



Analysis of Issues
Surrounding the Use of
Spray Adjuvants with
Herbicides
2021 Revision

David Bakke,
Pacific Southwest Regional
Pesticide-Use Specialist
(Retired), United States
Department of Agriculture
(USDA) Forest Service

Analysis of Issues Surrounding the Use of Spray Adjuvants with Herbicides 2021 Revision

David Bakke,
Pacific Southwest Regional Pesticide-Use Specialist (Retired)
United States Department of Agriculture (USDA) Forest Service

This paper is intended to serve as a source document for basic information concerning adjuvants commonly used with herbicides. Its intended audience is Forest Service interdisciplinary team members who are responsible for the analysis of projects that consider the use of these adjuvants. It is not a risk assessment, although it does provide some hazard information. It should be used in conjunction with existing national herbicide risk assessments.

I would like to acknowledge several people who reviewed drafts of this document; their reviews helped improve this paper immensely: Shawna Bautista, Forest Service Pacific Northwest Region Invasive Plant and Pesticide Use Program Manager; Kevin Chatelain, Strategic Account Manager, and Johnnie Roberts, Director of Formulation Development and Technical Support, Helena Agri-Enterprises; Tina Bond, former Product Specialist at Helena Products Group; Jim Ward, Director of Marketing at Loveland Products, Inc.; and Jim Glatzhofer, senior formulation chemist at Wilbur-Ellis Company.

The paper consists of eight parts. The first section is an introduction to the more common adjuvants used by the Forest Service in herbicide applications, grouped by type. The second part is a listing of common herbicide formulations and the accompanying adjuvant recommendations. The sources of this information are the herbicide labels. The third section lists the ingredients of the adjuvants described in Section 1. This information is from a variety of sources, including labels, Safety Data Sheets (SDS), manufacturer's product information, or studies involving the materials. In some cases, the ingredients cannot be specifically identified. This third section also contains a brief description of the hazard of the ingredients including two tables that list the results of standard acute toxicity testing in mammals and aquatic species. The fourth section is a set of five discussions involving various aspects of adjuvants that might be of use in environmental analysis. Sections five through eight provide reference data in support of this paper.

The listing of adjuvant and herbicide products in this document should not be considered as recommendations for use nor should their inclusion imply that they are the only products available for use. Always check current labels and registration status for any updated information. Inclusion of any product in this paper does not imply endorsement in any fashion by the USDA Forest Service.

Table of Contents

1. Introduction.....	3
a. Nonionic Surfactants.....	3
b. Cationic Surfactants.....	5
c. Sticker/Spreaders.....	5
d. Oil-Based Adjuvants.....	5
e. OMRI-Certified Wetter/Spreaders/Stickers.....	6

f. Activators - Fertilizer/Surfactant Mixtures	7
g. Special Purpose or Utility Adjuvants.....	7
h. Dyes and Colorants	8
2. Herbicide-Adjuvant combinations as recommended on herbicide labels (always refer to label first).....	10
3. Ingredients and Hazard Assessment	12
a. Nonionic Surfactants.....	13
Alkylphenol Ethoxylate-based Surfactants.....	13
Alcohol Ethoxylate-based Surfactants	23
Silicone-based Surfactants	29
b. Cationic Surfactants	37
c. Sticker/Spreaders	38
d. Oil-Based Adjuvants	44
Vegetable Oils.....	44
Vegetable Oils and Silicone Blends.....	55
Crop Oils and Crop Oil Concentrates	60
e. OMRI-Certified Wetter/Spreaders/Stickers.....	67
f. Activators - Fertilizer/Surfactant Mixtures	69
g. Special Purpose or Utility Adjuvants.....	76
Acidifiers.....	76
Drift Reduction Agents	79
Defoamers	83
Water Conditioning Agents	85
h. Dyes and Colorants	89
i. Table 1 – Standard Mammalian Acute Toxicity Testing Results.....	96
j. Table 2 – Standard Acute Aquatic Species Toxicity Testing Results	100
4. Issue Discussions Dealing With Adjuvants	106
a. Can surfactants cause pesticides to move more readily in the soil, or resolubilize, hence causing an increased risk of pesticide movement offsite into water? Can they cause effects to soil systems so that environmental decomposition of pesticides is affected?	106
b. Do adjuvants represent a unique risk to terrestrial or aquatic invertebrates?	115
c. Do mixtures of herbicides and adjuvants represent a greatly increased risk over the individual compounds alone (i.e. synergism)?	120
d. Do adjuvants represent a unique risk to aquatic organisms?	123
e. Do adjuvants represent a unique risk to mammals?.....	129
f. Do adjuvants affect the absorption rate of herbicides through the skin?.....	131
5. Toxicity Categories	135
6. List of Source Labels and SDSs.....	137
7. Acronyms and Abbreviations Used	139
8. References.....	141

1. Introduction

Adjuvants are spray solution additives that are mixed with an herbicide solution to improve efficacy, mixing, or application of the spray mixture. The Weed Science Society of America defines an adjuvant as any substance in an herbicide formulation or added to the spray tank to modify herbicidal activity or application characteristics (Penner 2000). Adjuvants can either enhance activity of an herbicide's active ingredient (activator adjuvant), offset any problems associated with spray application, such as adverse water quality or wind (special purpose or utility modifiers), or improve the mix compatibility of a spray solution. Activator adjuvants include surfactants, wetting agents, sticker-spreaders, and penetrants. Surfactants, or surface-acting agents, are a broad category of activator adjuvants that facilitate and enhance the absorbing, emulsifying, dispersing, spreading, sticking, wetting, or penetrating properties of herbicides. This paper deals mainly with commonly used activator adjuvants used in herbicide applications in forestry, range, and natural area management.

Adjuvants are not regulated by the U.S. Environmental Protection Agency (EPA). Labeling and registration of adjuvants is not required by the EPA, however there are some states that do require the registration of adjuvants. California and Washington, for example, are two states that do require adjuvant registration in their state. Manufacturers generally lab and field test adjuvants to ensure efficacy and appropriate rates for their intended use.

While the EPA does not regulate registration of adjuvants, there is a voluntary adjuvant certification program that was developed to bring consistency in product performance to adjuvants being used in the industry. Products that are certified must meet certain benchmarks derived by the American Society for Testing and Materials Association. Products that are submitted and meet all the required benchmarks are then given Crop Producers and Distributors Association (CPDA) certification. This gives another level of confidence to applicators that the adjuvant they have chosen will perform as it was intended

a. Nonionic Surfactants

Nonionic surfactants (NIS) are the most widely recommended and used of all spray adjuvants because they do not have a charge (versus a cation (positive charge) or anion (negative charge)) and will not negatively impact a spray application or mixture. Wetters, spreaders and organosilicone products fall into this classification. Nonionic surfactants lower the surface tension of water which helps the herbicide spread over and penetrate the waxy cuticle (outer layer) of a leaf or to penetrate through the small hairs present on the leaf surface. Because of the high surface tension of water, spray mixture droplets can maintain their roundness and sit on the leaf hairs or roll off of the waxy surface without much of the herbicide actually contacting the leaf. The primary purpose of a nonionic surfactant is to reduce the surface tension of the spray solution to allow more intimate contact between the spray droplet and the plant surface. They may also act to change the permeability of the leaf surface by affecting the cuticle.

Many of these compounds have the physical characteristics of both oil and water, containing a water-loving (hydrophilic) head and a long-chain hydrocarbon oil-loving (lipophilic) tail.

Nonionic surfactants can be characterized by their hydrophilic/lipophilic balance (HLB), on a scale of 1 to 20, with 1 being the most lipophilic (oil-loving) and 20 being the most hydrophilic (water-loving). Certain pesticides may describe an HLB range for the best results. A low HLB surfactant, when mixed with water will result in low dispersion or a milky mixture, while a high HLB surfactant in water may be a clear liquid or translucent. Most surfactants do not show an HLB number on their label. (Gadhav 2014; Green 1999)

There are several basic chemistries of nonionic surfactants. Examples of each¹:

Alkylphenol ethoxylate-based surfactants

R-11[®] Spreader Activator (Wilbur-Ellis Company)
 Activator 90 (Loveland Products)
 Target[™] Pro-Spreader Activator (Target Specialty Products, Inc.)
 Pro 90 (Integrated Agribusiness Professionals)
 Ad-Wet 90 (J.R. Simplot Co.)
 Induce[®] Nonionic Surfactant and Antifoaming Agent (Helena Agri-Enterprises, LLC)

Besides the alkylphenol ethoxylate, these surfactants usually include an alcohol as a solvent to prevent the surfactant from gelling in cold water, a silicone defoamer (polydimethylsiloxane), and water.

Alcohol ethoxylate-based surfactants

Denali EA[™] (Wilbur-Ellis Company)
 Wetcit (Oro Agri, Inc.)
 Rainier-EA[™] Nonionic Surfactant – Activator – Spreader (Wilbur-Ellis Co.)
 Liberate[®] Penetrant, Deposition Aid, Drift Control Agent (Loveland Products)

Silicone-Based Surfactants

Also known as organosilicones, these are increasing in popularity because of their superior spreading ability. This class contains a polysiloxane chain. Some of these are a blend of NIS and silicone while others are entirely silicone. The combination of NIS and a silicone surfactant can increase absorption into a plant so that the time between application and rainfall can be shortened. This is known as rainfastness. The surfactants extreme spreading ability may lead to droplet coalescence and subsequent runoff if applied at inappropriately high rates. Blends normally include an alcohol ethoxylate, a defoamer, and propylene glycol.

Freeway[®] (Loveland Products) –silicone blend
 Silwet L-77[®] (Helena Agri-Enterprises, LLC) – silicones
 Kinetic[®] (Helena Agri-Enterprises, LLC) – silicone blend
 Silwet[©] Eco Spreader (Momentum Performance Materials, Inc.) - silicones
 Hi-Wett[®] Super-Spreader (Loveland Products) – silicone blend

¹ The use of product names is for illustrative purposes only and is not intended as a recommendation for use or an endorsement of these products by the USDA Forest Service.

b. Cationic Surfactants

Ethoxylated fatty amines (Cationic)

Entry™ II (Monsanto Company) – No longer commercially available

POEA – Some commercial formulations of glyphosate have POEA surfactant, also known as tallow amine ethoxylate.

c. Sticker/Spreaders

A sticker can perform three types of functions. It can increase the adhesion or "stickiness" of solid particles that otherwise might be easily dislodged from a leaf surface. It can also reduce evaporation of the pesticide. The third function can be to provide a waterproof coating. Many of the stickers contain surfactants as their principal functioning agent and are sold as spreader-stickers, which give both a sticker action and a wetter-spreader action. These will perform the first two functions quite well. But since the surfactants that provide wetter-spreader action must be somewhat water soluble, they may not provide good protection from rain. This will be provided by products that contain latex (rubber), polyethylene (plastic), resins (rosin), polymenthenes (rosin-like), or other waterproofing agents.

Bond® Spreader Sticker Deposition Aid (Loveland Products)

Bond Max® Spreader Sticker Deposition Aid (Loveland Products)

Tactic™ Sticker – Organosilicone surfactant – deposition agent (Loveland Products)

Cohere® Nonionic Spreader Sticker (Helena Agri-Enterprises, LLC)

Surfix®-P (Helena Agri-Enterprises, LLC)

Sustain® Soil Deposition Adjuvant (Miller Chemical & Fertilizer Co.)

d. Oil-Based Adjuvants

Oils can be derived from two sources: soybeans and other crops; and oils that come from petroleum refineries. Oil-based adjuvants function to increase herbicide absorption through plant tissues and increase spray retention. They are especially useful in applications of herbicides to woody brush or tree stems to allow for penetration through the bark. Oil adjuvants, besides the oil also include an emulsifier for dispersion in water.

Vegetable or Seed Oils – The methylated seed oils are formed from 80-85% common seed oils, such as canola, soybean, or cotton and 10-20% NIS. They act to increase penetration of the herbicide. These are at least comparable in performance, and in some cases superior, to crop oil concentrates. In addition, silicone-seed oil blends are also available that take advantage of the spreading ability of the silicones and the penetrating characteristics of the seed oils.

The U.S. Food and Drug Administration (FDA) considers methyl and ethyl esters of fatty acids produced from edible fats and oils to be food grade additives (21 CFR 172.225) for use on dehydrating grapes to raisins as long as final amounts on raisins do not exceed 200 parts per

million (ppm). Because of the lack of exact ingredient statements on these surfactants, it is not always clear whether the oils that are used in them meet this FDA standard.

Competitor[®] Modified Vegetable Oil (Wilbur-Ellis Co.)
 MSO[®] Concentrate Methylated Seed Oil (Loveland Products)
 Hasten-EA[™] (Wilbur-Ellis Company)
 The surfactant in Pathfinder[®] II (a triclopyr formulation)
 Improved JLB Oil Plus (Brewer International)
 M.O.C. Methylated Oil Concentrate (Helena Agri-Enterprises, LLC)
 MSO[®] Concentrate with Leci-Tech (Loveland Products)
 Renegade-EA[®] Modified Vegetable Oil, Activator, and Surfactant (Wilbur-Ellis Co.)
 Super Spread[®] MSO (Wilbur-Ellis Company)
 MES-100[™] Modified Vegetable Oil Concentrate (Drexel Chemical Company)
 Spraytech Oil[™] Spray Adjuvant (Spraytech, Inc.)

Blends of vegetable oils and silicone-based surfactants

Syl-Tac-EA[™] (Wilbur-Ellis Company)
 Phase[®] (Loveland Products)
 Dyne-Amic[®] (Helena Agri-Enterprises, LLC)

Crop Oils and Crop Oil Concentrates - These are normally derivatives of paraffin-based petroleum oil. Crop oils are generally 95-98% paraffin or naphtha-based petroleum oil with 1-2% surfactant/emulsifier. Crop oils promote the penetration of a pesticide spray. Traditional crop oils are more commonly used in insect and disease control than with herbicides. Crop oil concentrates are a blend of crop oils (80-85%) and a nonionic surfactant (15-20%). The purpose of the nonionic surfactant in this mixture is to emulsify the oil in the spray solution and lower the surface tension of the overall spray solution. Crop oil concentrates are used with post-emergent herbicides.

Agri-Dex[®] (Helena Agri-Enterprises, LLC or Setre Chemical Co.)
 Mor-Act[®] Crop Oil Concentrate (Wilbur-Ellis Company)
 Herbimax[®] (Loveland Products)
 Grounded[®]-CA (Helena Agri-Enterprises, LLC)
 Inlet[®] Nonionic Wetter/Spreader Surfactant (Helena Agri-Enterprises, LLC)
 W.E.B. Oil (Wilbur-Ellis Company)

e. OMRI-Certified Wetter/Spreaders/Stickers

This is a unique category that includes many of the types of products already described above, but in addition are certified as suitable for organic production. The Organic Materials Review Institute (OMRI) is an international nonprofit organization that determines which input products are allowed for use in organic production and processing. OMRI Listed[®] products (OMRI 2019) are allowed for use in certified organic operations under the USDA National Organic Program.

The National Organic Standards were published in 2000 in the Federal Register at 7 CFR part 205 and were implemented in October 2002. Today, the National Organic Standards form the basis of OMRI's input reviews. Some examples of OMRI-Certified adjuvants:

Freeway[®] Organosilicone Super Wetter (Loveland Products, Inc.)
 Kinetic[®] (Helena Agri-Enterprises, LLC)
 Organic BioLink[®] Surfactant & Penetrant (Westbridge)
 Miller Nu Film P[®] Spreader and Sticker (Miller Chemical & Fertilizer Company)
 Sustain[®] Soil Deposition Adjuvant (Miller Chemical & Fertilizer Company)

f. Activators - Fertilizer/Surfactant Mixtures

Water quality, especially hard water, can greatly impact herbicide application and efficacy; as a result, ammonium sulfate and ammonium nitrate have been added to herbicide mixes to reduce the antagonism between poor water quality and herbicides. Herbicides that appear to benefit from the addition of ammonium are the relatively polar, weak acid herbicides such as glyphosate, the sulfonylureas (Oust, Escort, Telar, etc.), the imidazolinones (Arsenal, Plateau, Chopper, etc.), 2,4-D, and dicamba. In the case of glyphosate, the ammonium ions link to glyphosate molecules rather than allowing binding to any hard water calcium ions. The combination of ammonium and glyphosate better absorbed into plants than the calcium and glyphosate combination (Penner, 2000). Ammonium sulfate and nitrate should only be used with herbicides when recommended by the herbicide label. Velvetleaf and some grassy annual weeds in particular have been responsive to the addition of nitrogen fertilizer in the spray mix. Some broadleaves and grasses show little or no response with the inclusion of ammonium fertilizer solutions. There are challenges to the use of these ammonium products: they can corrode equipment; may affect spray mix compatibility; and there is always the potential for off-target damage.

Brandt[®] Magnify (Brandt Consolidated)
 Class Act[®] NG[®] (Winfield Solutions, LLC)
 Bronc[®] Plus Dry-EDT (Wilbur-Ellis Company)
 Cayuse[®] Plus (Wilbur-Ellis Company)
 phi[®] Kicker CA (J.R. Simplot Co.)

g. Special Purpose or Utility Adjuvants

The special purpose or utility adjuvants are used to offset or correct certain conditions associated with mixing and application such as impurities in the spray solution, extreme pH levels, and drift. These adjuvants include acidifiers, buffering agents, water conditioners, anti-foaming agents, compatibility agents, and drift control agents.

Acidifiers

Most herbicides perform best in slightly acidic water with a pH of 4-6.5 with the exception of sulfonylurea herbicides, which perform better in water with a pH of >7. Acidifier adjuvants

lower the pH of the water in the spray tank, although they do not necessarily maintain a constant pH level. Buffers tend to stabilize the pH at a relatively constant level.

LI 700[®] Surfactant Penetrant Acidifier (Loveland Products)
Tri-Fol[®] Acidifier and Buffering Agent (Wilbur Ellis Company)

Drift Reduction Agents

Drift reduction agents will generally increase the average droplet size so as to reduce the number of fine droplets that are especially susceptible to drift, or may act to thicken the solution (increase viscosity). Products that contain emulsified oils (e.g., In-Place[®] and InterLock[®]) narrow the droplet size distribution without significantly thickening the solution.

In-Place[®] Deposition Aid and Drift Management Agent (Wilbur Ellis Company)
Strike Zone[®] DF (Helena Agri-Enterprises, LLC)
InterLock[®] Deposition Aid, Canopy Penetrating & Drift Control Agent (Winfield Solutions, LLC)

Defoamers

Defoamers are used to reduce the foaming that might occur during agitation of the spray mixture. They typically are stabilized emulsions that contain a silicone compound (dimethylpolysiloxane) as their principal active ingredient. Some also include small amounts of silicon. The silicone compound acts to reduce the surface tension of the mixture, so foaming is eliminated or reduced. The silicon particles physically burst air bubbles.

Foaminator[®] Dry (Winfield Solutions, LLC)
FTF[™] Defoamer Defoaming Agent (Wilbur-Ellis Company)

Water Conditioning Agents

Conditioning or water-softening agents reduce problems caused by hard water. Hard water minerals bind with active ingredients of some pesticides, which may decrease pesticide performance. Before using a conditioning agent, test water for hardness; also refer to the pesticide label.

Bronc[®] Max Water Conditioning Agent (Wilbur-Ellis Company)
Quest[®] Water Conditioning Agent (Helena Agri-Enterprises, LLC)

h. Dyes and Colorants

Colorants are added to an herbicide mixture prior to application so that the actual treated area can be readily determined. This helps to prevent skips and overlaps. It can also be useful for reducing human exposures to recently treated vegetation. Dyes and colorants are not regulated by EPA or the states.

Hi-Light[®] Blue (BASF)
Colorfast[™] Purple (BASF)
Colorfast[™] Red (BASF)
Bas-Oil[®] Blue (BASF)
Bas-Oil[®] Red (BASF)
Mark-It Blue[®] (Lawn and Garden Products, Inc.)
Blazon[®] Blue (Milliken Chemical)
Dynamark[®] U.V. (Winfield Solutions, LLC)

2. Herbicide-Adjuvant combinations as recommended on herbicide labels (always refer to label first)

The following information should not take the place of reading the herbicide label. The information presented here is only intended to show the type of recommendations regarding adjuvants that are included on common forestry herbicide labels.

Aminocyclopyrachlor

- Method 50SG (Bayer Environmental Science) – 0.25% volume/volume (v/v) nonionic or 1% v/v methylated seed oil or vegetable oil. NIS should contain at least 70% NIS with a HLB of 12 to 17.
- Perspective (Bayer Environmental Science) – 0.25 – 0.5% nonionic v/v or 0.5 – 1.0% v/v methylated seed oil or vegetable oil or 1 – 2% v/v crop oil concentrate. NIS should contain at least 70% NIS. Oil adjuvants must contain at least 80% oil with at least 15% surfactant emulsifiers.

Aminopyralid

- Milestone[®] Specialty Herbicide (Corteva[™] Agriscience) – 0.25 – 0.5% v/v nonionic with at least 80% active principal

Chlorsulfuron

- Telar XP (Bayer Environmental Science) – Do not use LI-700 or any other acidifying adjuvant; otherwise add a quality surfactant at manufacturer's recommended rate.

Clethodim

- Tapout (Helena Chemical Co.) – 0.25% v/v nonionic or 1% v/v crop oil concentrate or methylated seed oil
- Envoy Plus (Valent U.S.A. Corp.) - 0.25% v/v nonionic or 1% v/v crop oil concentrate or methylated seed oil

Clopyralid

- Transline[™] (Corteva[™] Agriscience) – 0.25 – 0.5% non-ionic, or use surfactant manufacturer's label (also crop oils can be used)

2,4-D

- Weedar[®] 64 Broadleaf Herbicide (Nufarm, Inc.) - Use surfactant as per manufacturer's label
- Weedone LV6 EC Herbicide (Nufarm, Inc.) – Mix with NIS or crop oil concentrate if desired

Glyphosate

- Rodeo (Corteva[™] Agriscience) – use NIS with at least 80% active ingredient and add as per manufacturer's label
- Roundup Custom for Aquatic and Terrestrial Use (Bayer Environmental Science) - $\geq 0.5\%$ v/v NIS with at least 70% active ingredient
- Accord[®] XRT (Corteva[™] Agriscience) – 0.125 - 0.5% v/v NIS with at least 70% active ingredient
- Roundup Pro[®] Concentrate (Bayer Environmental Science) – none needed (contains POEA-based surfactant)

Fluazifop-p-butyl

- Fusilade[®] DX (Syngenta Crop Protection) – 0.25 – 0.5% v/v NIS or 0.5 – 1.0% v/v crop oil concentrate or seed oil. NIS should contain at least 75% NIS. Oil adjuvants must contain 15-20% emulsifiers.

Hexazinone

- Velpar[®] DF, and Velpar[®] L (DuPont) – none needed

Imazapic

- Plateau[®] (BASF) – for post-emergent applications – methylated seed oil or vegetable oil 1.5 – 2 pints/acre; $\geq 0.25\%$ v/v NIS with $>60\%$ active ingredient and an HLB between 12 and 17; silicone-based, as per surfactant manufacturer's label; silicone/oil blends as per surfactant manufacturer's label; fertilizer surfactant blends can be added at the rate of 2-3 pints/acre.

Imazapyr

- Arsenal[®] Applicators Concentrate (BASF) – foliar 0.25% v/v or higher NIS, with an HLB between 12 and 17 and at least 70% active ingredient; methylated seed oil or vegetable seed oil at 1.5 – 2 pints/acre; silicones as per manufacturer's label.
- Chopper[®] Gen2[™] (BASF) – foliar 1 - 12.5% v/v seed oil
- Nufarm Polaris[®] AC – (Nufarm Specialty Products) – foliar, NIS at minimum of 0.25% v/v.

Metsulfuron methyl

- Escort[®] XP (Bayer Environmental Science) – 0.25% minimum or surfactant manufacturer's rate with $>80\%$ ai; don't use products with acetic acid (LI-700).

Picloram

- Tordon[®] 22K (Corteva[™] Agriscience) – none needed, but can add as per surfactant manufacturer's label

Sulfometuron methyl

- Oust[®] XP (Bayer Environmental Science) – 0.25% v/v NIS if needed

Triclopyr

- Garlon[®] 3A (Corteva[™] Agriscience) – for foliar, use surfactant manufacturer's label
- Forestry Garlon[®] XRT (Corteva[™] Agriscience) – foliar, 1-2 qts/ac NIS; bark applications, use an oil; cut stump 80-87% v/v oil; diesel fuel, fuel oil, kerosene or a basal oil.
- Pathfinder[®] II (Corteva[™] Agriscience) – none needed, includes a crop oil surfactant.
- Garlon 4[®] Ultra (Corteva[™] Agriscience) – for foliar, no surfactant necessary although can make an oil-water emulsion for better effectiveness. Crop oil concentrate, kerosene, or diesel used for basal, cut stump applications.
- Vastlan[®] (Corteva[™] Agriscience) - For best results, use a surfactant with foliar applications. Broadcast Applications with Ground Equipment: To improve spray coverage, add a NIS. Label contains species-specific recommendations for NIS, crop oil concentrate, or methylated seed oil.

3. Ingredients² and Hazard Assessment

The assessment of hazards for these adjuvants is limited by the proprietary nature of the formulations. Unless the EPA classifies a compound in the formulation as hazardous, the manufacturer is not required to disclose its identity. At the current time, the disclosure of whether a material is hazardous is based primarily on acute toxicity. In many cases, ingredient names as stated on adjuvant labels or in the SDS are generic and do not allow this document to clearly describe the risks. As an example, the use of the two generic names *ethoxylated alkylphenol* and *ethoxylated alcohol* tells nothing about the degree of ethoxylation, or the type of alkylphenol or alcohol, both of which can have considerable impacts on how acutely toxic a compound might be.

Note that this section discusses individual ingredients. The hazards associated with the individual ingredients don't take into account the relative amounts of each ingredient in the formulated commercial product. As such, the signal word for the formulated product as well as acute toxicity information for the formulated product should be relied upon more so than the corresponding information for the individual ingredients.

There is little toxicity testing done on adjuvants. Most of the adjuvants have had some acute toxicity testing, as well as skin and eye irritation studies. The acute toxicity testing results are displayed in Table 1 for mammalian species and in Table 2 for aquatic species. 'NA' in these two tables indicates that either the particular test has not been conducted on the formulation, or these data were not available from the manufacturer.

As of June 1, 2015, all manufacturers of adjuvants were required to comply with the United Nations' Globally Harmonized System of Classification and Labelling of Chemicals (GHS); after that date all adjuvant labels and SDSs were to be amended to conform to GHS. Under GHS there are only two signal words³ allowed (Warning and Danger). In addition, pictograms have been placed in the label and SDS and the first aid and precautionary statement language have been changed. GHS does not apply to pesticide labels as pesticides are regulated under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Since adjuvants are not considered pesticides under FIFRA, and are therefore not registered by EPA, the labels and SDSs had to meet Federal Occupational Safety and Health Administration (OSHA) GHS requirements (29 CFR Parts 1910, 1915, and 1926). Therefore, adjuvants use Warning and Danger signal words, or if of low toxicity, may not use any signal word.

Although all adjuvant manufacturers were to comply with GHS in 2015, some issues have been seen where the signal words on the adjuvant label and the SDS may not match, or the personal protective equipment (PPE) listed on the adjuvant label does not match the PPE listed on the

² Adjuvant ingredients are not required to be disclosed as they are protected as Confidential Business Information unless they include hazardous ingredients required to be identified on the Safety Data Sheet (SDS). The listing of ingredients has been developed from the label, SDS, manufacturer's publicly released information, or from the open literature. Formulations of these adjuvants can often change, so caution must be used in relying on this list.

³ Signal words are required on pesticide and adjuvant labels, and provide an overall sense of the acute toxicity, or effects to eyes or skin, of the product. There are three signal words used by EPA on pesticides (Danger, Warning, and Caution) to signify decreasing levels of toxicity. In addition, the Danger signal word can be accompanied by the skull and crossbones symbol if the product is an acute poison. Refer to the table in Section 5.

SDS. This is largely due to the requirement under the GHS system for the SDS to now cover employees involved in the manufacturing of adjuvants. The EPA has clarified that adjuvants are not pesticides and therefore are not covered under FIFRA. However, OSHA and the EPA Worker Protection Branch clarified that when adding adjuvants to pesticides, as instructed to do so on the product labels, the resulting combined product mixture falls under the pesticide worker protection standard and, therefore, the pesticide label(s) prescribes appropriate PPE. It is important to note the information contained within the SDS for adjuvants pertain to the full chemical strength of the product which is not the version typically sold to an end-user consumer. Therefore, when using adjuvants, employees are required to adhere to the PPE requirements outlined in the locally produced risk assessment (job hazard analysis (JHA) or project safety plan), consistent with the PPE requirements listed on the label for application work.

Note that within the state of California, the Department of Pesticide Regulation (DPR) considers any spray adjuvant to be a pesticide, as defined in the state Food and Agriculture Code 12753. DPR registers spray adjuvants using the EPA pesticide labeling registration requirements. As such, in California, when an applicator is using spray adjuvants, they are required to follow all labeling requirements, including PPE, regardless of what is listed on the SDS (Damiano 2021).

The primary summary statement that can be made is that the more common risk factors for the use of these adjuvants are through skin or eye exposure. These adjuvants all have various levels of irritancy associated with skin or eye exposure. This points up the need for good industrial hygiene practices while utilizing these products, especially when handling the concentrate, such as during mixing. The use of chemical resistant gloves and goggles, especially while mixing, should be observed.

Note on categorization of ingredients – In 1987, EPA developed a four-category system of classifying inert ingredients based on their relative toxicity. This was done to prioritize evaluations of these chemicals. The categories were described as List 1, 2, 3, and 4 (the last subsequently broken down into 4A and 4B), with list 1 and 2 being compounds of known toxic hazard or high priority for testing, list 4 being those considered of low hazard, and list 3 which contains those compounds where not enough information was known to place them into any of the other categories. Officially this list has since been deemed obsolete by EPA since the reassessment of food tolerances/tolerance exemptions under the Food Quality Protection Act is now complete. The List 4 materials are still referenced in the USDA National Organic Program (7CFR §205.601(m)(1)) as allowed synthetic inert ingredients. Earlier versions of this paper identified these ingredients as belonging on one of these inert lists; this obsolete classification system is no longer included.

a. Nonionic Surfactants

Alkylphenol Ethoxylate-based Surfactants

R-11[®] Spreader Activator (Wilbur-Ellis Company)
CA Reg. #2935-50142, WA Reg. #2935-50142

Active Ingredients – 90%, Surfactant Content 80%

Nonylphenol polyethylene glycol ether (CAS 127087-87-0⁴) – a polyethoxylated nonylphenol surfactant with an unspecified number of ethoxylate groups (likely in range of 8-10), SDS identifies as 70-<80% by volume

Butyl alcohol (CAS 71-36-3), SDS identifies as 5%-<10% by volume (solvent)

Oxirane, aka ethylene oxide (CAS 75-21-8), likely contaminant

1,4-dioxane (CAS 123-91-1), likely contaminant

Warning signal word. Flammable liquid. May cause skin irritation, but not expected to be a skin sensitizer. Causes serious eye irritation. Prolonged inhalation may be harmful. Signal word and PPE listed on the label (chemical resistant gloves and eye protection) do not conflict with the PPE on latest SDS from 1/9/20.

The SDS does not contain any numerical mammalian toxicity data for the formulated product. Acute mammalian toxicity data is shown in Table 1. R-11[®] is considered slightly toxic via oral and dermal exposure and moderately toxic via inhalation exposure.

There are several aquatic toxicity values found in the literature for R-11[®] that are shown in Table 2. There is an acute toxicity value for rainbow trout in a 2004 study (Smith et al 2004), values for trout, bluegill, and daphnia in the Forest Service glyphosate risk assessment appendix (SERA 2011a). There is also an LD₅₀ value for *Daphnia pulex* in Stark and Walthall 2003, and values for two other fish species (fathead minnow and Sacramento splittail) in Siemering et al 2008. R-11[®] can be considered highly to moderately toxic to fish and moderately to slightly toxic to Daphnia.

The CAS number for the surfactant active ingredient refers to a generic description of ethoxylated nonylphenols, and therefore do not describe how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of nonylphenol ethoxylates in the 8-10 ethoxylate range. From the 2003 Forest Service human health and ecological risk assessment for nonylphenol polyethoxylate-based (NPE) surfactants (USDA 2003), the conclusions for human health risks:

Based on the estimated levels of exposure and the criteria for acute and chronic exposures, there is no evidence that typical exposures to NP9E-based surfactants will lead to dose levels that exceed the level of concern....From a practical perspective, eye irritation and skin sensitization are likely to be the only overt effects as a consequence of mishandling NP9E. These effects can be minimized or avoided by prudent industrial hygiene practices.

For the public, acute or accidental exposure scenarios involving consumption of contaminated water, consumption of contaminated vegetation, or subsistence consumption of fish represent some risk of effects....Based on the available information and under the foreseeable conditions of application, there is no route of

⁴ CAS refers to the Chemical Abstracts Service Registry identification number which is a unique numeric identifier for the stated chemical. The SDS is the primary source for these numbers.

exposure or scenario suggesting that the general public will be at any substantial risk from longer-term exposure to NP9E based surfactants.

The surfactant ingredient in R-11[®] Spreader Activator, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including aquatic species, such as fish and amphibians. From USDA 2003, however:

For aquatic species, the duration of any exposure would be short; the compounds of concern are broken down and their concentration reduced through dilution, as well as binding of the compounds to stream sediments....The ambient levels of NP9E assumed to be present from normal operations would be protective of all aquatic organisms.

Refer to USDA 2003 for a more detailed review of the nonylphenol ethoxylate surfactants.

Butyl alcohol (aka butanol) is likely added as a solvent. Butanol and the polyethoxylated nonylphenol surfactant are similar in acute oral toxicity (comparing oral LD₅₀ values from the SDS). Butanol is extensively and rapidly metabolized in mammals to carbon dioxide. Butanol is severely irritating to the eyes, leading to a signal word of Danger. It is approved for use in foods as an artificial flavoring and is Generally Regarded As Safe (GRAS) by the FDA.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Activator 90 Non-Ionic Surfactant Penetrant Anti-Foaming Agent (Loveland Products, Inc.)

CA Reg. #34704-50034, WA Reg. #34704-04001

Active Ingredients – 90%

Alkylphenol ethoxylate (Nonylphenol polyethylene glycol ether (i.e., nonylphenol polyethoxylate w unspecified # of ethoxylate groups) on SDS (CAS 127087-87-0))

Tall oil fatty acid (CAS 61790-12-3) (emulsifier)

Alcohol ethoxylate (linear alcohol) (CAS 34398-01-1)

Diethylene glycol (listed on SDS not label) (CAS 111-46-6) solvent

Water - 10% (listed on SDS)

Activator 90 has a Warning signal word. It may cause skin and eye irritation. It can be harmful if swallowed or inhaled. Signal word and PPE listed on the label (chemical resistant gloves and eye protection) do not conflict with the information in latest SDS from 5/20/19.

Mammalian acute toxicity data for the formulation are available in the SDS (refer to Table 1). Activator 90 is considered slightly toxic via oral or dermal exposure. It is considered moderately toxic via inhalation. It is not a skin sensitizer.

Aquatic acute toxicity data for the formulation are available on the SDS (refer to Table 2). The SDS describes a toxicity test involving the freshwater aquarium fish *Poecilia reticulata* (guppy) which indicated a 96-hour LC₅₀ of 12.7 mg/L and a 96-hour NOEC of 5.8 mg/L. The SDS also lists data for tests on *Daphnia magna* (water flea) showing a 24-hour EC₅₀ of 5.2 mg/L and a 24-

hour NOEC of 1.0 mg/L. The Forest Service risk assessment on glyphosate (SERA 2011a) provides values for rainbow trout, bluegill and Daphnia. This is comparable to effects of other nonylphenol polyethoxylate-based surfactants on fish and aquatic invertebrates (USDA, 2003) and can be considered moderately toxic to fish and Daphnia.

The active ingredient on the label refer to a generic description of ethoxylated nonylphenol, and therefore do not describe how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of nonylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

The linear ethoxylated alcohol is not adequately described to say anything definite about its toxicology. The CAS number represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular alcohol is unknown. The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. This ingredient has a GHS signal word of Danger due to its strong eye irritation, which can result in eye damage or blindness. It is also a skin irritant. EPA classifies it as a “Safer Choice” ingredient in surfactants because of its rapid rate of biodegradation, although it is acutely toxic to aquatic animals (more so than aquatic plants or algae).

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to tall oil fatty acid. Quality tall oil fatty acid consists mostly of oleic and linoleic acid. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value >10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

Diethylene glycol is a widely used solvent. It has a signal word of Warning, largely due to its toxic effect with repeated exposures. On an acute exposure basis, it is practically nontoxic with an acute oral LD₅₀ value in the rat of 12.5 g/kg. It is of low aquatic acute toxicity, with a 96-hour LC₅₀ in the bluegill of 1,000 mg/L and a 24-hour EC₅₀ in the waterflea of 10,000 mg/L.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Target[™] Pro-Spreader Activator (Target Specialty Products, Inc.)

CA Reg. #48813-50025

Active Ingredients – 90%

Alkyl phenol ethoxylate, not otherwise identified, likely an NPE

Propylene glycol (CAS 57-55-6), likely as a drying retardant

Tall oil fatty acids (not further identified)

SDS also lists poly(ethylene oxide), CAS 25322-68-3, from the APE
Pro 90 Spreader/Activator (Integrated Agribusiness Professionals)

CA Reg. #71058-50002

Active Ingredients – 90%

Branched alkylphenol ethoxylate (not further identified) (older SDS lists CAS 9016-45-9
at 55% which is an NPE of unspecified ethoxylate number)

Propylene glycol (CAS 57-55-6), likely added as a drying retardant

Tall oil fatty acids (not further identified)

SDS also lists poly(ethylene oxide), CAS 25322-68-3, from the APE (1-<3%)

Both products have the same identified generic ingredients without specific amounts, so although they are marketed by different companies, they will be handled together.

Both Pro-Spreader Activator and Pro 90 Spreader/Activator have a Warning signal word. Both may cause skin irritation and are noted as being seriously irritating to the eyes. Signal word and PPE listed on the label (chemical resistant gloves and eye protection) do not conflict with the information on latest SDS from 2/25/16 (Pro 90) and 4/4/16 (Target™ Pro-Spreader). They are both also noted as being harmful to the aquatic environment.

Identical mammalian acute toxicity data for both formulations are available on the SDSs (refer to Table 1). Both products are considered slightly toxic via oral or dermal exposure. There is no inhalation data available. Both are noted as causing serious eye irritation.

Identical aquatic acute toxicity data for both products are available on the SDSs (refer to Table 2). The SDSs describe an estimated toxicity value involving an unnamed fish species which indicate a 96-hour LC₅₀ of 7.1 mg/L. The SDSs also list estimated toxicity values for Daphnia spp. showing a 48-hour EC₅₀ of 49,702 mg/L. This would indicate that these two products are moderately toxic to fish and practically nontoxic to Daphnia.

The labels refer to a generic description of ethoxylated alkylphenol, and therefore do not describe the exact alkylphenol or how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of nonylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11®, above.

Propylene glycol is a tasteless, odorless and colorless clear oily liquid that is very soluble in water. It is the primary ingredient in low toxicity antifreezes (RV or marine antifreeze). GRAS material; used in some processed foods as a solvent for flavors and colors or as a humectant. Used as a humectant in hand sanitizers. It is a principal ingredient in vaping solutions. In these two adjuvants, it could be added as a solvent, as a humectant, or as a defoamer. Quickly metabolized in mammals after ingestion, although a large portion remains unmetabolized and excreted in urine. Half-life in humans is measured in hours, although it can be toxic in large doses over short time, otherwise propylene glycol is of low oral toxicity. Oral LD₅₀ values range from 8 to 46 g/kg. It is not a skin sensitizer nor an eye or skin irritant. It is not considered a carcinogen or mutagen. It is of low aquatic toxicity; LC₅₀ values for freshwater fish and invertebrates range from 11,000 to 77,400 ppm.

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to

tall oil fatty acid. Quality tall oil fatty acid consists mostly of oleic and linoleic acid. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value >10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds (for these two products, the SDSs describe levels of 1 to <3%). Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Ad-Wet 90 CA (J.R. Simplot Co.)

CA Reg. #7001-50005

Active Ingredients – 90%

Alkylphenol ethoxylate – SDS identifies as 4-nonylphenol, branched, ethoxylated, CAS #127087-87-0, at 40-50%

Glycols – not further identified

Free fatty acids – not further identified

Dimethylsiloxane

Ad-Wet 90 CA has a Warning signal word. It may cause serious eye irritation. Signal word and PPE listed on the label (chemical resistant gloves and eye/face protection) do not conflict with the latest SDS from 1/2/20, although the SDS includes a face mask (but not specifically a respirator) in Section 8.3.

The SDS does not contain any numerical mammalian toxicity data for the formulated product.

The SDS does not contain any numerical aquatic toxicity data for the formulated product.

The list of ingredients on the label are very generic and no additional information is in the SDS, not allowing for a clear idea of the toxicity of any of the components.

The CAS number for the surfactant active ingredient refers to a generic description of ethoxylated nonylphenols, and therefore do not describe how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of nonylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Glycols are listed in the ingredients and are not otherwise identified. Glycol is any of a class of organic compounds belonging to the alcohol family, in which, two hydroxyl (-OH) groups are attached to different carbon atoms. The term is often applied to the simplest member of the class, ethylene glycol, but could also be referring to propylene glycol. Both are found in other adjuvants discussed in this paper. Since Ad-Wet 90 CA is allowed to be used in aquatic applications, the likely glycol is propylene glycol, the active ingredient in RV and marine

antifreeze. Propylene glycol is quickly metabolized in mammals after ingestion, although a large portion remains unmetabolized and excreted in urine. Half-life in humans is measured in hours. It can be toxic in large doses over short time, otherwise propylene glycol is of low oral toxicity. Acute oral LD₅₀ values range from 8 to 46 g/kg. It is not a skin sensitizer nor an eye or skin irritant. It is not considered a carcinogen or mutagen. It is of low aquatic toxicity; LC₅₀ values for freshwater fish and invertebrates range from 11,000 to 77,400 ppm.

Free fatty acids are listed in the ingredients and are not otherwise identified. This generic title may be referring to some type of plant-based acid, such as oleic acid or linoleic acid, but this cannot be determined.

Dimethylsiloxane is likely referring to a linear polydimethylsiloxane. This descriptor is somewhat generic as it includes the segment *poly*, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. This may be referring to octamethyltrisiloxane, aka dimethicone, a commonly used polydimethylsiloxane. Although this may or may not be the actual product used in this formulation, many of the closely related linear silicones have similar tox profiles. Dimethicone is not absorbed in animal tissues to any great degree; most of tested doses are excreted in the feces with no metabolism. The signal word is Warning due to eye irritation. It is added to this formulation as either a surfactant or as a defoamer. The acute oral LD₅₀ in mice varied in different studies from 6.5 to 26.85 g/kg. No effects from subchronic feeding tests in beagles. Reproductive tests showed no impacts in rats. Chronic tests in rats and mice showed no cancers developed. Not a genotoxin. It is of low aquatic toxicity and not expected to bioaccumulate.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Ad-Wet 90 (J.R. Simplot Co.)

WA Reg. #7001-03002

Active Ingredients – 90%

Alkylphenol ethoxylate – not further identified

Diethylene glycol – not further identified (CAS 111-46-6?)

Tall oil fatty acids – not further identified

2-propanol CAS 67-63-0, 1-10%, listed on SDS (isopropyl alcohol)

Ad-Wet 90 has a Danger signal word. It may cause skin irritation and serious eye damage. It is a flammable liquid and vapor. Signal word and PPE listed on the label (chemical resistant gloves and eye/face protection) do not conflict with the latest SDS from 6/24/15, although the SDS includes passing reference to a face mask (a respirator?) in Section 8.

The SDS does not contain any numerical mammalian toxicity data for the formulated product and only provides toxicity data on 2-propanol (isopropyl alcohol), which is not listed on the label and is likely part of the formulation not considered as an active ingredient.

The SDS does not contain any numerical aquatic toxicity data for the formulated product.

The list of ingredients on the label are somewhat generic and no additional information is in the SDS, not allowing for a clear idea of the toxicity of any of the components.

The label refers generically to alkylphenol ethoxylate, and therefore does not describe the exact alkylphenol or how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Diethylene glycol is a colorless, practically odorless, poisonous liquid with a sweetish taste. It is a widely used solvent. It may be used in these formulations to retard drying (humectant) or as a surfactant. Diethylene glycol has a GHS signal word of Warning, largely due to its toxic effect with repeated exposures. It is of low acute toxicity. It is of low aquatic acute toxicity and is not expected to bioaccumulate.

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to tall oil fatty acid. Quality tall oil fatty acid consists mostly of oleic and linoleic acid. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value > 10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

Isopropyl alcohol, also known as rubbing alcohol, is likely included in Ad-Wet 90 as a solvent. Ad-Wet 90 is flammable due to the inclusion of isopropyl alcohol (at levels of 1-10% of the product). Isopropyl alcohol has a GHS signal word of Danger due to its flammability and its ability to cause eye irritation. Isopropyl alcohol acts as a central nervous system depressant with sufficient exposure, although it is of low acute toxicity (oral, dermal, and inhalation). It is of low aquatic toxicity to invertebrates and freshwater fish and is not expected to bioconcentrate. Readily biodegradable in the environment.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Induce[®] Nonionic Surfactant and Antifoaming Agent (Helena Agri-Enterprises, LLC) – WA label

WA Reg. # 5905-11002

Active Ingredients – 90%

Alkylphenol ethoxylates, not further identified

Alcohol ethoxylates, not further identified

Tall oil fatty acids, not further identified

Induce[®] Nonionic Surfactant and Antifoaming Agent has a Warning signal word. It may cause skin irritation and serious eye irritation. It is harmful if swallowed or inhaled. Signal word on the

label and SDS are not in conflict. The PPE listed on the label (chemical resistant gloves and eye protection) are not consistent with the latest SDS from 5/12/15. In addition to protective eyewear and gloves, the SDS also calls for an impervious apron and footwear in Section 8.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral, inhalation, and dermal exposure (but not a skin sensitizer). It is noted as being a severe eye irritant, but injury is reversible. The SDS notes that it may be fetotoxic but only at doses that are maternally toxic.

There are no quantitative aquatic acute toxicity data in the SDS. The SDS notes that the alcohol ethoxylate is considered a marine pollutant. There is an acute toxicity value for bluegill in a 2003 study (Haller and Stocker 2003) that is shown in Table 2. There are acute toxicity values for rainbow trout and *Daphnia* in the Forest Service glyphosate risk assessment (SERA 2011a). It is not known whether the product tested in those studies is the same formulation as this registered product. These values indicate that this product is moderately toxic to fish and slightly toxic to *Daphnia*.

The label refers generically to alkylphenol ethoxylate, and therefore does not describe the exact alkylphenol or how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

The alcohol ethoxylate on the label is further described as a mix of 12-16 carbon linear alcohols with 1-6 ethoxylate groups. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to tall oil fatty acid. Quality tall oil fatty acid consists mostly of oleic and linoleic acid. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value > 10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Induce[®] A Nonionic Low Foam Wetter/Spreader (Helena Agri-Enterprises, LLC) – CA label

CA Reg. # 5905-50091

Active Ingredients – 90%

Alkyl Aryl polyoxyalkane ethers, not further identified (likely an APE, either NPE or OPE)

Free fatty acids, not further identified

SDS also includes alkanolamides, not further identified (surfactant or emulsifier?)

SDS also includes dimethyl siloxane, not further identified (defoamer?)

SDS also identified Alcohol, C12-16, poly(1-6)ethoxylate

Induce[®] A Nonionic Low Foam Wetter/Spreader has a Warning signal word. It may cause skin irritation and serious eye irritation. It is harmful if swallowed or inhaled. Signal word on the label and SDS are not in conflict. The PPE listed on the label (chemical resistant gloves and eye protection) are not consistent with the latest SDS from 8/4/15. In addition to protective eyewear and gloves, the SDS also calls for an impervious apron and footwear in Section 8.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral, inhalation, and dermal exposure (but not a skin sensitizer). It is noted as being a severe eye irritant, but injury is reversible. The SDS notes that it may be fetotoxic but only at doses that are maternally toxic.

There are no quantitative aquatic acute toxicity data in the SDS. The SDS notes that the alcohol ethoxylate is considered a marine pollutant. There is an acute toxicity value for bluegill in a 2003 study (Haller and Stocker 2003) that is shown in Table 2. There are acute toxicity values for rainbow trout and Daphnia in the Forest Service glyphosate risk assessment (SERA 2011a). It is not known whether the product tested in those studies is the same formulation as this registered product. These values indicate that this product is moderately toxic to fish and slightly toxic to Daphnia.

The alkyl aryl polyoxyalkane ether is likely referring to some type of APE, although exactly which APE is not possible to say. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

The label lists free fatty acids as an ingredient. Obviously, this generic term does not allow any further clarification as to exactly which fatty acid is included in this product. Fatty acids include oleic acid, commonly associated with vegetable oils. Whether this term is referring to a fatty acid, one of its salts, or as some other compound is unknown.

The SDS lists alkanolamides as an ingredient, however this is a generic term, defined as a fatty acid used as a surfactant. Whether this is a further clarification of the term free fatty acids on the label is unknown. There are three alkanolamides typically used in surfactants: coconut diethanolamide (aka cocamide DEA), made from coconut oil (CAS 68603-42-9); soyamide DEA, made from soybean oil (CAS 68425-47-8); and, tallamide DEA (CAS 68155-20-4), made from tall oil fatty acids. Whether one of these or which of these is used in this product is unknown. Cocamide and soyamide DEA are used in personal care products so tox data is available on them; not much toxicity information is available on tallamide DEA. Both cocamide and soyamide DEA have signal words of Danger due to eye hazard and possible carcinogenicity. They are both slightly toxic orally and dermally in mammals. Cocamide DEA has aquatic LC₅₀

values for algae, daphnia, and fish that are all <10mg/L. As Induce[®] has an aquatic label, it is more likely that soyamide DEA is used as it is at least an order of magnitude less toxic than cocamide DEA to aquatic species.

Dimethyl siloxane is likely referring to a linear polydimethylsiloxane. This descriptor is somewhat generic as it includes the segment poly, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. This may be referring to octamethyltrisiloxane, aka dimethicone, a commonly used polydimethylsiloxane. Although this may or may not be the actual product used in this formulation, many of the closely related linear silicones have similar tox profiles. Dimethicone is not absorbed in animal tissues to any great degree; most of tested doses are excreted in the feces with no metabolism. The GHS signal word is Warning due to eye irritation. It is added to this formulation as either a surfactant or as a defoamer. The acute oral LD₅₀ in mice varied in different studies from 6.5 to 26.85 g/kg. No effects from subchronic feeding tests in beagles. Reproductive tests showed no impacts in rats. Chronic tests in rats and mice showed no cancers developed. Not a genotoxin. It is of low aquatic toxicity and not expected to bioaccumulate.

The alcohol ethoxylate listed in the SDS (sections 12 and 14) is further described as a mix of 12-16 carbon linear alcohols with 1-6 ethoxylate groups. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Alcohol Ethoxylate-based Surfactants

Denali-EA[™] (Wilbur-Ellis Company)

CA Reg. #2935-50204; WA Reg. #2935-15006

Active Ingredients – 68.9%, Surfactant content 60.9% (Noted as NPE-Free)

Polyoxyalkylene polyol fatty acid ester, SDS identifies as proprietary alkoxyate(s) – 30-40% - not further identified, nonionic surfactant

Alcohol ethoxylate, SDS identifies as proprietary – 20-30% - not further identified

2-hydroxy-1,2,3-propanetricarboxylic acid, synonym for citric acid (CAS 77-92-9) – 5-10%

SDS also lists formaldehyde, CAS 50-00-0

Water – 20-30% (from older SDS)

Denali EA[™] has a Warning signal word. It may cause eye irritation. It is also considered acutely toxic to aquatic organisms. There is no PPE listed on the label, although because of risk of eye

irritation, eye protection would be implied. Given that, the signal word and PPE implied on the label (eye protection) do not conflict with the latest SDS from 1/10/19.

The SDS does not contain any numerical toxicity data for the formulated product and only provides oral acute toxicity data on citric acid. Acute mammalian toxicity data is shown in Table 1. Denali EA™ is considered practically nontoxic via oral exposure and is considered slightly toxic via dermal and inhalation exposure.

There are no aquatic toxicity data in the SDS, although the SDS does state that Denali EA™ is acutely hazardous to the aquatic environment. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2 along with corresponding NOEC values (Glatzhofer 2020). It is considered slightly toxic to fish and moderately toxic to Daphnia. This product is approved for aquatic use by the state of Washington.

The list of ingredients on the label are somewhat generic and no additional information is in the most recent SDS.

The generic ingredient description of polyoxyalkylene polyol fatty acid ester could be referring to a polysorbate emulsifier or surfactant (a common name used are Tweens). Polysorbates are soluble or dispersible in water but differ widely in organic and oil solubilities. Ethoxylated sorbitan esters have 20 ethoxylate groups. Their variation is dependent on the esterified fatty acid associated with the ethoxylated sorbitan. Common polysorbates are polysorbate 20, polysorbate 40, polysorbate 60, and polysorbate 80. The first three have no signal word as they are of low acute toxicity and are not eye or skin irritants. They are of low aquatic toxicity. Polysorbate 80 may show a signal word of Warning due to eye and skin irritation (although many SDSs show no signal word for this polysorbate either).

The ethoxylated alcohol is not adequately described to say anything definite about its toxicology. The exact number of ethoxylate groups in this proprietary alcohol is unknown. The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

Citric acid is also present, likely added to provide the acidifier quality of this formulation. Citric acid is a weak organic acid occurring naturally in citrus fruits. It is very soluble in water. Considered GRAS, it has many uses in foods and food products, medicines, household and personal care products. EPA has completed several comprehensive reviews of citric acid. Citric acid carries a GHS signal word of Warning due to the risk of serious eye damage or irritation. It can also cause skin irritation. It is slightly toxic to practically non-toxic via oral exposure to rats and mice ($LD_{50} >3$ g/kg). Dermal $LD_{50} >5$ g/kg (slightly toxic), although it is not a skin

sensitizer. Citric acid is of low toxicity to freshwater fish (bluegill 96-hour LC₅₀ is 1,516 mg/L) and aquatic invertebrates (waterflea 72-hour EC₅₀ is 240 mg/L).

The 2019 SDS includes formaldehyde in sections 8 and 11, indicating it is a potential carcinogen. Formaldehyde may be intentionally added as a chelating agent, a preservative, or for some other purpose, although it is more likely an impurity or unreacted intermediate compound. Since it is not listed in the ingredients, it is likely only a minor component of the formulation. Formaldehyde has a Danger signal word because of its acute oral toxicity; skin irritant/corrosive; skin sensitizer; inhalation acute toxicity; and carcinogenicity. It is also a possible mutagen. Inhalation exposure is associated with cancer and lung disease (myeloid leukemia and nasal tumors).

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Wetcit (Oro Agri, Inc.)

CA Reg. #72662-50001; WA Reg. #72662-05001

Active Ingredients – 8.15%, surfactant content 8.15%, (noted as APE/NPE free)

Alcohol ethoxylate – 8.15%, SDS identifies as alcohol, C11-15 secondary, ethoxylated (CAS 84133-50-6)

Sweet Orange Extract, 5-10%, CAS 8028-48-6

Bulk of product identified as Proprietary Mixture (trade secret) on SDS

SDS lists ethanol (CAS 64-17-5)

SDS lists sodium hydroxide, aka lye (CAS 1310-73-2), as an acidity regulator?

SDS lists 2,6-di-tert-butyl-p-cresol (CAS 128-37-0), aka BHT (butylated hydroxytoluene), an antioxidant and preservative

Wetcit has a Warning signal word. It may cause skin and eye irritation or temporary eye damage and may be harmful if absorbed through skin or inhaled. It is also considered a potential long-term hazard to the aquatic environment. In terms of PPE, the label states that eye or face protection is required while the SDS also mentions chemical resistant gloves and recommends an impervious apron. The signal word on the label does not conflict with the latest SDS from 12/7/17.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral, inhalation, and dermal exposure (but not a skin sensitizer). It is noted as causing serious eye irritation in rabbits, but injury is reversible. The SDS notes that it is not considered a carcinogen.

Aquatic acute toxicity data for the formulation are available on the SDS (refer to Table 2). The SDS describes a toxicity test involving the freshwater fish *Danio rerio* (zebrafish) which indicated a 96-hour LC₅₀ of 18.7 mg/L. The SDS also lists data for tests on *Daphnia* (water flea) showing a 48-hour EC₅₀ of 11 mg/L. There are also several values for a freshwater green algae (*Pseudokirchnerella subcapitata*), including a 72-hour NOEC of 2.32 mg/L. The SDS notes that Wetcit is harmful to aquatic life with long lasting effects, although the data indicate it is only slightly toxic to fish and *Daphnia*.

The ingredients list on the label is very brief and somewhat unusual in that it states that over 91% of the formulation is ineffective as a spray adjuvant. The active ingredient is listed as an ethoxylated alcohol. The SDS further identifies this as an ethoxylated 11-15 carbon secondary alcohol; the CAS number refers to a linear alcohol. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

The SDS also lists sweet orange extract which is an essential oil pressed from the peels of sweet oranges. It is composed mostly of d-limonene (>90%) and is often used in place of pure d-limonene. Sweet orange extract has a signal word of Danger due to risk of death if aspirated into the lungs. It is a flammable liquid and a skin irritant and sensitizer (contact dermatitis). It is only slightly acutely toxic if swallowed. Sweet orange extract is very toxic to aquatic life with long-lasting effects (e.g., 96-hour LC₅₀ (fish) - 0.32 mg/L; 48-hour EC₅₀ (invertebrates) - 0.45 mg/L).

Section 8 of the SDS also lists ethanol, sodium hydroxide, and 2,6-di-tert-butyl-p-cresol as potential air contaminants from the use of Wetcit. But it is not known how much of the formulation is made up of these three ingredients. It is also unknown whether there are additional undisclosed ingredients.

Ethanol (or grain alcohol) is likely added to assist as a solvent for the sweet orange extract. Alcohol is readily absorbed into the bloodstream from the stomach and intestines. It acts as a central nervous system depressant. Ethanol has a signal word of Danger because of its flammability, but it can also cause eye irritation and organ damage. It may be a carcinogen. It is slightly toxic via acute oral exposure. Sodium hydroxide is a caustic material that can decompose proteins and lipids in living tissues resulting in chemical burns. It has a signal word of Danger due to its corrosiveness to skin and eyes. It can also be corrosive to metals. As a liquid it is clear, colorless, and odorless. Inhalation, ingestion, skin contact can all be damaging to those tissues. 2,6-di-tert-butyl-p-cresol (aka BHT, or butylated hydroxytoluene) is primarily used as an antioxidant food additive and is GRAS. It has a signal word of Warning due to its hazard to the aquatic environment. It is considered an eye and skin irritant. Although there is limited evidence of carcinogenicity in animals, there are no data for cancer in humans. It is acutely toxic to aquatic organisms and is expected to bioaccumulate in the aquatic environment.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Rainier-EA™ Nonionic Surfactant – Activator – Spreader (Wilbur-Ellis Company)

CA Reg. #2935-50200; WA Reg. #2935-15001

Active Ingredients – 98%, surfactant content 88%, noted as NPE-free

Polyoxyethylene polyol fatty acid ester – not further identified (a bio-oil?)

Butyl lactate (CAS 138-22-7) – 10-20% (surfactant?)

Alcohol ethoxylate phosphate ester – not further identified

SDS lists 1,4-dioxane and oxirane, both the results of using ethoxylated compounds

SDS lists acetaldehyde, CAS 75-07-0 (contaminant?)

SDS lists diethanolamine, CAS 111-42-2 (surfactant? thickener? or byproduct of ethylene oxide breakdown?)

Rainier-EA™ has a Caution signal word which is not part of the GHS. A compound that doesn't fit the Danger or Warning signal word typically has no signal word. It may cause slight eye irritation. The label-required PPE (chemical-resistant gloves) is not consistent with the SDS (which also requires eye protection). The SDS does not have a signal word associated with it due to its low toxicity, which is consistent with the label.

The SDS does not contain any numerical toxicity data for the formulated product or any of its ingredients. It may cause some minor eye irritation; prolonged skin contact may result in skin irritation; prolonged inhalation may be harmful.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients, and the SDS states that the product is not classified as environmentally hazardous. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. These data indicate this product is considered slightly toxic to fish and practically nontoxic to Daphnia. This product is approved for aquatic use by the state of Washington.

The list of ingredients on the label are somewhat generic and no clarifying additional information is in the most recent SDS.

The generic ingredient description of polyoxyethylene polyol fatty acid ester could be referring to a polysorbate emulsifier or surfactant (a common name used are Tweens). They are soluble or dispersible in water but differ widely in organic and oil solubilities. Ethoxylated sorbitan esters have 20 ethoxylate groups. Their variation is dependent on the esterified fatty acid associated with the ethoxylated sorbitan. The generic descriptions on the label and SDSs do not indicate which polysorbate is used; common ones are polysorbate 20, polysorbate 40, polysorbate 60, and polysorbate 80. The first three have no signal word as they are of low acute toxicity and are not eye or skin irritants. They are of low aquatic toxicity. Polysorbate 80 may show a signal word of Warning due to eye and skin irritation (although many SDSs show no signal word for this polysorbate either).

Butyl lactate is an ester (butyl ester of lactic acid) and is likely added as a solvent or as a co-surfactant. It has a signal word of Warning due to serious eye damage, also it can cause skin and eye irritation. Butyl lactate is slightly toxic with an oral LD₅₀ >2 g/kg in the rat and a dermal LD₅₀ >5 g/kg in the rabbit. Inhalation can cause irritation and effects in nasal passages, although it is considered only slightly irritating with a 4-hour inhalation LD₅₀ in the rat >5.14 g/m³. It is considered readily biodegradable, and would not be expected to bioaccumulate in the aquatic environment (estimated BCF of 3). In freshwater zebrafish, it has a 96-hour LC₅₀ of 75 mg/L and with the waterflea it has a 48-hour EC₅₀ of 320 mg/L.

Alcohol ethoxylate phosphate ester is likely an anionic phosphate ester surfactant, but without more identifying information the specific compound cannot be determined.

The SDS lists acetaldehyde which is likely a residual chemical intermediate, byproduct, or contaminant. It has a signal word of Danger due to its flammability. It can cause serious eye irritation, respiratory irritation. It is a suspected carcinogen. As Rainier-EA™ is not regarded as flammable, the levels of acetaldehyde in the formulation are likely low.

The SDS lists diethanolamine which could be included as an emulsifier and/or dispersing agent, but is more likely present as a contaminant. It has a signal word of Danger due to risk to eyes, but also can cause skin irritation and/or corrosion. It is considered harmful if swallowed (acute and chronic toxicity). Diethanolamine may affect the liver and kidneys with prolonged exposure. It is not a skin sensitizer. Considered a possible human carcinogen. It is of low aquatic toxicity.

Ethylene oxide and 1,4-dioxane are listed in the SDS and are a small component of any adjuvant that contains ethoxylated compounds. They are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Liberate® Penetrant, Deposition Aid, Drift Control Agent (Loveland Products)

CA Reg. # 34704-50030; WA Reg. # 34704-04008

Active Ingredients – 100%

Lecithin, CAS 8002-43-5

Methyl esters of fatty acids, CAS 67784-80-9

Alcohol ethoxylate, CAS 34398-01-1

Liberate® has a Warning signal word. It may cause eye irritation. It may be harmful if absorbed through skin or inhaled. Release to the environment should be avoided (although the SDS states that Liberate® is not considered environmentally hazardous). In terms of PPE, the label and SDS both state that gloves and eye or face protection is required. The SDS also mentions a respirator if spraying or misting (but likely referring to the undiluted formulation). The signal word on the label does not conflict with the latest SDS from 9/7/16.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered practically non-toxic via oral exposure and slightly toxic via dermal or inhalation exposure (but not a skin sensitizer). It is noted as an eye irritant in rabbits.

Aquatic acute toxicity data for the formulation are available on the SDS (refer to Table 2). The SDS describes a toxicity test involving the freshwater fish *Oncorhynchus mykiss* (rainbow trout) which indicated a 96-hour LC₅₀ of 17.6 mg/L and a corresponding 96-hour NOEC of 12.5 mg/L. The SDS also lists data for tests on *Daphnia magna* (water flea) showing a 48-hour EC₅₀ of 9.3 mg/L and a corresponding 48-hour NOEC of 7.5 mg/L. The SDS notes that Liberate® drift or runoff may affect non-target plants. The data indicate that this product is slightly toxic to fish and moderately toxic to *Daphnia*. This product is approved for aquatic use by the state of Washington.

Lecithin is a generic term to designate any group of yellow-brownish fatty substances occurring in animal and plant tissues usually available from sources such as soybeans, egg yolk, milk, marine sources, rapeseed, cottonseed, and sunflower oil. It has low solubility in water, but is an excellent emulsifier. Lecithins have emulsification and lubricant properties and are used as surfactants. Lecithin has no signal word as it is not considered hazardous. Lecithin is sold as a food additive and dietary supplement.

The CAS number in the SDS associated with the methyl esters of fatty acids leads to methylated soybean oil. An ester of methyl alcohol and soy acid, it is considered a replacement for petroleum ingredients, such as in biodiesel. Methylated soybean oil has no signal word as it is not considered hazardous. Exposure may cause mild irritation of nose and throat and mild irritation of skin and eyes.

The CAS number in the SDS associated with the alcohol ethoxylate leads to an ethoxylated linear alcohol that represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular product is unknown. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. This ethoxylated alcohol has a signal word of Danger due to its strong eye irritation, which can result in eye damage or blindness; it is also a skin irritant. It is rapidly biodegradable but is also acutely toxic to aquatic organisms with a 48-hour EC_{50} of 5-10 mg/L in waterfleas and a 96-hour LC_{50} of 5-10 mg/L in an unspecified species of fish.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Silicone-based Surfactants

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 4.b. in Section 4.

Freeway[®] (Loveland Products, Inc.)

CA Reg. #34704-50031, WA Reg. #34704-04005

Active Ingredients – 100%; surfactant content 99%

Silicone-polyether copolymer (CAS 67674-67-3) (silicone surfactant)

Alcohol ethoxylates (CAS 60828-78-6) (surfactant) (aka polyethylene glycol trimethylnonyl ether; Tergitol is a common brand name)

Propylene glycol (CAS 57-55-6)

Dimethylpolysiloxane (CAS 67762-90-7) (antifoam)

Freeway[®] has a Warning signal word. Freeway[®] can cause serious eye irritation. Release to waterways should be avoided. In terms of PPE, the label and SDS both state that gloves and eye or face protection is required. The SDS also mentions a respirator if there is a risk of inhaling mists or vapors (but likely referring to the undiluted formulation). The signal word on the label does not conflict with the latest SDS from 2/20/19.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). Based on the description of the hazards in the SDS, this product is considered slightly toxic via oral, dermal exposure, or inhalation exposure. The acute toxicity values in the SDS appear to be in error or represent a product with considerably more hazard than the SDS language implies, e.g., the oral LD₅₀ is shown as <5 g/kg and the inhalation LC₅₀ is >0.01 mg/L. It is considered a skin sensitizer with repeated exposures. It is noted as a serious eye irritant in rabbits.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. The SDS states that the product is not classified as environmentally hazardous. There is an acute toxicity value for bluegill in a 2003 study (Haller and Stocker 2003) that is shown in Table 2. It is not known whether the product tested in that study is the same formulation as this registered product. Based on this limited data, this product would be considered slightly toxic to fish.

The CAS number for the silicone-polyether copolymer refers to a four-silicon ethoxylated siloxane molecule. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers. They are also used in cosmetics (as antifoamers and skin conditioners), paints and other products. They consist of a hydrophobic polysiloxane backbone and a hydrophilic ethylene oxide chain. The number of ethoxylate groups is not specified in this particular CAS number. These have a signal word of Danger due to risk of serious eye damage/irritation as well as representing an acute health hazard if inhaled. This ethoxylated siloxane is considered toxic to aquatic life, representing a long-term hazard, but has a low potential for bioaccumulation. It has low mobility in soils.

The ingredient dimethylpolysiloxane is somewhat generic as it includes the segment *poly*, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. This may be dimethicone (CAS 9016-00-6). Although this may or may not be the actual product used in this formulation, many of the closely related linear silicones have similar tox profiles. Dimethicone is not absorbed after ingestion based on testing in rats, dogs, and mice and is excreted unchanged in the feces. For this reason, it is practically non-toxic on an acute oral basis (rat LD₅₀ values range from 7 to 27 g/kg). It is a component of antacids, gas relievers, and cosmetics. It is of low acute toxicity to aquatic organisms and is not expected to bioaccumulate.

The CAS number in the SDS associated with the alcohol ethoxylate leads to a branched secondary alcohol ethoxylate with a 12-14 carbon chain that represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular product is unknown. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. This ethoxylated alcohol has a signal word of Danger due to its strong eye

irritation, which can result in eye damage. It is rapidly biodegradable but is also acutely toxic to aquatic organisms with a 96-hour LC_{50} of 10-100 mg/L in an unspecified species of fish.

Propylene glycol is a tasteless, odorless and colorless clear oily liquid that is very soluble in water. It is the primary ingredient in low toxicity antifreezes (RV or marine antifreeze). GRAS material; used in some processed foods as a solvent for flavors and colors or as a humectant. Used as a humectant in hand sanitizers. It is a principal ingredient in vaping solutions. In this adjuvant, it could be added as a solvent, as a humectant, or as a defoamer. Quickly metabolized in mammals after ingestion, although a large portion remains unmetabolized and excreted in urine. Half-life in humans is measured in hours, although it can be toxic in large doses over short time, otherwise propylene glycol is of low oral toxicity. Oral LD_{50} values range from 8 to 46 g/kg. It is not a skin sensitizer nor an eye or skin irritant. It is not considered a carcinogen or mutagen. It is of low aquatic toxicity; LC_{50} values for freshwater fish and invertebrates range from 11,000 to 77,400 ppm.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Silwet L-77[®] (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50073 WA Reg. #5905-50073

Active Ingredients – 99.5%

Polyalkyleneoxide modified heptamethyltrisiloxane identified in older MSDS as CAS 27306-78-1, 80-90%

Allyloxypolyethyleneglycol methyl ether (CAS 27252-80-8), 10-20%

Silwet L-77[®] has a Warning signal word. It may be slightly irritating to the skin and can cause serious eye irritation. It is not a skin sensitizer. It may be harmful if swallowed or inhaled. In terms of PPE, the label and SDS both state that gloves and eye or face protection is required, although the SDS also states that a chemical resistant apron and footwear should be worn. The signal word on the label does not conflict with the latest SDS from 4/14/15.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral and dermal exposure. There are no acute inhalation data in the SDS although there is a statement that a substantially saturated vapor did not result in any deaths over six hours of exposure. It is not a skin sensitizer. It can cause some skin peeling with extended skin contact. It is a severe eye irritant. A 14-day dietary feeding study (no dosage specified) in rats showed that repeated high dosages causes reversible adverse effects on the male and female reproductive tracts. Further information is available on an older MSDS from OSI Specialties (1/10/01) - other effects seen were increased liver weight, altered blood cytology/chemistry, and thyroid enlargement. Evidence of partial or complete recovery was seen over a 28-day recovery period.

There are no quantitative aquatic acute toxicity data in the most recent SDS. An older MSDS from OSI Specialties (1/10/01) provides aquatic toxicity data (refer to Table 2). This older MSDS describes a toxicity test involving the zebrafish which indicated a 96-hour LC_{50} of 2.8 mg/L and a corresponding 96-hour NOEC of 0.6 mg/L. The MSDS also lists data for tests on

Daphnia magna (water flea) showing a 48-hour EC₅₀ of 22.6 mg/L and a corresponding 48-hour NOEC of 10 mg/L. In addition, the MSDS also lists a 96-hour EC₅₀ (growth) for green algae of 5.5 mg/L, with a corresponding 96-hour NOEC of 1 mg/L. There is an LD₅₀ value for *Daphnia pulex* in a 2003 study (Stark and Walthall 2003). It is not known whether the product tested in this study is the same formulation as this registered product. Based on these data, this product would be moderately toxic to fish slightly toxic to *Daphnia* and moderately toxic to green algae.

The CAS numbers for the two active ingredients come from the older OSI Specialties MSDS. The polyalkylenoxide modified heptamethyltrisiloxane is an ethoxylated siloxane. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic trisiloxane backbone and a hydrophilic ethylene oxide chain. This ingredient is based on a trisiloxane with some number of ethoxylate groups. This has a signal word of Warning due to eye irritation and damage; skin irritation and damage; and acute oral and inhalation toxicity. This trisiloxane is considered toxic to aquatic life with acute toxicity figures comparable to the Silwet L-77[®] formulation. It is not readily biodegradable.

The other listed active ingredient, allyloxy polyethylene glycol methyl ester is an alcohol ethoxylate, however the number of ethoxylate groups is unknown. It could be used in this formulation as an additional surfactant or wetting agent, although it may occur in silicone surfactants as an impurity from the manufacturing process (WSDA 2019). The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Kinetic[®] Nonionic Wetter/Spreader/Penetrant Adjuvant - California Label - (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50087, OMRI Listed

Active Ingredients – 99%

Polyalkyleneoxide modified polydimethylsiloxane, not further identified

Nonionic surfactants, not further identified

Kinetic[®] has a Warning signal word. It can cause skin and eye irritation and is noted as a possible skin sensitizer. It may be harmful if swallowed or inhaled. In terms of PPE, there is a conflict between the label and the SDS. The label only requires chemical resistant gloves, while the SDS, in addition to gloves, requires eye protection and a protective apron. The signal word on the label does not conflict with the latest SDS from 10/9/15.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral and dermal exposure. It is moderately toxic via inhalation.

Although it is only mildly irritating to the skin, the SDS states that dermal exposure may cause allergic skin reactions. Kinetic[®] is mildly irritating to the eyes.

There are no quantitative aquatic acute toxicity data in the most recent SDS. There is an acute toxicity value for bluegill in a 2003 study (Haller and Stocker 2003) that is shown in Table 2. There is an LD₅₀ value for *Daphnia pulex* in a 2003 study (Stark and Walthall 2003). It is not known whether the product tested in those studies is the same formulation as this registered product. These data would indicate that this product is slightly toxic to fish and practically nontoxic to *Daphnia*.

The polyalkylenoxide modified polydimethylsiloxane is an ethoxylated polydimethylsiloxane. The generic name does not allow for a determination of the number of dimethylsiloxane molecules or the degree of ethoxylation present. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers, but in this formulation, this is likely the main surfactant. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic siloxane backbone and a hydrophilic ethylene oxide chain. Similar to the alcohol ethoxylates, toxicity appears to be related to the number of ethoxylate groups, with more ethoxylate groups representing lower toxicity.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to Issue Discussions in Section 4.b.

The label indicates that the other active ingredient is a generic nonionic surfactant. Whether this is an alkylphenol ethoxylate or an ethoxylated alcohol, or some other type of surfactant is unknown.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Kinetic[®] Nonionic Surfactant and Silicone Surfactant Blend – Washington Label - (Helena Agri-Enterprises, LLC)

WA Reg. #5905-11004

Active Ingredients – 99%

Polyoxyethylene-polyoxypropylene copolymer, not further identified

Polysiloxane polyether copolymer, not further identified

Kinetic[®] has a Warning signal word. It can cause skin and eye irritation. It may be harmful if swallowed or inhaled. In terms of PPE, there is a conflict between the label and the SDS. The label requires chemical resistant gloves and eye protection, while the SDS also requires a protective apron. The signal word on the label does not conflict with the latest SDS from 8/11/17.

Limited mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral and dermal exposure. There are no acute inhalation toxicity data available.

There are no quantitative aquatic acute toxicity data in the most recent SDS. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. There is an acute toxicity value for bluegill in a 2003 study (Haller and Stocker 2003) that is also shown in Table 2. There is an LD₅₀ value for *Daphnia pulex* in a 2003 study (Stark and Walthall 2003). It is not known whether the product tested in those 2003 studies is the same formulation as this Washington-state registered product. These data would indicate this product is moderately toxic to fish and practically nontoxic to Daphnia. This product is approved for aquatic use in the state of Washington.

The polyoxyethylene-polyoxypropylene copolymer represents a family of copolymers, combining ethylene oxide and propylene oxide. Used as a surfactant and antifoamer. The polyoxypropylene is a hydrophobic molecule and is combined with two flanking hydrophilic ethylene oxide chains. The name is generic and does not provide any idea of the exact nature and number of the two copolymers. These copolymers are also used as a treatment for alfalfa bloat in cattle. These copolymers are excreted quickly through urine with little metabolism. Some SDSs have no signal word due to low toxicity, others have a signal word of Warning due to inhalation risk. Acute oral LD₅₀ values in rats range from 2,300 - 22,400 mg/kg (considered slightly toxic to practically non-toxic). The dermal LD₅₀ values in rabbits range from >5 – 20 g/kg (practically non-toxic). Aquatic acute toxicity is low.

The polysiloxane polyether copolymer is likely referring to an ethoxylated polydimethylsiloxane. The generic name does not allow for a determination of the number of dimethylsiloxane molecules or the degree of ethoxylation present. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wettors or as defoamers, but in this formulation, this is likely the main surfactant. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic siloxane backbone and a hydrophilic ethylene oxide chain. Similar to the alcohol ethoxylates, toxicity appears to be related to the number of ethoxylate groups, with more ethoxylate groups representing lower toxicity.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to Issue Discussions in Section 4.b.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Silwet[®] Eco Spreader (Momentum Performance Materials, Inc.)

CA Reg. #1051186-50002

Active Ingredients – 100%, OMRI Certified

Siloxane Polyalkyleneoxide copolymer (50 - <100%), not further identified

SDS lists polyalkylene oxide

SDS lists 2-propanol (aka isopropyl alcohol, CAS 67-63-0)

A label for Silwet[®] Eco Spreader was not found on-line. The company's website provides a technical data sheet and an SDS. The signal word in the SDS is Warning, due to an inhalation hazard. PPE listed in the SDS includes eye protection and chemical resistant gloves. It is non-irritating to the eyes but moderately irritating to the skin, but is not a skin sensitizer.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral and dermal exposure. It is considered slightly to moderately toxic via inhalation. In three mammalian test systems, it was not considered mutagenic. A 14-day dietary feeding study (no dosage specified) in rats showed that repeated high dosages causes reversible adverse effects on the male and female reproductive tracts; other effects seen were increased liver weight, altered blood cytology/chemistry, and thyroid enlargement. Evidence of partial or complete recovery was seen over a 28-day recovery period.

There are limited aquatic toxicity data in the SDS (refer to Table 2). This SDS describes a toxicity test involving rainbow trout which indicated a 96-hour LC₅₀ of 2.1 mg/L and a corresponding 96-hour NOEC of 1 mg/L. The SDS lists the active ingredient as an environmentally hazardous substance. The value for rainbow trout would indicate this product is moderately toxic to fish.

The only identified ingredient, siloxane polyalkyleneoxide copolymer, is likely referring to an ethoxylated polydimethylsiloxane. The generic name does not allow for a determination of the number of dimethylsiloxane molecules or the degree of ethoxylation present. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers, but in this formulation, this is likely the main surfactant. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic siloxane backbone and a hydrophilic ethylene oxide chain. Similar to the alcohol ethoxylates, toxicity appears to be related to the number of ethoxylate groups, with more ethoxylate groups representing lower toxicity.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to Issue Discussions in Section 4.b.

The SDS also lists 2-propanol, otherwise known as isopropyl (or rubbing) alcohol. This is likely added to the formulation as a solvent. It has a signal word of Danger due to its flammability; it is also a serious eye irritant and central nervous system depressant. It is not classifiable as a human carcinogen. It is slightly toxic through oral and dermal exposure and is practically nontoxic through inhalation exposure. Isopropyl alcohol is of low aquatic toxicity, with a 96-hour LC₅₀ in rainbow trout of 13,000 mg/L and an EC₅₀ to the waterflea of 10,000 mg/L.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Hi-Wett® (Loveland Products, Inc.)

CA Reg. #34704-50093; WA Reg. #34704-15002

Active Ingredients – 100%

Polydimethylsiloxane polyether copolymer – not further identified, in SDS polyalkyleneoxide modified heptamethyltrisiloxane (30-50%)

Alcohol ethoxylate – not further identified (non-ionic surfactant)

Polyoxyethylene-polyoxypropylene copolymer – not further identified

Hi-Wett[®] has a Warning signal word. It can cause serious eye irritation and is slightly irritating to the skin (but is not a sensitizer). It may be harmful if inhaled. In terms of PPE, the label and SDS both state that gloves and eye or face protection is required, although the SDS also states that a respirator should be worn during operations where spraying or misting occur. The signal word on the label does not conflict with the latest SDS from 2/26/19.

Mammalian acute toxicity data are available on the SDS (refer to Table 1). This product is considered slightly toxic via oral and dermal exposure. It is considered moderately toxic via inhalation.

There are limited aquatic toxicity data in the SDS (refer to Table 2). This SDS describes a toxicity test involving rainbow trout which indicated a 96-hour LC₅₀ of 4.5 mg/L. The SDS describes this product as not being classified as environmentally hazardous. The value for rainbow trout would indicate this product is moderately toxic to fish.

The identified ingredient in the SDS, polyalkylenoxide modified heptamethyltrisiloxane, is an ethoxylated siloxane. In this case, the siloxane is based on a three-silicon structure. The generic name does not allow for a determination of the number of heptamethyltrisiloxane molecules or the degree of ethoxylation present. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers, but in this formulation, this is likely the main surfactant. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic siloxane backbone and a hydrophilic ethylene oxide chain. Similar to the alcohol ethoxylates, toxicity appears to be related to the number of ethoxylate groups, with more ethoxylate groups representing lower toxicity.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to Issue Discussions in Section 4.b.

Ethoxylated alcohol, not otherwise described, is listed as an ingredient in Hi-Wett[®]. This could be in the formulation as a surfactant. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

The polyoxyethylene-polyoxypropylene copolymer represents a family of copolymers, combining ethylene oxide and propylene oxide. Used as a surfactant and antifoamer. The polyoxypropylene is a hydrophobic molecule and is combined with two flanking hydrophilic ethylene oxide chains. The name is generic and does not provide any idea of the exact nature and number of the two copolymers. These copolymers are also used as a treatment for alfalfa bloat in cattle. These copolymers are excreted quickly through urine with little metabolism. Some SDSs have no signal word due to low toxicity, others have a signal word of Warning due to inhalation risk. Acute oral LD₅₀ values in rats range from 2,300 - 22,400 mg/kg (considered slightly toxic to practically non-toxic). The dermal LD₅₀ values in rabbits range from >5 – 20 g/kg (practically non-toxic). Aquatic acute toxicity is low.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

b. Cationic Surfactants

Ethoxylated Tallow Amine (Entry™ II; polyoxyethyleneamine (POEA) surfactant)

Entry™ II is no longer registered in California; likely no longer commercially available
Active Ingredients – 35%

Ethoxylated Tallow Amine 35% by weight (CAS 61791-26-2) aka polyoxyethyleneamine or POEA

Water 64.5%?

Isopropylamine 0.5% (CAS 75-31-0)

POEA is found in some commercial glyphosate formulations.

Entry™ II (35% POEA) has a Danger signal word due to eye damage (burns). It is also a skin irritant, may be a skin sensitizer. It is harmful if swallowed. A recent SDS from Stepan Chemical Company for a product called Toximul TA-5 (a much more concentrated 90-100% POEA) also has a Danger signal word due to severe effects to the skin and eyes, and burns to the digestive tract if swallowed. It is also considered an acute and long-term hazard to the aquatic environment. Both the Entry™ II SDS and the Toximul SDS call for protective eyewear and gloves; while the more concentrated Toximul also calls for chemical resistant clothing.

Limited mammalian acute toxicity data are available on the Toximul TA-5 SDS (refer to Table 1). This product is considered moderately toxic via dermal exposure (although severe skin burns and skin sensitization are noted on the SDS). It is considered slightly toxic via oral exposure. It is considered moderately toxic via inhalation.

There are limited aquatic toxicity data in the Entry™ II MSDS and the Toximul TA-5 SDS (refer to Table 2). The Entry™ II MSDS describes tests that involved a 70% concentration of POEA. The test involving rainbow trout indicated a 96-hour LC₅₀ of 4.2 mg/L and the same test on bluegill sunfish with an LC₅₀ of 1.3 mg/L. The waterflea had a 48-hour EC₅₀ of 2 mg/L. For the more concentrated Toximul TA-5 (90-100% POEA), the 96-hour LC₅₀ for fish (species not indicated) ranged from 0.2 – 1 mg/L. The waterflea had a 48-hour EC₅₀ of 0.5 mg/L. These values indicate that POEA is moderately toxic to aquatic species.

POEA is not a single surfactant. POEA surfactants are mixtures. For a comprehensive look at the hazards and risks of POEA as a surfactant in some glyphosate formulations, refer to SERA 1997a and SERA 2011a.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

The Toximul TA-5 SDS lists acetaldehyde which is likely a residual chemical intermediate, byproduct, or contaminant. It has a signal word of Danger due to its flammability. It can cause serious eye irritation, respiratory irritation. It is a suspected carcinogen. As Toximul TA-5 is not regarded as flammable, the levels of acetaldehyde in the formulation are likely low.

The Toximul TA-5 SDS lists ethylene glycol which is likely present as a minor contaminant from an interaction of ethylene oxide and water. It has a signal word of Warning due to its acute oral toxicity. Ethylene glycol is irritating to the eyes and skin as well as the respiratory tract. Target organs in mammals are the kidneys and nervous system. It is of low aquatic toxicity.

c. Sticker/Spreaders

Bond[®] Spreader Sticker Deposition Aid (Loveland Products, Inc.)

CA Reg. #34704-50033; WA Reg. #34704-04003

Active Ingredients – 55%

Synthetic latex – 45% (not further identified)

Alcohol ethoxylate (primary aliphatic oxyalkylated alcohol) – 10%, a linear alcohol with unspecified carbon chain length.

Bond[®] has a Warning signal word. This material is a skin irritant but is not a skin sensitizer. It is noted as being a serious eye irritant. It is somewhat toxic to aquatic organisms. Bond[®] may no longer be commercially available as only a 2010 MSDS is available and the product isn't featured on the Loveland website. This older MSDS has a signal word of Caution, so there is a conflict between the label and the MSDS as to signal word. As for PPE, the label only calls for gloves, while the MSDS only calls for eye protection.

Mammalian acute toxicity data are in the MSDS (refer to Table 1). This product is considered slightly toxic via dermal exposure and is not a skin sensitizer. It is considered practically non-toxic via oral exposure. It is considered slightly toxic via inhalation.

There are limited aquatic toxicity data in the MSDS; one test on waterfleas (refer to Table 2). The test indicated a 48-hour EC₅₀ of 614 mg/L, although this same value is referred to as an LD₅₀ in Stark and Walthall 2003, which appears to be the study which determined this value. There is an acute toxicity value for rainbow trout listed in a Washington State document (WSDA 2018), which is shown in Table 2. These data would indicate this product is practically non-toxic to fish and Daphnia. This product is approved for aquatic use by the state of Washington.

Bond[®] is a mixture of synthetic latex and a linear alcohol (identified in the MSDS as a primary aliphatic oxyalkylated alcohol). The large percentage of inert ingredients (45%) in this formulation is troublesome; it is unknown if the inerts are all or mostly water or made up of other ingredients.

The exact composition of the synthetic latex is not specified; it is likely an acrylic latex.

The exact composition of the primary aliphatic oxyalkylated alcohol is not specified. It is an ethoxylated alcohol, but the degree of ethoxylation and the range of carbon molecules in the alcohol is unspecified.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Bond Max[®] Spreader Sticker Deposition Aid (Loveland Products, Inc.)

CA Reg. #34704-50060; WA Reg. #34704-08003

Active Ingredients – 57.5%

Alcohol ethoxylate (CAS 68154-97-2, alcohols, C10-12, ethoxylated propoxylated)

1,2-propanediol (propylene glycol) CAS 57-55-6

Synthetic latex – not further identified

Bond Max[®] has a Warning signal word. This material is a skin irritant but is not a skin sensitizer. It is noted as being a serious eye irritant. It may be irritating to the respiratory system if inhaled, and is noted as possibly causing mucous membrane irritation if ingested. There is no conflict between the label and the SDS as to signal word. As for PPE, both the label and SDS call for gloves and eye protection. The SDS warns that the product may penetrate gloves and that frequent glove changes are advisable.

Mammalian acute toxicity data are in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure but is not a skin sensitizer. It is considered slightly toxic via oral exposure and inhalation. It is a severe eye irritant.

There are limited aquatic toxicity data in the SDS (refer to Table 2). Tests on bluegill (*Lepomis macrochirus*) indicate a 96-hour LC₅₀ of 360 mg/L (noted as from a similar product). There is also a 96-hour NOEC for the same species of 220 mg/L. The SDS notes that drift or runoff may affect non-target plants. The limited toxicity data would indicate this product as being practically nontoxic to fish.

Bond Max[®] is a mixture of synthetic latex, propylene glycol, and an alcohol ethoxylate. The large percentage of inert ingredients (42.5%) in this formulation is troublesome; it is unknown if the inerts are all or mostly water or made up of other ingredients.

The exact composition of the synthetic latex is not specified; it is likely an acrylic latex.

Propylene glycol is a tasteless, odorless and colorless clear oily liquid that is very soluble in water. It is the primary ingredient in low toxicity antifreezes (RV or marine antifreeze). GRAS material; used in some processed foods as a solvent for flavors and colors or as a humectant. Used as a humectant in hand sanitizers. It is a principal ingredient in vaping solutions. In this adjuvant, it could be added as a solvent, as a humectant, or as a defoamer. Quickly metabolized in mammals after ingestion, although a large portion remains unmetabolized and excreted in urine. Half-life in humans is measured in hours, although it can be toxic in large doses over short time, otherwise propylene glycol is of low oral toxicity. Oral LD₅₀ values range from 8 to 46 g/kg. It is not a skin sensitizer nor an eye or skin irritant. It is not considered a carcinogen or

mutagen. It is of low aquatic toxicity; LC₅₀ values for freshwater fish and invertebrates range from 11,000 to 77,400 ppm.

The ethoxylated alcohol in this formulation, based on the CAS number in the SDS, is a linear alcohol with 10-12 carbon atoms and an unknown ethoxylate chain length. This alcohol has a Danger or Warning signal word (varies depending on the product SDS) due to eye irritation or damage. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Tactic™ Sticker – Surfactant – Deposition Aid (Loveland Products, Inc.)

CA Reg. #34704-50041; WA Reg. #34704-05008

Active Ingredients – 63.4%

Synthetic latex copolymer, CAS 52831-07-9

1,2-propanediol (propylene glycol), CAS 57-55-6

alcohol ethoxylate, CAS 34398-01-1, (a linear alcohol with unspecified carbon chain length)

silicone polyether copolymer, CAS 67762-90-7

Tactic™ has a Warning signal word. It may be a slight skin irritant, but is not a skin sensitizer. Tactic™ may be harmful if inhaled. There is no conflict between the label and the SDS as to signal word. As for PPE, both the label and SDS call for gloves and eye protection, but the SDS also notes that respiratory protection should be used during operations where spraying or misting occurs.

Mammalian acute toxicity data are in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure but is not a skin sensitizer. It is considered practically nontoxic via oral exposure and slightly toxic via inhalation. There is no information on eye irritation.

There are limited aquatic toxicity data in the SDS (refer to Table 2). Tests on freshwater guppy (*Poecilia reticulata*) indicate a 96-hour LC₅₀ of 160 mg/L. Tests on *Daphnia magna* indicate a 24-hour EC₅₀ of 99.1 mg/L. The SDS notes that drift or runoff may affect non-target plants. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are also shown in Table 2. These data would indicate this product is practically nontoxic to fish and *Daphnia*. This product is approved for aquatic use by the state of Washington.

Tactic™ is a blend of synthetic latex and a silicone-based wetter/spreader, along with an ethoxylated linear alcohol and propylene glycol. The large percentage of inert ingredients

(36.6%) in this formulation is troublesome; it is unknown if the inerts are all or mostly water or made up of other ingredients.

The exact composition of the synthetic latex is not specified; it is likely an acrylic latex. The CAS number leads to carboxylated styrene-butadiene polymer, a synthetic rubber; however, no relevant health data could be pulled from the internet on SDS documents for the specific CAS number. Appears to be a rather benign substance.

The ingredient dimethylpolysiloxane is somewhat generic as it includes the segment *poly*, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. This may be dimethicone (CAS 9016-00-6). Although this may or may not be the actual product used in this formulation, many of the closely related linear silicones have similar tox profiles. Dimethicone is not absorbed after ingestion based on testing in rats, dogs, and mice and is excreted unchanged in the feces. For this reason, it is practically non-toxic on an acute oral basis (rat LD₅₀ values range from 7 to 27 g/kg). It is a component of antacids, gas relievers, and cosmetics. It is of low acute toxicity to aquatic organisms and is not expected to bioaccumulate.

The linear ethoxylated alcohol is not adequately described to say anything definite about its toxicology. The CAS number represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular alcohol is unknown. The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. It has a GHS signal word of Danger due to its strong eye irritation, which can result in eye damage or blindness. It is also a skin irritant. EPA classifies it as a “Safer Choice” ingredient in surfactants because of its rapid rate of biodegradation, although it is acutely toxic to aquatic animals (more so than aquatic plants or algae).

Propylene glycol is a tasteless, odorless and colorless clear oily liquid that is very soluble in water. It is the primary ingredient in low toxicity antifreezes (RV or marine antifreeze). GRAS material; used in some processed foods as a solvent for flavors and colors or as a humectant. Used as a humectant in hand sanitizers. It is a principal ingredient in vaping solutions. In this adjuvant, it could be added as a solvent, as a humectant, or as a defoamer. Quickly metabolized in mammals after ingestion, although a large portion remains unmetabolized and excreted in urine. Half-life in humans is measured in hours, although it can be toxic in large doses over short time, otherwise propylene glycol is of low oral toxicity. Oral LD₅₀ values range from 8 to 46 g/kg. It is not a skin sensitizer nor an eye or skin irritant. It is not considered a carcinogen or mutagen. It is of low aquatic toxicity; LC₅₀ values for freshwater fish and invertebrates range from 11,000 to 77,400 ppm.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Cohere® Nonionic Spreader Sticker Adjuvant (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50083

Active Ingredients – 88%

Alkanolamide surfactants - not further identified
Alkylaryl polyethoxyethanol sulfates – not further identified
1,2-propanediol (propylene glycol, CAS 57-55-6)
SDS also lists three compounds listed by California as suspected of being carcinogens: 1,4-dioxane; acetaldehyde; and, formaldehyde (likely impurities).

Cohere[®] has a Warning signal word. It is noted as causing skin irritation and serious eye irritation. It may be harmful if swallowed or inhaled. There is no conflict between the label and SDS as regards the signal word, but there is a conflict between the label and the SDS as regards PPE: the label only refers to gloves, while the SDS also states that eye protection should be worn.

There is limited mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. There is no information on skin sensitization. It is considered practically non-toxic via oral exposure. It is noted as severely irritating to the eyes.

There are no aquatic toxicity data or ecotoxicity information in the SDS.

Cohere[®] contains alkanolamine surfactant and alkylaryl polyethoxyethanol sulfate neither of which are further identified. There is also ethylene glycol (1,2-propanediol). The SDS also lists three compounds likely found as contaminants: 1,4-dioxane, acetaldehyde, and formaldehyde.

The alkanolamine surfactant is a generic term, defined as a fatty acid used as a surfactant. There are three alkanolamides typically used in surfactants: coconut diethanolamide (aka cocamide DEA), made from coconut oil (CAS 68603-42-9); soyamide DEA, made from soybean oil (CAS 68425-47-8); and, tallamide DEA (CAS 68155-20-4), made from tall oil fatty acids. Whether one of these or which of these is used in this product is unknown. Cocamide and soyamide DEA are used in personal care products so toxicity data is available on them; not much toxicity information is available on tallamide DEA. Both cocamide and soyamide DEA have signal words of Danger due to eye hazard and possible carcinogenicity. They are both slightly toxic orally and dermally in mammals. Cocamide DEA has aquatic LC₅₀ values for algae, daphnia, and fish that are all <10mg/L.

The alkylaryl polyethoxyethanol sulfate can be referring to an alkylphenol, such as nonylphenol. If that is the case here, this term could be referring to an ethoxylated nonylphenol sulfate surfactant or more likely an emulsifier. Examples include an anionic surfactant, ammonium nonylphenol ethoxylate sulfate (CAS 9051-57-4) and sodium nonylphenol ethoxylate sulfate (CAS 9014-90-8). These are nonylphenol molecules of various degrees of ethoxylation and a sulfate group with the ammonium or sodium molecule attached to the sulfate. Ammonium nonylphenol ethoxylate sulfate has a Warning signal word, is listed as flammable, and as a skin irritant.

Propylene glycol is a tasteless, odorless and colorless clear oily liquid that is very soluble in water. It is the primary ingredient in low toxicity antifreezes (RV or marine antifreeze). GRAS material; used in some processed foods as a solvent for flavors and colors or as a humectant. Used as a humectant in hand sanitizers. It is a principal ingredient in vaping solutions. In this adjuvant, it could be added as a solvent, as a humectant, or as a defoamer. Quickly metabolized in mammals after ingestion, although a large portion remains unmetabolized and excreted in

urine. Half-life in humans is measured in hours, although it can be toxic in large doses over short time, otherwise propylene glycol is of low oral toxicity. Oral LD₅₀ values range from 8 to 46 g/kg. It is not a skin sensitizer nor an eye or skin irritant. It is not considered a carcinogen or mutagen. It is of low aquatic toxicity; LC₅₀ values for freshwater fish and invertebrates range from 11,000 to 77,400 ppm.

The SDS includes formaldehyde indicating it is a potential carcinogen. Formaldehyde may be intentionally added as a chelating agent, a preservative, or for some other purpose. It may also be an impurity or unreacted intermediate compound. Since it is not listed in the ingredients, it is likely only a minor component of the formulation. Formaldehyde has a Danger signal word because of its acute oral toxicity; skin irritant/corrosive; skin sensitizer; inhalation acute toxicity; and carcinogenicity. It is also a possible mutagen. Inhalation exposure is associated with cancer and lung disease (myeloid leukemia and nasal tumors).

The SDS lists acetaldehyde which is likely a residual chemical intermediate, byproduct, or contaminant. It has a signal word of Danger due to its flammability. It can cause serious eye irritation, respiratory irritation. It is a suspected carcinogen. As Cohere[®] is not regarded as very flammable, the levels of acetaldehyde in the formulation are likely low.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Surfix[®]-P Sticker (Helena Agri-Enterprises, LLC)

WA Reg. #5905-10001

Active Ingredients – 95.7% (SDS says 90.6%)

Pinene polymers (95.7%, SDS says 90.6%) (CAS 31393-98-3)

Surfix[®]-P has no signal word. It is not considered hazardous. It is noted as causing minor skin and eye irritation. There is no conflict between the label and SDS as regards the signal word or PPE (chemical-resistant gloves and eye protection).

There is limited mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. There is no information on skin sensitization. It is considered practically non-toxic via oral exposure. There is some risk of minor eye irritation, but is noted as clearing within 24 hours.

There are no aquatic toxicity data or ecotoxicity information in the SDS.

Surfix[®]-P contains pinene polymers which are not further identified. The label indicates that Surfix[®]-P contains 95.7% active ingredients, while the SDS indicates 90.6% active ingredients. It is unclear why there is this discrepancy. Pinene is a constituent of pine resin as well as other conifers. Two isomers of pinene exist (alpha- and beta-pinene), and these are used singly or in combination to develop pinene polymers. There is some limited evidence of skin sensitization, although most of the pinene polymers with the same CAS number do not show this. Practically non-toxic via oral exposure.

Sustain[®] Soil Deposition Adjuvant (Miller Chemical & Fertilizer Company)

CA Reg. #90930-50015

Active Ingredients – 100%

Pinene (terpene) polymers – not further identified

Petrolatum – not further identified

Alkyl amine ethoxylate – not further identified (could this be POEA?)

Sustain[®] has no signal word. It is not considered hazardous. It is noted as possibly causing minor skin and eye irritation. There is no conflict between the label and SDS as regards the lack of a signal word. There is a PPE conflict between the label (chemical-resistant gloves) and the SDS (rubber gloves, eye protection, rubber apron, rubber boots).

There is mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal and inhalation exposure. There is no information on skin sensitization. It is considered practically non-toxic via oral exposure.

There are no aquatic toxicity data or ecotoxicity information in the SDS. It is noted that large spills could damage vegetation and that contamination of waterways could cause fish kills.

Sustain[®] contains pinene polymers which are not further identified. Pinene is a constituent of pine resin as well as other conifers. Two isomers of pinene exist (alpha- and beta-pinene), and these are used singly or in combination to develop pinene polymers. There is some limited evidence of skin sensitization, although most of the pinene polymers with the same CAS number do not show this. Practically non-toxic via oral exposure.

The ingredient petrolatum is likely referring to white petrolatum (CAS 8009-03-8), a compound derived from petroleum that is insoluble in water. SDS searches indicate low toxicity to mammals via dermal or oral exposure. Some risk of aquatic toxicity to fish (96-hour LC₅₀ in minnow of >100 mg/L), although its lack of water solubility would indicate low risk of water contamination.

The alkyl amine ethoxylate represents a very generic description that could represent a large number of potential compounds. Because of the OMRI certification of Sustain[®], it is likely that this is a plant-based formulation like an ethoxylated soy or coco alkylamine that is used as a surfactant in Sustain[®].

d. Oil-Based AdjuvantsVegetable OilsCompetitor[®] Modified Vegetable Oil (Wilbur-Ellis Company)

CA Reg. #2935-50173; WA Reg. #2935-04001

Active Ingredients – 98%

Ethyl oleate (CAS 111-62-6)

Sorbitan alkylpolyethoxylate ester (ethoxylated sorbitan ester - emulsifier, a food-grade additive)

Dialkyl polyoxyethylene glycol (surfactant)

SDS says ethyl oleate 80-<90%, nonionic surfactants 20-<30%

Competitor[®] does not have a signal word. It may cause slight eye and moderate skin irritation and is not a skin sensitizer. The label does not identify any required PPE which is not consistent with the SDS (which requires eye protection and gloves). The SDS does not have a signal word associated with it due to its low toxicity.

The SDS does not contain any numerical toxicity data for the formulated product or any of its ingredients. It may cause some minor eye irritation; prolonged skin contact may result in skin irritation. There is limited acute toxicity data in an older (2005) MSDS (refer to Table 1). Competitor[®] is considered practically non-toxic via oral exposure and is considered slightly toxic via dermal and inhalation exposure.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. The SDS states that the product is not classified as environmentally hazardous. There are acute toxicity values for rainbow trout and daphnia shown in Table 2. These data would indicate this product is slightly toxic to fish and daphnia. This product is approved for aquatic use by the state of Washington.

According to the label, Competitor[®] is made up of ethyl oleate, sorbitan alkylpolyethoxylate ester, and dialkyl polyoxyethylene glycol. The label also describes Competitor[®] as a modified vegetable oil containing a nonionic emulsifier system. The SDS is much less descriptive, describing the ingredients as ethyl oleate and nonionic surfactants.

Ethylated canola oil is a generic description of a product of a reaction of a fatty acid derived from canola oil with ethyl alcohol. Most SDSs have no signal word and are not considered acutely hazardous, but are considered flammable, although Competitor is not considered flammable. These are often found as components of biodiesel fuels. Exposure may cause skin and eye irritation, respiratory irritation, and irritation if swallowed. None appear to be listed under California's Proposition 65. Ethyl oleate is practically non-toxic via oral exposure ($LD_{50} >5$ g/kg) and slightly toxic via dermal exposure ($LD_{50} >5$ g/kg). There is no signal word associated with ethyl oleate due to its low hazard.

Ethoxylated sorbitan esters are known as polysorbates (trade names: Scattics, Alkest, Canarcel, Tween). They are an important class of emulsifiers and surfactants used in a variety of settings, including pharmaceuticals and food. They are soluble or dispersible in water but differ widely in organic and oil solubilities. Their variation is dependent on the esterified fatty acid with which the ethoxylated sorbitan is associated. The generic description on the label does not indicate which polysorbate is used. Most commercial polysorbates carry no signal word due to low hazard and toxicity.

The dialkyl polyoxyethylene glycol represents a generic term that appears to be referring to a form of polyethylene glycol ether that has been reacted with an alcohol. A common one is polyethylene glycol dimethyl ether (CAS 24991-55-7). But the description is too generic to verify that this is the basic description, and if it is, what the molecular weight of the compound is (based on the number of ethylene oxide molecules).

MSO[®] Concentrate Methylated Seed Oil (Loveland Products, Inc.)

CA Reg. #34704-50067, WA Reg. #34704-04009

Active Ingredients – 100%

Methylated vegetable oil – not further described

Alcohol ethoxylate - not further described (surfactant)

Tall oil fatty acids – not further described

MSO[®] Concentrate Methylated Seed Oil has a Warning signal word. It may cause slight eye and skin irritation and is not a skin sensitizer. May be harmful if swallowed or inhaled. The label-and SDS to not conflict as regards PPE (eye protection and gloves).

Mammalian acute toxicity data are in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure but is not a skin sensitizer. It is considered slightly toxic via oral exposure and inhalation. It is a minimal eye irritant.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. These data would indicate this product is slightly toxic to aquatic species. It is approved for aquatic use in Washington and California.

MSO[®] Concentrate Methylated Seed Oil is made up of a methylated vegetable oil, an ethoxylated alcohol, and a tall oil fatty acid. These are all generic descriptions and no CAS numbers are associated with them in the current SDS. An older MSDS identified the ethoxylated alcohol with the CAS number 34398-01-1. Whether this is still the same alcohol is unknown. Based on the CAS number, the ethoxylated alcohol is an 11-carbon chain linear alcohol.

Methylated vegetable oil is a generic description of a product of a reaction of a fatty acid derived from vegetable or seed oil with methyl alcohol. Most common seed oils produced are soy, palm kernel, and rapeseed (canola). It is unknown what species of plant or seed oil is used in this product. Most have no signal word and are not considered acutely hazardous, but are considered flammable. These are often found as primary components of biodiesel fuels. Exposure may cause minor skin and eye irritation, respiratory irritation, and irritation if swallowed. None appear to be listed under California's Proposition 65. There is very little acute toxicity data or ecotoxicity data available on-line for any of the individual methylated seed oils.

The linear ethoxylated alcohol is not adequately described to say anything definite about its toxicology. The CAS number in the older MSDS represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular alcohol is unknown. The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. It has a signal word of Danger due to its strong eye irritation, which can result in eye damage or blindness. It is also a skin irritant. EPA classifies it as a "Safer Choice" ingredient in surfactants because of its rapid rate of biodegradation, although it is acutely toxic to aquatic animals (more so than aquatic plants or algae).

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to tall oil fatty acid. Quality tall oil fatty acid consists mostly of oleic and linoleic acid. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value > 10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Hasten-EA™ Modified Vegetable Oil Concentrate (Wilbur-Ellis Co.)

CA Reg. #2935-50202, WA Reg. #2935-15003

Active Ingredients – 100%, Noted as NPE-free

Ethylated seed oil (from product bulletin, an ethylated canola oil with high oleic acid content) – not further described

Polyoxyalkylene fatty ester – not further described

Hasten-EA™ does not have a signal word. It may be mildly irritating to the skin with prolonged contact and mildly to non-irritating to the eyes. The label does not identify any required PPE which is not consistent with the SDS (which requires eye protection and gloves). The SDS does not have a signal word associated with it due to its low toxicity.

The SDS does not contain any numerical toxicity data for the formulated product or any of its ingredients. The SDS does contain narrative statements that indicate no adverse effects are expected from skin contact or inhalation. It may cause some temporary eye irritation. It is not expected to be a skin sensitizer. An older SDS from September 2014 contains acute toxicity information (see Table 1).

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients; the SDS states that the product is not classified as environmentally hazardous. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. An older SDS from September 2014 does contain these same acute toxicity values but also a 96-hour NOEC for rainbow trout of 250 mg/L and for daphnia a 48-hour NOEC of 50 mg/L. These values would indicate this product is practically nontoxic to fish and slightly toxic to daphnia. This product is approved for aquatic use by the state of Washington.

The ingredients in Hasten-EA™ are identified as an ethylated seed oil and a polyoxyalkylene fatty ester. Neither are more specifically identified on the label or SDS. A product bulletin refers to ethylated canola oil as the ethylated seed oil.

Ethylated seed oil is a generic description of a product of a reaction of a fatty acid derived from vegetable or seed oil with ethyl alcohol. Most common seed oils produced are soy, palm kernel, and rapeseed (canola). A Wilbur-Ellis product bulletin for Hasten-EA™ identifies this as ethylated canola oil. Most ethylated seed oils have no signal word and are not considered acutely hazardous, but are considered flammable. These are often found as primary components of biodiesel fuels. Exposure may cause minor skin and eye irritation, respiratory irritation, and irritation if swallowed. None appear to be listed under California's Proposition 65. There is very little acute toxicity data or ecotoxicity data available on-line for any of the individual ethylated seed oils.

The polyoxyalkylene fatty ester is likely referring to some type of ethoxylated fatty acid ester, acting as an emulsifier, but the generic nature of the term does not allow for identifying the specific fatty acid or alcohol that makes up the fatty acid ester, or how many ethoxylate units are attached. A possible compound that is being referred to here is an ethoxylated methyl ester, or methyl ester ethoxylate (MEE) (such as methyl laurate ethoxylate or methyl oleate ethoxylate).

If Hasten-EA™ contains ethoxylated ingredients, ethylene oxide and 1,4-dioxane will likely be a small component. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Pathfinder® II surfactant (Corteva Agriscience)

In the triclopyr formulation, Pathfinder® II, EPA Reg. #62719-176

“The diluent in Pathfinder® is derived from a naturally occurring nonpetroleum substance with a low odor”, from company website, not further described.

Pathfinder® II herbicide is a ready-to-use material that contains triclopyr herbicide in the butoxyethyl ester formulation combined with oil for use in treating woody plants. The surfactant is not identified except as a ‘naturally occurring non-petroleum diluent’.

Pathfinder® II has a Caution signal word. It may cause skin irritation and slight eye irritation. From the SDS, the 96-hour oral LD₅₀ for rats is 4,183 mg/kg (females), while the dermal LD₅₀ for rabbits is >2,000 mg/kg. These values are not appreciably different from those for the butoxyethyl ester form of triclopyr alone. For information on the hazards and risks of using triclopyr herbicide, refer to SERA 2011b.

Improved JLB Oil Plus (Brewer International)

CA Reg. # - not necessary as per California DPR, not a surfactant but a diluent (label says diluent for basal applications)

Active Ingredients – 100%

SDS states it is a mixture of MSO and natural oils including limonenes (correspondence from 1992 indicates sunflower seed oil)

Limone (CAS 138-86-3)

Improved JLB Oil Plus has a Warning signal word. According to the manufacturer, it is exempt from California registration because the state considers it a diluent, not a surfactant. It is a mild skin irritant and noted as a potential skin sensitizer. It is a severe eye irritant. The label notes it as

harmful if swallowed. The SDS does not contain a signal word, in conflict with the label. The label does not list any PPE which is in conflict with the SDS which calls for protective eyewear and impervious gloves.

The SDS does not contain any numerical toxicity data for the formulated product or any of its ingredients. It may cause serious eye irritation. It may cause skin irritation and can lead to skin sensitization (allergies). An older MSDS from December 2000 does contain some acute toxicity values (see Table 1).

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. The SDS states that the product is not expected to be harmful to aquatic organisms.

Considered a mixture of all-natural oils, it is made up of natural vegetable oils (unspecified) and limonene (as a penetrant). The manufacturer's website describes it as a *100% blend of natural vegetable oils*. It is intended to be used in place of diesel or kerosene in stem basal applications. The SDS describes it as a mixture of methylated seed oil (MSO) and natural oils, including limonene.

Methylated seed oil is a generic description of a product of a reaction of a fatty acid derived from vegetable or seed oil with methyl alcohol. Most common seed oils produced are soy, palm kernel, and rapeseed (canola). It is unknown what species of plant or seed oil is used in this product. Most have no signal word and are not considered acutely hazardous, but are considered flammable. These are often found as primary components of biodiesel fuels. Exposure may cause minor skin and eye irritation, respiratory irritation, and irritation if swallowed. None appear to be listed under California's Proposition 65. There is very little acute toxicity data or ecotoxicity data available on-line for any of the individual methylated seed oils. Some information from the manufacturer from the early 1990's indicated the oil as being sunflower seed oil, if this is indeed what is still in the formulation, this would be considered a food-grade additive.

Limonene is a naturally occurring class of monoterpenes; the major component in oil of citrus fruit peels. The isomer D-limonene occurs more commonly in nature and is a food grade additive (flavoring). Used as a dietary supplement and fragrance in personal care products. A botanical insecticide and herbicide, also used as a surfactant. It has a signal word of Danger as it may be fatal if swallowed and enters airway (aspiration hazard). It is flammable (both liquid and vapor). Limonene causes skin and eye irritation and may cause skin sensitization. The oral LD₅₀ in rats is 4.4 g/kg. In chronic exposures in rats, a NOAEL 250 mg/kg/day was determined. Concentrated limonene can be toxic to aquatic organisms, especially algae, and has a high risk of bioaccumulation.

M.O.C. Methylated Oil Concentrate (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50095

Active Ingredients – 100% (Modified vegetable oil concentrate)

Methylated soybean oil (SDS identifies as fatty acid, methyl esters CAS 67762-38-3, 90-100% by weight)

Alkylphenol ethoxylate, not further described

M.O.C. has a Warning signal word. It may cause serious eye irritation. It can cause skin irritation and is not a skin sensitizer. May be harmful if swallowed or inhaled. There is a conflict with

PPE; the label requires eye protection and gloves for PPE while the SDS also requires an impervious apron and footwear. There is no conflict between the label and SDS as regards the signal word.

There is limited mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure but is not a skin sensitizer. It is considered slightly toxic via oral exposure. There is no inhalation toxicity information. It is a serious eye irritant.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients.

M.O.C. is made up of a methylated soybean oil and an alkylphenol ethoxylate. The alkylphenol ethoxylate is a generic description and no CAS numbers are associated with it in the SDS.

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for *Daphnia* ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

The exact type of alkylphenol ethoxylate contained in this product cannot be determined. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

MSO[®] Concentrate with Leci-Tech (Loveland Products, Inc.)

CA Reg. #34704-50053; WA Reg. #34704-07001

Active Ingredients – 100%, Surfactant Content – 15%

Methylated vegetable oil – CAS 67784-80-9 (Soybean oil, methyl esters)

Alcohol ethoxylate – CAS 34398-01-1, polyethylene glycol monoundecyl ether

Phosphatidylcholine, CAS 97281-47-5, derived from soy, soybean lecithin (emulsifier or surfactant)

MSO[®] Concentrate has a Warning signal word. It may cause eye irritation. It can cause skin irritation but is not a skin sensitizer. May be harmful if swallowed or inhaled. There is no conflict with PPE between the label and the SDS; both require eye protection and gloves. There is no conflict between the label and SDS as regards the signal word.

There is mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure but is not a skin sensitizer. It is considered slightly toxic via oral and inhalation exposure. It is an eye irritant.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. It is noted as not being classified as environmentally harmful. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. Based on these data, this product is considered slightly toxic to aquatic species. It is approved for aquatic use by the state of Washington.

Phosphatidylcholine, also known as soybean lecithin, is likely added to this formulation as an emulsifier or as a surfactant. Phosphatidylcholines are such a major component of lecithin that in some contexts the terms are sometimes used as synonyms. However, lecithin extracts consist of a mixture of phosphatidylcholine and other compounds. Lecithins are fatty substances that naturally occur in animal and plant tissues. There is no signal word associated with lecithins or phosphatidylcholine as these are not considered hazardous. Exposure to phosphatidylcholine or lecithin may cause irritation of respiratory tract, skin irritation, and eye irritation.

The linear ethoxylated alcohol is not adequately described to say anything definite about its toxicology. The CAS number represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular alcohol is unknown. The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. It has a GHS signal word of Danger due to its strong eye irritation, which can result in eye damage or blindness. It is also a skin irritant. EPA classifies it as a “Safer Choice” ingredient in surfactants because of its rapid rate of biodegradation, although it is acutely toxic to aquatic animals (more so than aquatic plants or algae).

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for Daphnia ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Renegade-EA[®] Modified Vegetable Oil, Activator, and Surfactant (Wilbur-Ellis Company)

CA Reg. #2935-50201; WA Reg. #2935-15002

Active Ingredients – 83.4%, Contains 19.45% NIS surfactant, Label states “NPE Free Oil”

Methyl soyate, not further identified

Ammonium nitrate, not further identified - activator

Urea, not further identified - activator

“Other Components” (unspecified – non-ionic surfactant, likely an ethoxylated alcohol)

SDS also mentions butyl alcohol (CAS 71-36-3); 1,4-dioxane (CAS 123-91-1); acetaldehyde (CAS 75-07-0) and oxirane (ethylene oxide, CAS 75-21-8)

Renegade-EA[®] has a Warning signal word. It is irritating to the skin and may be a skin sensitizer. It is seriously irritating to the eyes. It is a combustible liquid. The label does not identify any required PPE which is not consistent with the SDS (which requires eye protection and gloves), although the SDS also recommends face protection and an apron. The label and SDS are consistent in the Warning signal word.

The SDS does not contain any numerical toxicity data for the formulated product but does contain information on one of the ingredients - butanol. Acute mammalian toxicity data for the formulation is shown in Table 1. Renegade-EA[®] would be considered practically non-toxic via oral exposure and slightly toxic via dermal and inhalation exposures.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. The SDS states that the product is not classified as environmentally hazardous. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2, along with the corresponding NOEC values (Glatzhofer 2020). Based on these data this product is considered slightly toxic to aquatic species. It is approved for aquatic use by the state of Washington.

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for Daphnia ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

The label states that that this product contains a solution of urea and ammonium nitrate (UAN). Both are important nitrogen fertilizers but are added to herbicides to increase herbicide activity by increasing herbicide absorption. The most commonly used grade of these fertilizer solutions is UAN 32 (32%N), which consists of 45% ammonium nitrate, 35% urea and 20% water. Other grades are UAN 28, UAN 30 and UAN 18. The solutions are quite corrosive towards mild steel and are therefore generally equipped with a corrosion inhibitor to protect tanks, pipelines, nozzles, etc. In a search of SDSs for UAN 32, some carry Warning signal words, others do not have a signal word due to low hazard. Most SDSs do not show toxicity information for the mixture, only for the components, but for the mixture (UAN 32) there is an oral LD₅₀ for rat of >2g/kg; a 96-hour LC₅₀ for rainbow trout of 103 mg/L and for fathead minnow of 100-500 mg/L. There are small amounts of free ammonia associated with the mixture (<0.2%). Ammonium nitrate has a Warning signal word, causing serious eye irritation as well as being irritating to the nose, throat, and mucous membranes. Urea has no signal word as it is not considered hazardous. It may irritate the eyes, skin, and respiratory tract and repeated or prolonged contact with skin can cause dermatitis.

The label refers to a nonionic surfactant. This could be referring to butanol or an unidentified ethoxylated alcohol. Butyl alcohol (aka butanol) is likely added as a solvent or surfactant in this product. Butanol has a Danger signal word due to serious eye irritation or damage. The 96-hour oral LD₅₀ in rats and mice ranges from 146 to >1,500 mg/kg. Butanol is extensively and rapidly metabolized in mammals to carbon dioxide. Butanol is severely irritating to the eyes, leading to a

signal word of Danger. It is approved for use in foods as an artificial flavoring and is GRAS. Butanol is of low toxicity to aquatic life and is not expected to bioaccumulate.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

The SDS lists acetaldehyde which is likely a residual chemical intermediate, byproduct, or contaminant. It has a signal word of Danger due to its flammability. It can cause serious eye irritation, respiratory irritation. It is a suspected carcinogen.

Super Spread[®] MSO (Wilbur-Ellis Company)

CA Reg. # 2935-50176; WA Reg. #2935-03001

Active Ingredients – 100%, surfactant content 15% minimum

Methyl soyate, not further described

Nonylphenol ethoxylate, not further described - surfactant

SDS also mentions oxirane (ethylene oxide, CAS 75-21-8)

Super Spread[®] MSO has a Warning signal word. It can cause serious eye damage and irritation. It can be mildly irritating to the skin with prolonged contact but is not expected to be a skin sensitizer. The label identifies eye protection as the only required PPE which is not consistent with the SDS (which requires eye protection and gloves). The label and SDS are consistent in the Warning signal word.

The SDS does not contain any numerical toxicity data for the formulated product. Acute mammalian toxicity data for the formulation is shown in Table 1. Super Spread[®] MSO is considered practically non-toxic via oral exposure and slightly toxic via dermal and inhalation exposures.

The SDS does not contain any aquatic toxicity data for the formulation or any of its ingredients. The SDS states that the product is not classified as environmentally hazardous, and it is registered for aquatic uses (but not in Washington State).

The label only lists two ingredients, methyl soyate and nonylphenol ethoxylate, yet the SDS states that the formulation is made up of methyl esters, surfactants, and formulation aids. Assuming the methyl ester is referring to the methyl soyate and the surfactant is referring to nonylphenol ethoxylate, it remains unclear whether there are additional ingredients added as formulation aids.

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for Daphnia ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

The active ingredient on the label refers to a generic description of nonylphenol ethoxylate, and therefore does not describe how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of nonylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

MES-100[™] Modified Vegetable Oil Concentrate (Drexel Chemical Company)

CA Reg. # 19713-50002, WA Reg. # 19713-50002

Active Ingredients – 100%

Methylated seed oil, not further identified

Alkylphenol ethoxylate, not further identified

MES-100[™] has a Warning signal word. It can cause eye irritation. It can be seriously irritating to the skin. It can be harmful if swallowed or inhaled. There is no information in the SDS concerning whether it is a skin sensitizer. The label identifies protective gloves as the only required PPE which is not consistent with the SDS (which requires eye protection and gloves). The label and SDS are consistent in the Warning signal word.

There are limited mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. There is no inhalation toxicity information. It is noted as being non-mutagenic for bacteria and/or yeast.

There are no aquatic toxicity data in the SDS.

Methylated seed oil is a generic description of a product of a reaction of a fatty acid derived from vegetable or seed oil with methyl alcohol. Most common seed oils produced are soy, palm kernel, and rapeseed (canola). It is unknown what species of plant or seed oil is used in this product. Most have no signal word and are not considered acutely hazardous, but are considered flammable. These are often found as primary components of biodiesel fuels. Exposure may cause minor skin and eye irritation, respiratory irritation, and irritation if swallowed. None appear to be listed under California's Proposition 65. There is very little acute toxicity data or ecotoxicity data available on-line for any of the individual methylated seed oils.

The active ingredient on the label refer to a generic description of alkylphenol ethoxylate, and therefore does not describe how many ethoxylate groups are present or what type of alkylphenol is used. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either octylphenol or nonylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Spraytech Oil™ Spray Adjuvant (Spraytech, Inc.)

CA Reg. # 65328-50001

May no longer be sold; may no longer be supported by Spraytech, Inc.

Active Ingredients – 95%

Emulsifiable soybean oil (emulsifiable vegetable oils and polyethoxylated esters and derivatives thereof), CAS 67784-80-9

This product appears to no longer be commercially supported by Spraytech, Inc., or any other company. It may no longer be widely available, but existing stock is still being used. There is no SDS available online and the latest MSDS is from 1996.

Spraytech Oil™ has a Warning signal word. It can cause serious eye irritation. It can be seriously irritating to the skin and can lead to dermatitis. It can be harmful if swallowed and subsequently aspirated. There is no information in the MSDS concerning whether it is a skin sensitizer. The label does not list any required PPE which is not consistent with the MSDS (which requires eye protection and gloves). The label and MSDS are consistent in the Warning signal word.

There are limited mammalian acute toxicity data in the MSDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. There is no inhalation toxicity information.

There are no aquatic toxicity data in the SDS. The label states that Spraytech Oil™ should be kept out of lakes, streams, and ponds.

The active ingredient is described on the label as an emulsifiable soybean oil. Whether this means an ethylated or methylated soybean oil is unknown. It is also unknown whether this means the formulation includes an added emulsifier, and if so what type of emulsifier. The MSDS described the formula as also including polyethoxylated esters, which could be referring to an ethoxylated alcohol surfactant.

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for Daphnia ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Vegetable Oils and Silicone BlendsSyl-Tac-EA™ (Wilbur-Ellis Co.)

CA Reg. # 2935-50203, WA Reg. #2935-15004

Active Ingredients – 100%, Surfactant content 40%, Label states “NPE Free Oil”

Ethylated seed oil (ethyl and methyl esters of canola oil, 60-<70%, in SDS)

Polyether-polymethylsiloxane-copolymer – (polysiloxane, CAS 125997-17-3, 30-<40%, in SDS)

Polyoxyalkylene fatty ester – not further described

Syl-Tac-EA™ has no signal word due to its low hazard. It may cause temporary eye irritation. Prolonged skin contact may cause temporary irritation. Syl-Tac-EA™ is expected to be a low ingestion hazard and no effects from inhalation are expected. The label does not list any required PPE which is not consistent with the SDS (which requires eye protection and gloves). The label and SDS are consistent in not having a signal word.

There are no mammalian acute toxicity data in the most recent SDS. There are acute toxicity data in an older SDS from 2014 (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure. The 2014 SDS describes Syl-Tac-EA™ as not being a skin sensitizer.

There are no aquatic toxicity data in the most recent SDS. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. There are the same acute toxicity data in an older SDS from 2014 which also shows a 96-hr NOEC of 30 mg/L in rainbow trout and a 48-hour NOEC in daphnia of 50 mg/L. These data would indicate this product is slightly toxic to fish and practically nontoxic to daphnia. This product is approved for aquatic use by the state of Washington.

The label describes the ingredients as an ethylated seed oil, a polyether-polymethylsiloxane-copolymer, and polyoxyalkylene fatty ester. These are all rather generic descriptions. The SDS further defines the ethylated seed oil as ethyl and methyl esters of canola oil and provides a CAS number and name of polysiloxane for the polyether-polymethylsiloxane-copolymer.

Methylated canola oil is a generic description of a product of a reaction of a fatty acid derived from canola oil with methyl alcohol. Ethylated canola oil is derived from a similar reaction with ethyl alcohol. Most SDSs have no signal word and are not considered acutely hazardous, but are considered flammable. These are often found as components of biodiesel fuels. Exposure may cause skin and eye irritation, respiratory irritation, and irritation if swallowed. None appear to be listed under California’s Proposition 65. There is very little acute toxicity data or ecotoxicity data available on-line for any of the individual methylated seed oils.

The CAS number for the polyether polymethylsiloxane copolymer refers to a three-silicon ethoxylated siloxane molecule with 6-9 ethoxylate groups. Ethoxylated siloxanes are added to adjuvants as nonionic surfactants (superspreaders/wetters) or as defoamers. They consist of a hydrophobic polysiloxane backbone and a hydrophilic ethylene oxide chain. Many of the online SDSs have no signal word, a few have a Warning signal word (due to skin, eye irritation, as well as respiratory irritation). This ethoxylated siloxane is considered toxic to aquatic life, representing a long-term hazard, but has a low potential for bioaccumulation. It has low mobility in soils.

The polyoxyalkylene fatty ester is likely referring to some type of ethoxylated fatty acid ester, acting as an emulsifier, but the generic nature of the term does not allow for identifying the

specific fatty acid or alcohol that makes up the fatty acid ester, or how many ethoxylate units are attached. A possible compound that is being referred to here is an ethoxylated methyl ester, or methyl ester ethoxylate (MEE) (such as methyl laurate ethoxylate or methyl oleate ethoxylate).

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Phase[®] Surfactant – Antifoaming Agent (Loveland Products, Inc.)

CA Reg. #34704-50037, WA Reg. #34704-05007

Active Ingredients – 100%

Polyether modified polysiloxane (SDS has CAS 63148-62-9)

Methyl esters of fatty acids (SDS has CAS 67784-80-9, methylated soybean oil)

Alcohol ethoxylate (SDS has CAS 34398-01-1)

Phase[®] has a Warning signal word. It may cause minor eye irritation. It can be harmful if swallowed, inhaled, or in contact with the skin. It is not a skin sensitizer. The label and SDS require the same PPE - eye protection and gloves. The label and SDS are consistent in the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered moderately toxic via inhalation exposure.

There are no aquatic toxicity data in the SDS, although there is a statement that says Phase[®] is not environmentally hazardous. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. These data would indicate this product is slightly toxic to fish and practically nontoxic to daphnia. This product is approved for aquatic use by the state of Washington.

The exact identity of the silicone-based components of Phase[®] is unspecified. Whether it is of the same toxicity as the active ingredient in Sylgard[®] 309 is unknown, however these silicone-based compounds are generally of low acute toxicity. There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Polyether modified polysiloxane is likely referring to a linear polydimethylsiloxane. This descriptor is somewhat generic as it includes the segment poly, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. This may be referring to octamethyltrisiloxane, aka dimethicone, a commonly used polydimethylsiloxane. Although this may or may not be the actual product used in this formulation, many of the closely related linear silicones have similar tox profiles. Dimethicone is not absorbed in animal tissues to any great degree; most of tested doses are excreted in the feces with no metabolism. The GHS signal word is Warning due to eye irritation. It is added to this formulation as either a surfactant or as a defoamer. The acute oral LD₅₀ in mice varied in different studies from 6.5 to 26.85 g/kg. No effects from subchronic feeding tests in beagles. Reproductive tests showed no impacts in rats.

Chronic tests in rats and mice showed no cancers developed. Not a genotoxin. It is of low aquatic toxicity and not expected to bioaccumulate.

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC_{50} for *Daphnia* ranging from 332-5,243 mg/L and a 96-hour LC_{50} in (unspecified) fish of >1,000 mg/L.

The linear ethoxylated alcohol is not adequately described to say anything definite about its toxicology. The CAS number represents a range of compounds with different degrees of ethoxylation, therefore the exact number of ethoxylate groups in this particular alcohol is unknown. The degree of ethoxylation has more of a bearing on the toxicity than the length of the carbon chains or the branching of the alcohols. Manufacturers market these products as alternatives to alkylphenol ethoxylates in surfactant formulations. It has a GHS signal word of Danger due to its strong eye irritation, which can result in eye damage or blindness. It is also a skin irritant. EPA classifies it as a “Safer Choice” ingredient in surfactants because of its rapid rate of biodegradation, although it is acutely toxic to aquatic animals (more so than aquatic plants or algae).

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Dyne-Amic[®] Modified Vegetable Oil/Surfactant Blend (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50071

Active Ingredients – 99%

Methyl esters of C16-C18 fatty acids – not further identified (label states the product contains soy oil)

Polyalkyleneoxide modified polydimethylsiloxane – not further identified (silicone surfactant)

Alkylphenol ethoxylate – not further identified (nonionic surfactant)

Poloxalene (Label and SDS both list CAS 9003-11-6)

Polypropylene glycol butyl ether oleate (Label and SDS list CAS 37281-78-0), anti-foam

Dyne-Amic[®] has a Warning signal word. Dyne-Amic[®] may be mildly irritating to the skin and may be slightly irritating to the eyes. It may be harmful if swallowed or inhaled. It is not a skin sensitizer. The label and SDS require the same PPE – chemical-resistant gloves. The label and SDS are consistent in the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure. There is a note in the SDS that Dyne-Amic[®] contains a compound identified by California under Proposition 65 to cause cancer,

birth defects, or other reproductive harm but it is unclear from the SDS or the Proposition 65 list what compound is being referred to.

There are no aquatic toxicity data in the SDS. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. These data would indicate this product is slightly toxic to fish and daphnia. This product is approved for aquatic use by the state of Washington.

Dyne-Amic[®] is a mixture of a silicone-based surfactant, esterified soy oil, and an alkylphenol ethoxylate; however, the exact formulation of these ingredients is unknown. There are two CAS numbers on the label, one that corresponds to polyoxypropylene oleate butyl ether, while the other indicates poloxalene.

Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for Daphnia ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

The polyalkylenoxide modified polydimethylsiloxane is likely referring to an ethoxylated polydimethylsiloxane. The generic name does not allow for a determination of the number of dimethylsiloxane molecules or the degree of ethoxylation present. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers, but in this formulation, this is likely the main surfactant. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic siloxane backbone and a hydrophilic ethylene oxide chain. Similar to the alcohol ethoxylates, toxicity appears to be related to the number of ethoxylate groups, with more ethoxylate groups representing lower toxicity.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to Issue Discussions in Section 4.b.

The label refers to a generic description of alkylphenol ethoxylate, and therefore does not describe the exact alkylphenol or how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Poloxalene represents a family of polyoxyethylene and polyoxypropylene copolymers that combine ethylene oxide and propylene oxide. Used as a surfactant and antifoamer. The polyoxypropylene is a hydrophobic molecule and is combined with two flanking hydrophilic ethylene oxide chains. The name is generic and does not provide any idea of the exact nature and number of the two copolymers. These copolymers are also used as a treatment for alfalfa bloat in cattle. These copolymers are excreted quickly through urine with little metabolism. Some SDSs have no signal word due to low toxicity, others have a signal word of Warning due to inhalation risk. Acute oral LD₅₀ values in rats range from 2,300 - 22,400 mg/kg (considered slightly toxic to

practically non-toxic. The dermal LD₅₀ values in rabbits range from >5 – 20 g/kg (practically non-toxic). Aquatic acute toxicity is low.

Polyoxypropylene oleate butyl ether (CAS 37281-78-0) is probably a minor component of Dyne-Amic[®], likely used as an antifoam agent. Most on-line references refer to a 20 mole polyoxypropylene compound. When 20 moles of polyoxypropylene are present, it is a compound recognized as GRAS by the FDA when used as an antifoam agent in food packaging (21 CFR 176.200). But very little toxicity information is readily available on the internet.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Crop Oils and Crop Oil Concentrates

Agri-Dex[®] Crop Oil Concentrate (Helena Agri-Enterprises, LLC)

CA Reg. # 5905-50094

Active Ingredients – 99%, surfactant content 17%, contains petroleum distillates

Heavy range paraffinic oil, not further identified

Polyol fatty acid esters and polyethoxylated derivatives thereof, not further identified
(surfactant/emulsifier)

Agri-Dex[®] has a Warning signal word. It may be mildly irritating to the skin (although the SDS also says it is non-irritating), but is not a skin sensitizer. It may be irritating to the eyes (although the SDS also says it is non-irritating). It can be harmful if swallowed, inhaled, or in contact with the skin. There is a conflict between the label and SDS as regards PPE. The label only calls for protective gloves, while the SDS also calls for protective eyewear and an impervious apron and footwear. There is no conflict between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure.

There are no aquatic toxicity data in the SDS. An older Technical Data Sheet does list aquatic toxicity data (refer to Table 2) which are also shown in WSDA 2008. There is an acute toxicity value for rainbow trout in a 2004 study (Smith et al 2004) that is also shown in Table 2. This product is practically nontoxic to fish and aquatic invertebrates. It is approved for aquatic use by the state of Washington.

One of the primary ingredients is a heavy-range paraffin-base mineral oil. Through internet searches, heavy range paraffinic oil may be referring to CAS 64742-54-7 or 64742-65-0. From an internet search of SDSs associated with these CAS numbers, there is commonly no signal word as these oils are not considered hazardous. These compounds are a complex combination of hydrocarbons consisting of hydrocarbons having carbon numbers predominantly in the range of C20 through C50. These are not expected to be skin or eye irritants or skin sensitizers. For CAS 64742-54-7 the dermal LD₅₀ in rabbit ranges from >2 - >5 g/kg; the oral LD₅₀ in rats ranges from

>2 - >15 g/kg; and the inhalation LC₅₀ in rats ranges from 2.18 - >5 mg/L. For CAS 64742-65-0, the dermal LD₅₀ in rabbits is >5g/kg and the oral LD₅₀ in rats is >5g/kg. Both have low acute toxicity in aquatic organisms (rainbow trout 96-hour EC₅₀ is >5000 mg/L; Daphnia 48-hour EC₅₀ is >1000 mg/L). These compounds are not readily biodegradable, but will degrade (6-31% after 28 days).

The name polyol fatty acid ester refers to unspecified fatty acid esters of unspecified alcohols. Similarly, the name polyethoxylated polyol fatty acid ester refers to a group of chemicals that consist of unspecified fatty acid esters of unspecified polyethoxylated alcohols (SERA 1997a). An example would be a fatty acid methyl ester, used in biodiesel and detergents. A possible compound that is being referred to here is an ethoxylated fatty methyl ester, or methyl ester ethoxylate (MEE) (such as methyl laurate ethoxylate, methyl oleate ethoxylate, soy methyl ester ethoxylate), however even here, the degree of ethoxylation is not stated (and could vary). Without further identity, no definitive statements can be made concerning the toxicity of these compounds.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Mor-Act[®] Adjuvant (Wilbur-Ellis Company) - CA label

CA Reg. #2935-50184

Mor-Act[®] Crop Oil Concentrate (Wilbur-Ellis Company) – WA label

WA Reg. #2935-03007

Active Ingredients – 98.8%

Petroleum oil, not further identified

Tall oil, not further identified

Alkyl phenol ethoxylate (identified in the SDS as nonylphenol polyethylene glycol ether)

SDS also mentions 1,4-dioxane (CAS 123-91-1) and oxirane (ethylene oxide, CAS 75-21-8)

Mor-Act[®] has a Warning signal word. It causes eye irritation. Prolonged inhalation may be harmful. Prolonged exposure may cause skin irritation, but is not expected to be a skin sensitizer. There is a conflict between the Washington state label and SDS as regards PPE. The Washington state label calls for chemical-resistant gloves, protective eyewear, and a respirator or facemask, while the SDS does not call for the respirator or facemask. It is interesting that the California label does not require the respirator or facemask. There is no conflict between the label and SDS as regards the Warning signal word.

There are no mammalian acute toxicity data in the SDS. Acute mammalian toxicity data is shown in Table 1 and there appears to be some toxicity difference between the two state labels as regards oral toxicity, although as these values are both indeterminate, it is unclear whether there is any actual difference in formulation. Mor-Act[®] is slightly toxic to practically non-toxic via oral exposure and slightly toxic via dermal and inhalation exposures.

There are no aquatic toxicity data in the SDS. There is a statement in the SDS that Mor-Act[®] is not classified as environmentally hazardous, although the nonylphenol ethoxylate is identified as a marine pollutant.

One of the ingredients is a generically described petroleum oil. This is likely referring to a paraffinic mineral oil, but there is some uncertainty in this assumption as they may be naphthenic mineral oils. If it is some type of paraffinic mineral oil, these can have either Danger, Warning, or no signal word. They are generally of low acute toxicity except that they represent a serious health risk if aspirated into the lungs, potentially resulting in chemical pneumonia. They can be eye irritants. Prolonged contact with the skin may be irritating as well. Highly refined paraffinic mineral oils are used in many personal care products as well as pharmaceuticals. They are also used as the basis for many horticultural oils, which can affect terrestrial insects through suffocation. They are of low acute toxicity to aquatic organisms. They are not readily biodegradable but ultimately will biodegrade.

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to tall oil fatty acid, which is likely the ingredient in this product. Quality tall oil fatty acid consists mostly of oleic and linoleic acid and is likely added as a surfactant or emulsifier. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value >10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

The ingredient listed in the SDS as nonylphenol polyethylene glycol ether refers to a generic description of ethoxylated nonylphenol, and therefore does not describe how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of nonylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Herbimax[®] Petroleum Oil-Surfactant Adjuvant (Loveland Products, Inc.)

CA Reg #34704-50032; WA Reg. #34704-04006

Active ingredients – 99.3%

Petroleum hydrocarbons – 83%

Light paraffinic distillate, not further identified

Odorless aliphatic petroleum solvent, not further identified

Alkylphenol ethoxylate, not further identified (surfactant)

Tall oil fatty acid - not further identified

Last two ingredients listed as 16.32% combined

Herbimax[®] has a Danger signal word. This product causes serious eye irritation. Causes skin irritation but is not a skin sensitizer. Can be fatal if swallowed and subsequently aspirated into the lungs. Herbimax[®] is a flammable liquid. There is a conflict between the label required PPE (protective gloves and eyewear) and the PPE required in the SDS (which also requires chemical-resistant footwear). There is no conflict between the label and SDS as regards the Danger signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered moderately toxic via inhalation exposure, with the risk of chemical pneumonia.

There are limited aquatic toxicity data in the SDS (refer to Table 2). This product is moderately toxic to fish, with a 96-hour LC₅₀ in bluegill of 2.2 mg/L, although the SDS states that Herbimax[®] is not classified as environmentally hazardous. The SDS also provides results of a 24-hour EC₅₀ test in the marine invertebrate *Dendronereides heteropoda* with a result of 4,720 mg/L. There are no test data on freshwater invertebrates.

The paraffin base petroleum oil assigned the CAS numbers in Herbimax[®] is described as a light paraffinic mineral oil. It consists of hydrocarbons having 15 to 30 carbon chains. This oil carries a Danger signal word. Also is considered a carcinogen although this may represent a more unrefined product with contaminants. In an on-line search of SDSs, this can have either Danger, Warning, or no signal word. They are generally of low acute toxicity except that they represent a serious health risk if aspirated into the lungs, potentially resulting in chemical pneumonia. They can be eye irritants. Prolonged contact with the skin may be irritating as well. Highly refined paraffinic mineral oils are used in many personal care products as well as pharmaceuticals. They are also used as the basis for many horticultural oils, which can affect terrestrial insects through suffocation. They are generally of low acute toxicity to aquatic organisms. They are not readily biodegradable but ultimately will biodegrade.

The label lists odorless aliphatic petroleum solvent, but an older SDS provides a CAS number that leads to light aliphatic solvent naphtha, or naphtha. Whether the older SDS still represents the current formulation is not known. Through an SDS search, the signal word is either Danger or Warning. It is generally of low acute toxicity except that it represents a serious health risk if aspirated into the lungs, potentially resulting in chemical pneumonia. It can be an eye irritant. Prolonged contact with the skin may be irritating as well. It is rated as a carcinogen and reproductive toxin, although this is the result of several contaminants in the compound (e.g., benzene, toluene, etc.). High levels of acute naphtha exposure can result in central nervous system depression. Naphtha is a flammable material. Considered toxic to aquatic organisms.

The label refers to a generic alkylphenol ethoxylate, and therefore does not describe the exact alkylphenol or how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the pine wood-pulp manufacturing process. By distillation and chemical reactions, tall oil can be converted to tall oil fatty acid, which is likely the ingredient in this product. Quality tall oil fatty acid consists

mostly of oleic and linoleic acid and is likely added as a surfactant or emulsifier. Based on SDS documents for 100% tall oil fatty acids, it carries no signal word and the acute health hazards are low. It has an LD₅₀ value > 10 g/kg and a dermal LD₅₀ of >2 g/kg. It did not cause eye irritation in tested rabbits. It is not a skin sensitizer. Tall oil fatty acids do not exhibit toxicity when administered via the diet to rats at 2,500 mg/kg/day for 90 days. A two-generation reproduction toxicity study in rats was available for tall oil fatty acids; fetal susceptibility was not observed. Neither maternal nor developmental adverse effects were observed following oral administration of tall oil fatty acids at doses as high as 5,000 mg/kg/day.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Grounded[®]-CA (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50096

Active Ingredients – 100%, surfactant content 15%

Mineral Oil – 85% (SDS has CAS 8012-95-1)

Polyoxyethylated polyol fatty acid ester and polyol fatty acid ester – 15%, not further identified (surfactant/emulsifier)

Grounded[®]-CA has a Warning signal word. This product causes skin and eye irritation but is not a skin sensitizer. Can be harmful if swallowed or inhaled. May be harmful if in contact with the skin. There is a conflict between the label required PPE (chemical-resistant gloves) and the PPE required in the SDS (which also requires protective eyewear, impervious apron, and impervious footwear). There is no conflict between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure. The SDS notes that prolonged contact with the skin may cause irritation and dermatitis, but Grounded[®]-CA is not judged to be a corrosive or irritant by OSHA standards.

There are no aquatic toxicity data in the SDS.

The main ingredient (85%) in Grounded[®]-CA is mineral oil. By the CAS number this is highly refined food grade mineral oil. These can have either Danger, Warning, or no signal word. They are generally of low acute toxicity (96-hour oral LD₅₀ in rat is >5 to >24 g/kg). Heavy exposure to oil mist may cause lipoid pneumonia. They can be eye irritants. Prolonged contact with the skin may be irritating as well. Ingestion may cause diarrhea (it is used as a laxative), abdominal discomfort, and vomiting. Highly refined paraffinic mineral oils are used in many personal care products as well as pharmaceuticals. They are also used as the basis for many horticultural oils, which can affect terrestrial insects through suffocation. They are of low acute toxicity to aquatic organisms (96-hour LC₅₀ in rainbow trout ranges from >100 - 5,000 mg/L). They are not readily biodegradable but ultimately will biodegrade.

The surfactant in Grounded[®]-CA is generically described. The name polyol fatty acid ester refers to unspecified fatty acid esters of unspecified alcohols. Similarly, the name polyoxyethylated

polyol fatty acid ester refers to a group of chemicals that consist of unspecified fatty acid esters of unspecified polyethoxylated alcohols (SERA 1997a). An example would be a fatty acid methyl ester, used in biodiesel and detergents. A possible compound that is being referred to here is an ethoxylated fatty methyl ester, or methyl ester ethoxylate (MEE) (such as methyl laurate ethoxylate, methyl oleate ethoxylate, soy methyl ester ethoxylate), however even here, the degree of ethoxylation is not stated (and could vary). Without further identity, no definitive statements can be made concerning the toxicity of these compounds.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Grounded[®]-W (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50105; WA Reg. #5905-13001

Active Ingredients – 100%, surfactant content 15%

Mineral Oil – 85% (SDS has CAS 8012-95-1)

Polyoxyethylene sorbitan fatty acid esters, sorbitan fatty acid esters – 15%, not further identified (surfactant)

Grounded[®]-W has a Warning signal word. This product may cause mild skin and eye irritation but is not a skin sensitizer. Can be harmful if swallowed or inhaled. May be harmful if in contact with the skin. There is a conflict between the label required PPE (waterproof gloves) and the PPE required in the SDS (which requires protective eyewear, impervious apron, and impervious footwear). There is no conflict between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure.

There are no aquatic toxicity data in the SDS.

The main ingredient (85%) in Grounded[®]-W is mineral oil. By the CAS number this is highly refined food grade mineral oil. These can have either Danger, Warning, or no signal word. They are generally of low acute toxicity (96-hour oral LD₅₀ in rat is >5 to >24 g/kg). Heavy exposure to oil mist may cause lipoid pneumonia. They can be eye irritants. Prolonged contact with the skin may be irritating as well. Ingestion may cause diarrhea (it is used as a laxative), abdominal discomfort, and vomiting. Highly refined paraffinic mineral oils are used in many personal care products as well as pharmaceuticals. They are also used as the basis for many horticultural oils, which can affect terrestrial insects through suffocation. They are of low acute toxicity to aquatic organisms (96-hour LC₅₀ in rainbow trout ranges from >100 - 5,000 mg/L). They are not readily biodegradable but ultimately will biodegrade.

The surfactant in Grounded[®]-W are more specifically described than Grounded[®]-CA. Ethoxylated sorbitan esters are known as polysorbates (trade names: Scattics, Alkest, Canarcel, Tween). They are an important class of emulsifiers used in a variety of settings, including pharmaceuticals and food. They are soluble or dispersible in water but differ widely in organic and oil solubilities. Their variation is dependent on the esterified fatty acid with which the

ethoxylated sorbitan is associated. The generic description on the label does not indicate which polysorbate is used. Most commercial polysorbates carry no signal word due to low hazard and toxicity.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Inlet® Nonionic Wetter/Spreader Surfactant (Helena Agri-Enterprises, LLC)

CA Reg. #5905-50099

Active Ingredients – 90%

Polyalkoxylated and non-alkoxylated aliphatics, alkanolamides (surfactant, thickener) and derivatives thereof, not further identified

Inlet® has a Warning signal word. This product causes skin and eye irritation; it is not stated in the SDS whether it is a skin sensitizer. Can be harmful if swallowed or inhaled. May be harmful if in contact with the skin. There is a conflict between the label required PPE (protective eyewear and chemical-resistant gloves) and the PPE required in the SDS (which also requires an impervious apron and impervious footwear). There is no conflict between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure. It is considered practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure. The SDS notes it is moderately irritating to the skin and mildly irritating to the eyes.

There are no aquatic toxicity data in the SDS.

The ingredients listed in the label and SDS are generically described. The term polyalkoxylated and non-alkoxylated aliphatics represents such a wide list of possibilities, that it is not possible to identify what it is meant to represent in terms of any actual compound. From a search on-line, there are surfactants referred to as alkoxylated surfactants (e.g., Triton HW-1000), referred to as non-alkylphenol polyethoxylate and non-silicone.

The alkanolamide surfactant is a generic term, defined as a fatty acid used as a surfactant. There are three alkanolamides typically used in surfactants: coconut diethanolamide (aka cocamide DEA), made from coconut oil (CAS 68603-42-9); soyamide DEA, made from soybean oil (CAS 68425-47-8); and, tallamide DEA (CAS 68155-20-4), made from tall oil fatty acids. Whether one of these or which of these is used in this product is unknown. Cocamide and soyamide DEA are used in personal care products so toxicity data is available on them; not much toxicity information is available on tallamide DEA. Both cocamide and soyamide DEA have signal words of Danger due to eye hazard and possible carcinogenicity. They are both slightly toxic orally and dermally in mammals. Cocamide DEA has aquatic LC₅₀ values for algae, daphnia, and fish that are all <10mg/L.

W.E.B. Oil (Wilbur-Ellis Company)

WA Reg. # 2935-70023

Active Ingredients – 98%; contains petroleum distillates
Mineral Oil, not otherwise described, 98%
Alkylphenol polyoxyethylene, not otherwise described, 2%

W.E.B. Oil has a Danger signal word. This product may cause temporary eye irritation. It is not expected to cause skin irritation (except through prolonged skin contact), nor is it expected to be a skin sensitizer. It can be fatal if swallowed and subsequently enters airway. There is a conflict between the label required PPE (none listed) and the PPE required in the SDS (which requires protective eyewear and chemical-resistant gloves). There is no conflict between the label and SDS as regards the Danger signal word.

There are no mammalian acute toxicity data in the SDS. The SDS states that aspiration into the lungs may cause pulmonary edema and chemical pneumonia. It is not considered a carcinogen or to cause reproductive or developmental effects.

There are no aquatic toxicity data in the SDS. The SDS states that it is not considered environmentally hazardous, although the label prohibits aquatic use.

The main ingredient is a mineral oil, described on the label as a highly refined and emulsifiable mineral oil. Mineral oil can have either Danger, Warning, or no signal word. It is generally of low acute toxicity (96-hour oral LD₅₀ in rat is >5 to >24 g/kg). Heavy exposure to oil mist may cause lipoid pneumonia. It can be an eye irritant. Prolonged contact with the skin may be irritating as well. Ingestion may cause diarrhea (it is used as a laxative), abdominal discomfort, and vomiting. Mineral oils are also used as the basis for many horticultural oils, which can affect terrestrial insects through suffocation. They are of low acute toxicity to aquatic organisms (96-hour LC₅₀ in rainbow trout ranges from >100 - 5,000 mg/L). They are not readily biodegradable but ultimately will biodegrade.

There is an alkylphenol polyoxyethylene listed on the SDS, but not the label, likely as an emulsifier. This is a generic description of alkylphenol ethoxylate, and therefore does not describe the exact alkylphenol or how many ethoxylate groups are present. Based on adjuvant chemistries for water-based herbicides, this ingredient is likely made up of either nonylphenol or octylphenol ethoxylates in the 8-10 ethoxylate range. Refer to the discussion for R-11[®], above.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

e. OMRI-Certified Wetter/Spreaders/Stickers

Freeway[®] Organosilicone Super Wetter (Loveland Products, Inc.)

Refer to discussion of Freeway[®] under Silicone-based surfactants, above.

Kinetic[®] Nonionic Wetter/Spreader/Penetrant (Helena Agri-Enterprises, LLC) – CA Registration

Refer to discussion of Kinetic[®] under silicone-based surfactants, above.

Kinetic[®] Nonionic Wetter/Spreader/Penetrant (Helena Agri-Enterprises, LLC) – WA Registration

Refer to discussion of Kinetic[®] under silicone-based surfactants, above.

Organic BioLink[®] Surfactant & Penetrant (Westbridge Agricultural Products)

CA Reg. #51517-5002; WA Reg. #51517-10001

Active Ingredients – 40% (remainder is water)

Yucca extracts (CAS 223749-05-1) 30%

Garlic extracts (CAS 8008-99-9) 10%

BioLink[®] has a Warning signal word. It can cause eye irritation and mild skin irritation. There is a conflict between the label-required PPE (protective eyewear) and the PPE required in the SDS (which also requires chemical resistant gloves). There is no conflict between the label and SDS as regards the Warning signal word.

There are no mammalian acute toxicity data in the SDS. The SDS notes that it is a potential nose and throat irritant. Ingestion may cause nausea, vomiting, diarrhea, and abdominal discomfort. Prolonged exposure may cause skin irritation.

There are no aquatic toxicity data in the SDS. There is a statement in the SDS that says there are no known significant environmental effects.

There are two active ingredients, both botanical extracts: garlic and yucca.

Garlic extract is obtained by distillation of crushed bulbs of the common garlic, *Allium sativum*. From a search of SDSs, signal words varied depending on the concentration of the garlic extract in the product. Low concentrations show no signal word. 5-10% concentrations have a Warning signal word; higher concentrations have a Danger signal word. Inhalation exposure may cause skin sensitization and asthma. May be harmful (or fatal) if swallowed or inhaled; may be irritating to mucous membranes and upper respiratory tract. High concentrations can be flammable (both the liquid and vapor). High concentration materials can be harmful to fish and the aquatic environment.

Yucca extract is derived from *Yucca schidigera* (Mojave yucca) and can be used as naturally-derived food grade surfactant. Yucca products are GRAS. From a search of SDSs, many have no signal word while others have a Warning signal word. Slight transient skin irritation; eye irritant (although some SDSs indicate serious eye irritation or eye damage). Not a skin sensitizer. May cause respiratory irritation. One aquatic toxicity test for *Daphnia* resulted in a 48-hour EC₅₀ of 40.61 mg/L.

Miller Nu Film P[®] Spreader and Sticker (Miller Chemical & Fertilizer Co.)

CA Reg. #90930-50022

Active Ingredients – 100%

Pinene (polyterpenes) polymers – not further identified, label says the main active ingredient is Pinolene[®], a terpenic polymer

Petrolatum, not further identified (CAS 8009-03-8)

Alkyl amine ethoxylate, not further identified

Nu Film P[®] has no signal word. It may cause eye and skin irritation. There is a conflict between the label-required PPE (chemical-resistant gloves) and the PPE required in the SDS (which also requires eye protection). There is no conflict between the label and SDS as regards the absence of a signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure and practically nontoxic via oral exposure. It is considered slightly toxic via inhalation exposure. The SDS states that large oral doses may cause nausea, vomiting, and stomach pain.

There are no aquatic toxicity data in the SDS.

Nu Film P[®] contains pinene polymers which are not further identified beyond the trademarked name Pinolene. Pinene is a constituent of pine resin as well as other conifers. Two isomers of pinene exist (alpha- and beta-pinene), and these are used singly or in combination to develop pinene polymers. There is some limited evidence of skin sensitization. Practically non-toxic via oral exposure.

The ingredient petrolatum is likely referring to white petrolatum (CAS 8009-03-8), a compound derived from petroleum that is insoluble in water. SDS searches indicate low toxicity to mammals via dermal or oral exposure. Some risk of aquatic toxicity to fish (96-hour LC₅₀ in minnow of >100 mg/L), although its lack of water solubility would indicate low risk of water contamination.

The alkyl amine ethoxylate is a very generic description that could represent a large number of potential compounds. Because of the OMRI certification of Nu Film P[®], it is likely that this is a plant-based formulation like an ethoxylated soy or coco alkylamine that is used as a surfactant in this product.

Sustain[®] Soil Deposition Adjuvant (Miller Chemical & Fertilizer Co.)

Refer to discussion of Sustain[®] under Sticker/Spreaders, above.

f. Activators - Fertilizer/Surfactant Mixtures

Brandt[®] Magnify Water Conditioning Agent, Surfactant, Antifoaming Agent (Brandt Consolidated, Inc.)

CA Reg # 48813-50014

Active Ingredients – 51.02%

Oligomeric D-glucopyranose decyl octyl glycosides, not further identified (possibly CAS 68515-73-1, a derivative of corn sugar)

Ammonium sulfate (CAS 7783-20-2), 20-30%, source of N fertilizer

Ammonium nitrate (CAS 6484-52-2), 10 - <20%, source of N fertilizer

Brandt® Magnify has a Warning signal word. Causes serious eye irritation or damage. No adverse effects due to inhalation or skin exposure are expected. It is not expected to be a skin sensitizer. There is no conflict between the label required PPE and the PPE required in the SDS (both require gloves and eye protection. There is no conflict between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation as well as the ammonium nitrate ingredient. This product is considered slightly toxic via dermal exposure and practically nontoxic via oral and inhalation exposure. The SDS states that large oral doses may cause nausea, vomiting, and stomach pain.

There are limited aquatic toxicity data in the SDS (refer to Table 2). This product is practically nontoxic to fish, with a 96-hour LC₅₀ in rainbow trout of >100 mg/L. It is moderately toxic to aquatic invertebrates, with a 48-hour EC₅₀ in *Daphnia magna* of 7.7 mg/L. It is approved for aquatic use by the state of Washington.

There are three active ingredients in this formulation, one is a surfactant, the other two are ammonium nitrate and ammonium sulfate.

The surfactant is identified on the label as oligomeric D-glucopyranose decyl octyl glycosides, otherwise known as alkyl (C₈ – C₁₀) polyglycoside. In 2013, EPA compiled toxicity study data on this and several closely related alkyl polyglycosides, collectively referred to as APGs (EPA 2013). APGs are nonionic surfactants derived from naturally occurring sugars (e.g., corn starch, glucose). In addition to their use in pesticide formulations, APGs are also used in laundry detergents, cleaners, rinse aids in dishwashers, and in personal care products. They are water soluble. These are of low acute oral and dermal toxicity (the SDS lists the oral LD₅₀ in rats of 2217 mg/kg). In subchronic and chronic toxicity tests in rats, the NOAEL was 1,000 mg/kg/day, the highest dose tested (90-day oral toxicity; developmental toxicity; reproductive screening toxicity); a LOAEL was not established. For alkyl (C₈ – C₁₀) polyglycoside, aquatic toxicity is low, with a 96-hour LC₅₀ in fish of 101 mg/L and a 48-hour EC₅₀ in *Daphnia* of 20 mg/L.

Ammonium nitrate is the nitrate salt of the ammonium cation. It is highly soluble in water. It is predominantly used in agriculture as a high-nitrogen fertilizer. In its dilute form as found in these products, it is mildly irritating to the eyes and skin; in its concentrated form, it can cause chemical burns. Ammonium nitrate has gained some notoriety as a component of low cost but dangerous explosive mixtures. Ammonium nitrate has a signal word of Warning. It is considered an oxidizer, and can cause serious eye irritation. It is also irritating to the nose, throat, and mucous membranes. It is slightly toxic via oral or dermal exposure. The 96-hour oral LD₅₀ in rats is 2.2 – 2.8 g/kg. Ammonium nitrate is of low aquatic toxicity, with a 96-hour LC₅₀ in rainbow trout of 6,000 mg/L and a 24-hour EC₅₀ in *Daphnia magna* of 555 mg/L. There is also a 96-hour LC₅₀ for the toadfrog (species and life stage not identified) of 39.3 mg/L. A recent study with red-legged frog embryos and larvae showed that ammonium nitrate was more toxic to this species of frog than the tested fish, with a 16-day LC₅₀ of 72 mg/L and a 16-day NOAEC of 6.4 mg/L ammonium-nitrogen equivalent (Schuytema and Nebeker 1999). Ammonium nitrate is a nutrient in water; therefore, spills may cause algal blooms. Ammonium nitrate will be taken up

by bacteria. Nitrate is more persistent in water than the ammonium ion; nitrate degradation is fastest in anaerobic conditions.

Ammonium sulfate is also used as a nitrogen fertilizer. It is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

The label states that there is an antifoaming agent in Brandt[®] Magnify. This is not described in the list of ingredients but is likely some type of polysiloxane.

The large percentage of inert ingredients (49.5%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Class Act[®] NG[®] Water Conditioning Agent/Nonionic Surfactant Blend (Winfield Solutions, LLC)

CA Reg. # 1381-50014; WA Reg. # 1381-01004

Active Ingredients – 50.5%; surfactant content 10%

Alkyl polyglucoside 0-4% by weight (CAS 68515-73-1), corn sugar derivative, used as a wetting agent

Corn syrup (CAS 8029-43-4)

Ammonium sulfate 33-35% by weight (CAS 7783-20-2), source of N fertilizer

Class Act[®] NG[®] has a Warning signal word. Prolonged contact can cause eye and skin irritation. No adverse effects due to inhalation is expected. It is not expected to be a skin sensitizer. There is a conflict between the label required PPE (none) and the PPE required in the SDS (requires gloves and eye protection). There is no conflict between the label and SDS as regards the Warning signal word.

There are limited mammalian acute toxicity data in the SDS (refer to Table 1). This product is considered slightly toxic via dermal exposure and practically nontoxic via oral exposure. There are no inhalation toxicity data. The SDS states that ingestion may cause gastric upset and that inhalation may aggravate pre-existing respiratory conditions.

There are aquatic toxicity data in the SDS (refer to Table 2). This product is practically nontoxic to fish, with a 96-hour LC₅₀ in rainbow trout of 447 mg/L and a NOEC of 40 mg/L. It is practically nontoxic to aquatic invertebrates, with a 48-hour EC₅₀ in *Daphnia magna* of 377 mg/L, with a NOEC of 40 mg/L. It is approved for aquatic use by the state of Washington.

There are three active ingredients in this formulation: ammonium sulfate, corn syrup, and an alkyl polyglucoside.

Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Corn syrup is a food syrup which is made from the starch of corn and contains varying amounts of maltose and higher oligosaccharides, depending on the grade. Commonly used as a sweetener in foods. It has no signal word due to its low hazard. It is of low acute toxicity with an oral LD₅₀ in the rat of 25.8 g/kg. It is not irritating to the eyes or skin and is not considered a hazard for inhalation or ingestion. Corn syrup appears to be added to increase absorption of herbicides.

The alkyl polyglucoside identified on the label is likely acting as a surfactant. The carbon chain length of the alkyl is unspecified. In 2013, EPA compiled toxicity study data on several closely related alkyl polyglucosides, collectively referred to as APGs (EPA 2013). APGs are nonionic surfactants derived from naturally occurring glucose (e.g., corn starch, glucose). In addition to their use in pesticide formulations, APGs are also used in laundry detergents, cleaners, rinse aids in dishwashers, and in personal care products. They are water soluble. These are of low acute oral and dermal toxicity (the SDS lists the oral LD₅₀ in rats of 2,217 mg/kg). In subchronic and chronic toxicity tests in rats, the NOAEL was 1,000 mg/kg/day, the highest dose tested (90-day oral toxicity; developmental toxicity; reproductive screening toxicity); a LOAEL was not established. Aquatic toxicity is low, with a 96-hour LC₅₀ in fish of 101 mg/L and a 48-hour EC₅₀ in *Daphnia* of 20 mg/L.

The large percentage of inert ingredients (49.5%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Bronc[®] Plus Dry-EDT (Wilbur-Ellis Company)

CA Reg. # 2935-50175; WA Reg. # 2935-03002

Active Ingredients – 99.04%

Ammonium sulfate, CAS 7783-20-2

Carbonyl diamine (aka urea, CAS 57-13-6)

Polyoxyethylene-polyoxypropylene, not further identified (likely as a surfactant)

Beta-Hydroxy-tricarboxylic acid (aka citric acid, CAS 77-92-9)

Polyacrylamide polymer, not further identified, likely acting as a deposition agent

Poly(dimethylsiloxane), CAS 9016-00-6 (anti-foam)

Bronc[®] Plus Dry-EDT has a Warning signal word. It can cause serious eye irritation. There is a conflict between the label required PPE (eye protection) and the PPE required in the SDS (requires gloves as well as eye protection). There is no conflict between the label and SDS as regards the Warning signal word.

There are no mammalian acute toxicity data in the SDS for the formulation. The SDS states that prolonged skin contact may cause skin irritation.

There are no aquatic toxicity data in the SDS. The SDS states that the product is not classified as environmentally hazardous. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2, along with values for minnow (Glatzhofer 2020). These values would indicate that this product is practically nontoxic to fish and daphnia. It is approved for aquatic use by the state of Washington.

Bronc[®] Plus Dry-EDT contains numerous ingredients as listed on the label. Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Carbonyl diamine, also known as urea, is the main nitrogen-containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water, and practically non-toxic (the oral LD₅₀ for rats is 8 - 15 g/kg). Dissolved in water, it is neither acidic nor alkaline. Urea is widely used in fertilizers as a source of nitrogen and is an important raw material for the chemical industry. Urea is GRAS. It does not carry a signal word because it is not considered hazardous. It may irritate the eyes, skin, and respiratory tract. Repeated or prolonged contact with skin can cause dermatitis. It is practically non-toxic to aquatic organisms and is rapidly hydrolyzed to ammonia and carbon dioxide. It is not expected to bioconcentrate.

The polyoxyethylene-polyoxypropylene copolymer represents a family of copolymers, combining ethylene oxide and propylene oxide. Used as a surfactant and antifoamer. The polyoxypropylene is a hydrophobic molecule and is combined with two flanking hydrophilic ethylene oxide chains. The name is generic and does not provide any idea of the exact nature and number of the two copolymers. These copolymers are also used as a treatment for alfalfa bloat in cattle. These copolymers are excreted quickly through urine with little metabolism. Some SDSs have no signal word due to low toxicity, others have a signal word of Warning due to inhalation risk. Acute oral LD₅₀ values in rats range from 2,300 - 22,400 mg/kg (considered slightly toxic to practically non-toxic). The dermal LD₅₀ values in rabbits range from >5 – 20 g/kg (practically non-toxic). Aquatic acute toxicity is low.

Beta-hydroxy-tricarboxylic acid, also known as citric acid, is likely added to provide the acidifier quality of this formulation. Citric acid is a weak organic acid occurring naturally in citrus fruits. It is very soluble in water. Citric acid is GRAS as it has many uses in foods and food products, medicines, household and personal care products. EPA has completed several comprehensive reviews of citric acid. Citric acid carries a signal word of Warning due to the risk of serious eye damage or irritation. It can also cause skin irritation. It is slightly toxic to practically non-toxic via oral exposure to rats and mice ($LD_{50} >3$ g/kg). Dermal $LD_{50} >5$ g/kg (slightly toxic), although it is not a skin sensitizer. Citric acid is of low toxicity to freshwater fish (bluegill 96-hour LC_{50} is 1,516 mg/L) and aquatic invertebrates (waterflea 72-hour EC_{50} is 240 mg/L).

The polyacrylamide polymer is highly water-absorbent, forming a soft gel when hydrated. It is likely added to Bronc[®] Plus Dry-EDT as a binding or thickening agent. An SDS search of polyacrylamide indicates none or Warning signal word. May be harmful if inhaled or absorbed through skin. May cause skin and eye irritation. The oral LD_{50} in the rat >1 g/kg. If ingested, it may cause digestive tract irritation. If inhaled, it may affect respiration and may cause ataxia or convulsions. While polyacrylamide itself is relatively non-toxic, it is known that commercially available polyacrylamide contains minute residual amounts of acrylamide remaining from its production. Acrylamide is a known neurotoxin and carcinogen. Polyacrylamide is of low aquatic toxicity with a 96-hour LC_{50} in rainbow trout of >750 mg/L.

The ingredient polydimethylsiloxane is somewhat generic as it includes the segment *poly*, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. Based on the CAS number in the SDS, this is dimethicone. Dimethicone is not absorbed after ingestion based on testing in rats, dogs, and mice and is excreted unchanged in the feces. For this reason, it is practically non-toxic on an acute oral basis (rat LD_{50} values range from 7 to 27 g/kg). It is a component of antacids, gas relievers, and cosmetics. It is of low acute toxicity to aquatic organisms and is not expected to bioaccumulate.

Cayuse[®] Plus ammonium sulfate and surfactant combination (Wilbur-Ellis Company)

CA Reg. # 2935-50171; WA Reg. # 2935-00003

Active Ingredients – 33.5%; surfactant content 7.84%; label states NPE-free

Ammonium sulfate, CAS 7783-20-2; 20 - $<30\%$; 2.49 pounds per gallon

Alcohol ethoxylate phosphate ester, surfactant

Ethylene glycol, CAS 107-21-1, 3 - $<5\%$

Diethylene glycol, CAS 111-46-6, 1 - $<3\%$

SDS also lists formaldehyde, CAS 50-00-0

SDS also lists oxirane, CAS 75-21-8

Cayuse[®] Plus has no signal word due to its low hazard. May cause temporary eye irritation. Not expected to be a skin irritant or skin sensitizer. Low ingestion hazard. There is a conflict between the label required PPE (none required) and the PPE required in the SDS (requires chemical-resistant gloves and eye protection). There is no conflict between the label and SDS as regards the lack of a signal word.

There are no mammalian acute toxicity data in the SDS for the formulation. The SDS states that prolonged inhalation may be harmful but that Cayuse[®] Plus is not a respiratory sensitizer. There are acute mammalian toxicity data included in Table 1. Cayuse[®] Plus is considered slightly toxic via oral, dermal, and inhalation exposure.

There are no aquatic toxicity data in the SDS. The SDS states that the product is not classified as environmentally hazardous, although it is not registered for use in water.

Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Alcohol ethoxylate phosphate ester is likely an anionic phosphate ester surfactant, but without more identifying information the specific compound cannot be determined.

The SDS lists ethylene glycol which is likely present as a minor contaminant from an interaction of ethylene oxide and water. It has a signal word of Warning due to its acute oral toxicity. Ethylene glycol is irritating to the eyes and skin as well as the respiratory tract. Target organs in mammals are the kidneys and nervous system. It is of low aquatic toxicity.

Diethylene glycol is a widely used solvent. It has a GHS signal word of Warning, largely due to its toxic effect with repeated exposures. On an acute exposure basis, it is practically nontoxic with an acute oral LD₅₀ value in the rat of 12.5 g/kg. It is of low aquatic acute toxicity, with a 96-hour LC₅₀ in the bluegill of 1,000 mg/L and a 24-hour EC₅₀ in the waterflea of 10,000 mg/L.

The SDS includes formaldehyde indicating it is a potential carcinogen. Formaldehyde may be intentionally added as a chelating agent, a preservative, or for some other purpose. It may also be an impurity or unreacted intermediate compound. Since it is not listed in the ingredients, it is likely only a minor component of the formulation. Formaldehyde has a Danger signal word because of its acute oral toxicity; skin irritant/corrosive; skin sensitizer; inhalation acute toxicity; and carcinogenicity. It is also a possible mutagen. Inhalation exposure is associated with cancer and lung disease (myeloid leukemia and nasal tumors).

Ethylene oxide (oxirane) and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

The large percentage of inert ingredients (66.5%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

pht[®] Kicker CA (J.R. Simplot Company)

CA Reg. # may be exempt from registration?

Active Ingredients – 17.3%

Ammoniacal nitrogen, 8%
 Sulfur, 9.3%
 Both from ammonium sulfate, CAS 7783-20-2, 30-40%

pH stable antifoam, not otherwise described

Kicker CA has no signal word due to its low hazard. It may cause temporary eye irritation. It is not expected to be a skin irritant or skin sensitizer. Kicker CA has a low ingestion hazard. There is a conflict between the label required PPE (none required) and the PPE required in the SDS (requires protective gloves and eye protection). There is no conflict between the label and SDS as regards the lack of a signal word.

There are no mammalian acute toxicity data in the SDS for the formulation.

There are no aquatic toxicity data in the SDS.

Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

The label states that there is a pH-stable antifoaming agent in Kicker CA. This is not described in the list of ingredients but is likely some type of polysiloxane.

The large percentage of non-disclosed ingredients (60-70%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

g. Special Purpose or Utility Adjuvants

Acidifiers

LI-700[®] Penetrant, Acidifier, Deposition Aid, Drift Control Agent (Loveland Products, Inc.)

CA Reg. # 34704-50035, WA Reg. # 34704-04007

Active Ingredients – 80%

Lecithin (phosphatidylcholine), CAS 8002-43-5 (soybean lecithin base)

Propionic acid (methylacetic acid) CAS 79-09-4, 35%

Alkyl polyoxyethylene ether, not further identified (likely to be ethoxylated alcohol, older MSDS characterizes this as a liquid detergent)

Water 20%

LI-700[®] has a Danger signal word, because of its corrosiveness to eyes and skin that is primarily due to the presence of methylacetic acid, also referred to as propionic acid. It is harmful if inhaled. LI-700[®] is not exceptionally acutely toxic orally or dermally. It is not a skin sensitizer. There is no conflict between the label required PPE (protective gloves, protective clothing, and face protection) and the PPE required in the SDS (although the SDS refers to impervious protective clothing and both goggles and a face shield). There is no conflict between the label and SDS as regards the Danger signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation. This product is considered slightly toxic via dermal and inhalation exposure and practically nontoxic via oral exposure. The SDS does note that LI-700 causes severe skin burns and eye damage. The SDS also states that chronic exposure to the fumes may cause teeth erosion and jaw necrosis and that bronchial irritation with chronic cough and pneumonia are common. Chronic exposure presents the possible risk of irreversible effects.

There are no aquatic toxicity data in the latest SDS. But an older SDS (6/19/15) does include aquatic toxicity data (refer to Table 2). The SDS lists a 96-hour LC₅₀ for rainbow trout of 130 mg/L and for bluegill of 210 mg/L and a 96-hour NOEC for rainbow trout of <100 mg/L and for bluegill of 100 mg/L. For aquatic invertebrates, there is a 48-hour EC₅₀ of 190 mg/L for *Daphnia magna* and a 48-hour NOEC of 100 mg/L. There is an acute toxicity value for bluegill in a 2003 study (Haller and Stocker 2003) that is also shown in Table 2 that would indicate this product is more toxic than the values in the SDS. There is an acute toxicity value for rainbow trout in a 2004 study (Smith et al 2004) that is shown in Table 2. It is not known whether the product tested in these two studies is the same formulation as this registered product. These data would indicate that this product is slightly toxic to practically nontoxic to fish and practically nontoxic to daphnia. It is approved for aquatic use by the state of Washington.

Phosphatidylcholine, also known as soybean lecithin, is likely added to this formulation as an emulsifier or as a surfactant. Phosphatidylcholines are such a major component of lecithin that in some contexts the terms are sometimes used as synonyms. However, lecithin extracts consist of a mixture of phosphatidylcholine and other compounds. Lecithins are fatty substances that naturally occur in animal and plant tissues. There is no signal word associated with lecithins or phosphatidylcholine as these are not considered hazardous. Exposure to phosphatidylcholine or lecithin may cause irritation of respiratory tract, skin irritation, and eye irritation.

Methyl acetic acid, also known as propionic acid, is a naturally occurring carboxylic acid. It is GRAS when used at low levels in foods as a preservative. It is naturally present at low levels in dairy products. It is present in the gastro-intestinal tract in mammals as an end-product of carbohydrate digestion. It has a signal word of Danger because of its skin and eye corrosivity. In addition, the vapors may irritate the eyes, nose, and throat. It is moderately toxic via dermal exposure, with a dermal LD₅₀ in rabbits of 500 mg/kg, but is only slightly toxic via oral or inhalation exposures. It is of moderate aquatic toxicity, with a 96-hour LC₅₀ in rainbow trout of 51 mg/L and a 48-hour EC₅₀ in *Daphnia magna* of 22.7 mg/L. It is expected to have very high mobility in soil, but is also rapidly biodegraded.

The nonionic surfactant contained in LI-700[®] is identified as alkyl polyoxyethylene ether. This generic term is insufficient to determine the exact compound. It is made up of an alkyl chain of some length combined with a hydrophilic oxyethylene chain of some length. A common example of such a surfactant is polyoxyethylene lauryl ether, also known as polyethylene glycol dodecyl ether; a common brand name is Brij.

Ethylene oxide (oxirane) and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Tri-Fol[®] Acidifier and Buffering Agent (Wilbur-Ellis Co.)

CA Reg. # 2935-50152; WA Reg. # 2935-50152; OMRI-Certified

Active Ingredients – 34%; noted as NPE-free

2-hydroxy-1,2,3-propanetricarboxylic acid, 25% (SDS says citric acid, CAS 77-92-9, 20-
<30%)

Calcium Chloride 9%, SDS says 5- <10% (CAS 10043-52-4)

Tri-Fol[®] has a Caution signal word. It is a mild eye and skin irritant. It is not expected to be a skin sensitizer. There is no conflict between the label required PPE (chemical-resistant gloves and eye protection) and the PPE required in the SDS. There is a conflict between the label signal word of Caution and the absence of a signal word in the SDS.

There are no mammalian acute toxicity data in the SDS for the formulation, although there are data for the two active ingredients. There is a mammalian acute toxicity value for oral exposure shown in Table 1. Based on this value, Tri-Fol[®] would be considered practically non-toxic via oral exposure.

There are no aquatic toxicity data in the SDS.

The acidifier in Tri-Fol[®] is citric acid (25% of the formulation). Citric acid is a weak organic acid occurring naturally in citrus fruits. It is very soluble in water. The FDA regards it as GRAS. It has many uses in foods and food products, medicines, household and personal care products. EPA has completed several comprehensive reviews of citric acid. Citric acid carries a signal word of Warning due to the risk of serious eye damage or irritation. It can also cause skin irritation. It is slightly toxic to practically non-toxic via oral exposure to rats and mice (LD₅₀ >3 g/kg). Dermal LD₅₀ >5 g/kg (slightly toxic), although it is not a skin sensitizer. Citric acid is of low toxicity to freshwater fish (bluegill 96-hour LC₅₀ is 1,516 mg/L) and aquatic invertebrates (waterflea 72-hour EC₅₀ is 240 mg/L).

Calcium chloride is used as an anti-browning agent in processed fruits and vegetables, and is GRAS. It is used as a deicer for roads. It has a signal word of warning due to its potential as an eye irritant. Calcium chloride is slightly toxic via oral exposure (oral LD₅₀ in rats ranges from 1 to 4.2 g/kg). In concentrated liquid forms, it can be very irritating to the skin and eyes. As a solid, it is slightly toxic via dermal exposure (dermal LD₅₀ in rabbit of >5 g/kg). It is of low

aquatic toxicity with a 96-hour LC₅₀ in bluegill of 10,650 mg/L and a 48-hour EC₅₀ in Daphnia of 2,400 mg/L. It rapidly degrades in the environment.

The large percentage of inert ingredients (66%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Drift Reduction Agents

In-Place[®] Deposition Aid and Drift Management Agent (Wilbur-Ellis Co.)

CA Reg # 2935-50169; WA Reg. # 2935-01003

Active Ingredients – 100%, noted as NPE-free

Modified vegetable oil, not further identified (older SDS identifies as a modified soybean oil, CAS 67784-80-9, 90-100%)

Aliphatic mineral oil, not further identified

Amine salts of organic acids, not further identified (older SDS identifies as 1 - <3%)

Aromatic acid, not further identified, although SDS calls it an organic acid (older SDS identifies as 1 - <3%)

In-Place[®] has a Warning signal word. It may cause an allergic skin reaction (a sensitizer). It may cause temporary eye irritation. Prolonged skin contact may cause temporary irritation. There is a conflict between the label-required PPE (chemical resistant gloves) and the PPE required in the SDS (which also requires eye protection and recommends both a face shield and an impervious apron). There is no conflict with the signal word between the label and SDS.

There are no mammalian acute toxicity data in the SDS for the formulation, although there are data for two of the active ingredients: the proprietary amine salts of organic acids; and the proprietary organic acid. The SDS states that skin contact can cause dermatitis. There are mammalian acute tox data for the formulation in Table 1. In-Place[®] is considered practically non-toxic via oral exposure and slightly toxic via dermal and inhalation exposure.

There are no aquatic toxicity data in the SDS. There are acute aquatic toxicity data in Table 2. Based on these data, In-Place[®] is considered practically non-toxic to fish and slightly toxic to daphnia.

The list of ingredients for In-Place[®] are too generic to be able to support much of a discussion about them, although some information is available from an older SDS and previous communications with the company.

The modified vegetable oil is identified in an older SDS (10/27/14) as a modified soybean oil with a CAS number of 67784-80-9 and making up at least 90% of the formulation. Whether this information is still current is unknown. This older SDS does not include the mineral oil that is in the current SDS, so it may be that the percentage of the formulation made of the modified vegetable oil has been reduced and replaced to some extent with mineral oil. Methylated soybean oil, aka methyl soyate, is the most commonly used biodiesel fuel in the United States. It is used in cosmetics, detergents, soaps and lubricants as a surfactant, solvent, or emollient. It is insoluble in water. It has no signal word as it is not considered hazardous. Mild irritation of nose and throat may occur; mild irritation of skin and eyes may occur. Some companies identify it as a skin

sensitizer. It is readily biodegradable and does not bioaccumulate. It is of low aquatic toxicity with a 48-hour EC₅₀ for Daphnia ranging from 332-5,243 mg/L and a 96-hour LC₅₀ in (unspecified) fish of >1,000 mg/L.

The term aliphatic mineral oil is likely referring to a paraffinic mineral oil. Mineral oil can have either Danger, Warning, or no signal word. It is generally of low acute toxicity (96-hour oral LD₅₀ in rat is >5 to >24 g/kg). Heavy exposure to oil mist may cause lipoid pneumonia. It can be an eye irritant. Prolonged contact with the skin may be irritating as well. Ingestion may cause diarrhea (it is used as a laxative), abdominal discomfort, and vomiting. Mineral oils are also used as the basis for many horticultural oils, which can affect terrestrial insects through suffocation. They are of low acute toxicity to aquatic organisms (96-hour LC₅₀ in rainbow trout ranges from >100 - 5,000 mg/L). They are not readily biodegradable but ultimately will biodegrade.

The reference to proprietary amine salts of organic acids is too vague to determine what it might be. In older communications with the company, the Forest Service was told that the amine salts of organic acids were slight skin and eye irritants. In an older SDS (10/27/14), the percentage of this ingredient is listed as 1 - <3%; whether this is still valid information is unknown. The current SDS provides an oral LD₅₀ value for the rat of 1,400 mg/kg (slightly toxic).

The reference to proprietary organic aromatic acid is too vague to determine what it might be. In older communications with the company, the Forest Service was told this aromatic acid is GRAS. In an older SDS (10/27/14), the percentage of this ingredient is listed as 1 - <3%; whether this is still valid information is unknown. The current SDS provides an oral LD₅₀ value for the rat of 2,742 mg/kg and for the mouse of 2,742 mg/kg (both slightly toxic). There is a 24-hour dermal LD₅₀ value for the rabbit of >2,000 mg/kg. The current SDS also lists a 4-hour inhalation LC₅₀ in the rat of >12.2 mg/L (slightly toxic).

Strike Zone[®] DF Drift Control Agent and Deposition Aid (Helena Agri-Enterprises, LLC)

CA Reg. # 5905-50084; WA Reg. # 5905-50084

Active Ingredients – 92%

Complex carbohydrate polymer, not further identified (likely some type of starch)

Alcohol ethoxylate, not further identified

Polyoxyethylene-polyoxypropylene copolymer, not further identified (likely as a surfactant)

Strike Zone[®] DF has a Warning signal word. It may cause eye irritation and mild skin irritation. It may be harmful if swallowed, inhaled, or in contact with skin. It is not a skin sensitizer. There is a conflict between the label-required PPE (chemical resistant gloves) and the PPE required in the SDS (which also requires eye protection and impervious apron and footwear). There is no conflict with the signal word between the label and SDS.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation. This product is considered slightly toxic via dermal and inhalation exposure and practically nontoxic via oral exposure.

There are no aquatic toxicity data in the SDS.

The list of ingredients for Strike Zone[®] DF are too generic to be able to support much of a discussion about them.

Complex carbohydrate polymers are polymers of the simple sugars. In other words, the complex carbohydrates are long chains of simple sugar units bonded together (for this reason the complex carbohydrates are often referred to as polysaccharides). The ingredient name is too generic to identify; however, this is likely a starch of some type (or less likely perhaps glycogen or cellulose).

Alcohol ethoxylate, not otherwise described, is listed as an ingredient in Strike Zone[®] DF. This could be in the formulation as a surfactant. Alcohol ethoxylates are not considered to be skin sensitizers, nor considered to be mutagenic, carcinogenic, or genotoxic. In a 2013 Environment Canada document on alcohol ethoxylates, these compounds affect fish and aquatic invertebrates more so than aquatic plants or algae. Aquatic toxicity increases with increasing carbon chain length and decreasing ethoxylate chain length. Linear ethoxylated alcohols are more toxic than branched. Commercial alcohol ethoxylates consist of a mixture of various homologues which differ in their relative toxicity.

The polyoxyethylene-polyoxypropylene copolymer represents a family of copolymers, combining ethylene oxide and propylene oxide. Used as a surfactant and antifoamer. The polyoxypropylene is a hydrophobic molecule and is combined with two flanking hydrophilic ethylene oxide chains. The name is generic and does not provide any idea of the exact nature and number of the two copolymers. These copolymers are also used as a treatment for alfalfa bloat in cattle. These copolymers are excreted quickly through urine with little metabolism. Some SDSs have no signal word due to low toxicity, others have a signal word of Warning due to inhalation risk. Acute oral LD₅₀ values in rats range from 2,300 - 22,400 mg/kg (considered slightly toxic to practically non-toxic). The dermal LD₅₀ values in rabbits range from >5 – 20 g/kg (practically non-toxic). Aquatic acute toxicity is low.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Interlock[®] Deposition Aid, Canopy Penetrating & Drift Control Agent (Winfield Solutions, LLC)

CA Reg. # 1381-50004; WA Reg. # 1381-05004

Active Ingredients – 100%

Modified vegetable oil, not further identified

Polyoxyethylene sorbitan fatty acid ester, not further identified

Vegetable oil, not further identified

Alkyl benzenesulfonic acid, calcium salt listed in SDS, CAS 84989-14-0, <1.5%
(surfactant?)

Isobutyl alcohol listed in SDS, CAS 78-83-1, <0.5%

InterLock[®] has a Caution signal word. It may be harmful if inhaled. It may cause minor eye and skin irritation. If swallowed it may cause minor irritation of the digestive tract. It is not a skin sensitizer. There is a conflict between the label-required PPE (none) and the PPE required in the

SDS (which requires protective gloves and eye protection). There is no conflict with the signal word between the label and SDS.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation. This product is considered slightly toxic via dermal and inhalation exposure and practically nontoxic via oral exposure.

There are no aquatic toxicity data in the SDS. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are shown in Table 2. These data would indicate this product is practically nontoxic to fish and daphnia. It is approved for aquatic use by the state of Washington.

The modified vegetable oil and the vegetable oil are too generic a description to determine what they might be. The modified oil could be referring to any of several methylated or ethylated vegetable or seed oils such as soybean or canola. Generally, of low acute toxicity. Similarly, vegetable oils are of low toxicity, often used as foods, and are GRAS.

Ethoxylated sorbitan esters are known as polysorbates (trade names: Scattics, Alkest, Canarcel, Tween). They are an important class of emulsifiers used in a variety of settings, including pharmaceuticals and food. They are soluble or dispersible in water but differ widely in organic and oil solubilities. Their variation is dependent on the esterified fatty acid with which the ethoxylated sorbitan is associated. The generic description on the label does not indicate which polysorbate is used. Most commercial polysorbates carry no signal word due to low hazard and toxicity.

The calcium salt of alkyl benzenesulfonic acid is present in low amounts (<1.5%). Often used as a surfactant, although whether that is its role in InterLock[®] is unknown. This compound has a signal word of Warning due to the potential for serious eye damage and skin irritation. It is harmful if swallowed. It has an oral LD₅₀ in the rat that ranges from 1,080 to 1,630 mg/kg and a dermal LD₅₀ in the rat of >2,000 mg/kg. The calcium salt of alkyl benzenesulfonic acid is harmful to aquatic life, although it is readily biodegradable in water. The 96-hour LC₅₀ in fish ranges from 1.7 to 7.7 mg/L. The 48-hour EC₅₀ in Daphnia is 5.7 mg/L with a NOEC of 3.2 mg/L.

Isobutyl alcohol, or isobutanol, is also listed as a minor ingredient in InterLock[®], making up less than 0.5% of the formulation. Isobutanol is widely used in industry, as a solvent in chemical reactions, as well as being a useful starting material for organic synthesis. Isobutanol is a flammable liquid that should be stored and used in well-ventilated areas. It is moderately irritating to the skin and greatly irritating to the eyes, mucous membranes and respiratory tract. Exposure to high concentrations of its vapor can cause temporary narcosis. It has a signal word of Danger due to risk of serious eye irritation and/or injury (may cause burns). The acute 4-hour inhalation LC₅₀ in rabbits is 2.6 mg/L. The 96-hour oral LD₅₀ in rats is 2,460 mg/kg and the dermal LD₅₀ in rabbits is 3,400 mg/kg. In terms of aquatic organisms, the 96-hour EC₅₀ in rainbow trout is 1,330 mg/L, with similar values in fathead minnow, bluegill, and daphnia. The most sensitive aquatic species appears to be *Xenopus laevis* with a 48-hour LC₅₀ of 18.3 mg/L.

Ethylene oxide and 1,4-dioxane will likely be a small component of any adjuvant that contains ethoxylated compounds. Some SDSs include them, others do not, but they are a common, albeit minor, contaminant in any ethoxylate (alcohol ethoxylate, alkylphenol ethoxylate, etc.). These two impurities are discussed in USDA 2003.

Defoamers

Foaminator[®] Dry Antifoaming/Defoaming agent (Winfield Solutions, LLC)

Active Ingredients – 15%

Dimethylpolysiloxane, not further identified

Polypropylene glycol, not further identified

Silicon dioxide, not further identified

Foaminator[®] Dry has a Warning signal word. It may cause moderate but temporary eye irritation. It may cause respiratory irritation; the label warns against inhaling the dust. Skin exposure may cause minor irritation. Foaminator[®] Dry may be harmful if swallowed. If ingested, it may cause severe irritation of the mouth, throat and stomach, and result in nausea, vomiting, and diarrhea. There is a conflict between the label and SDS as regards PPE; the label does not require any PPE while the SDS requires chemical resistant gloves and eye protection. There is no conflict between the label and SDS as regards the signal word.

There are no mammalian acute toxicity data in the SDS.

There are no aquatic toxicity data in the SDS.

The ingredient dimethylpolysiloxane is somewhat generic as it includes the segment *poly*, although the dimethyl indicates that this is a straight chain silicone rather than a cyclic silicone. This may be dimethicone (CAS 9016-00-6). Although this may or may not be the actual product used in this formulation, many of the closely related linear silicones have similar tox profiles. Dimethicone is not absorbed after ingestion based on testing in rats, dogs, and mice and is excreted unchanged in the feces. For this reason, it is practically non-toxic on an acute oral basis (rat LD₅₀ values range from 7 to 27 g/kg). It is a component of antacids, gas relievers, and cosmetics. It is of low acute toxicity to aquatic organisms and is not expected to bioaccumulate.

Polypropylene glycol (PPG) is a generic name for a large class of polymers. The exact size of the PPG in Foaminator[®] Dry is not specified, however the term polypropylene glycol is reserved for low to medium range molar mass polymers. Molecular weights between 1,200 and 3,000 are used as surfactants, antifoaming agents, also as solvents; used in personal care products, detergents, soaps. PPG is an indirect food additive for use only as a component of adhesives. Toxicity of PPG increases as molecular weight decreases. PPGs with molecular weights of 2,000 or greater are of low toxicity, with oral LD₅₀ values from 2 to >15 g/kg and acute dermal LD₅₀ values >10 g/kg. Toxicity to aquatic organisms is also low. Lower weight PPGs (molecular weights of 200 to 1,200) are of higher toxicity and also can cause central nervous system stimulation.

Silicon dioxide, also known as silica, is identified as part of the active ingredients in Foaminator[®] Dry, although it is more commonly used as an inert carrier. Hydrophobic silica is

used as a defoamer component and is likely the form of silica found in this product. Hydrophobic silica is a form of silica that has hydrophobic groups chemically bonded to the surface. The hydrophobic groups are normally alkyl or polydimethylsiloxane chains. Silica can be found in food and feed as an anti-caking agent. Hydrophobic silica generally has no signal word due to its low toxicity. It is of low acute toxicity, with an oral LD₅₀ value in rats of >1 g/kg. The dermal LD₅₀ in rabbits is >5 g/kg. Silicosis is a hazard from long-term inhalation of silica, however hydrophobic silica does not have this same risk. Silica does have some insecticidal properties, but this is through physical abrasion of protective oils, causing desiccation rather than through direct insect toxicity; it is not known whether hydrophobic silica has this same risk to insects.

As per the SDS, ethylene oxide may be a small component of this product. This impurity is discussed in USDA 2003.

The large percentage of inert ingredients (85%) in this product is troublesome. As this is a dry formulation, this inert fraction is not water.

FTF™ Defoamer Defoaming Agent (Wilbur-Ellis Company)

CA Reg. # 2935-50196; WA Reg. # 2935-13002

Active Ingredients – 29.53%

Silica Filled Polydimethylsiloxane, not further identified (CAS 67762-90-7)

Polypropylene glycol, not further identified

Siloxane Polyalkyleneoxide copolymer

Glycerin listed in SDS, CAS 56-81-5, 5 - <10% (listed in SDS)

FTF™ Defoamer has a Caution signal word. It may cause moderate eye irritation. It can be harmful if swallowed, absorbed through the skin, or inhaled. The PPE required by the label (protective eyewear and protective gloves) matches the PPE required in the SDS. There is a conflict between the label signal word (Caution) and the SDS signal word (none).

There are no mammalian acute toxicity data in the SDS.

There are no aquatic toxicity data in the SDS.

Silica filled polydimethylsiloxane is identified as part of the active ingredients in FTF™ Defoamer. Silica filled polydimethylsiloxane is another term for hydrophobic silica. Hydrophobic silica is used as a defoamer component. Hydrophobic silica is a form of silica that has hydrophobic groups chemically bonded to the surface. The hydrophobic groups are normally alkyl or polydimethylsiloxane chains. Silica can be found in food and feed as an anti-caking agent. Hydrophobic silica generally has no signal word due to its low toxicity. It is of low acute toxicity, with an oral LD₅₀ value in rats of >1 g/kg. The dermal LD₅₀ in rabbits is >5 g/kg. Silicosis is a hazard from long-term inhalation of silica, however hydrophobic silica does not have this same risk. Silica does have some insecticidal properties, but this is through physical abrasion of protective oils, causing desiccation rather than through direct insect toxicity; it is not known whether hydrophobic silica has this same risk to insects.

Polypropylene glycol (PPG) is a generic name for a large class of polymers. The exact size of the PPG in FTF™ Defoamer is not specified, however the term polypropylene glycol is reserved for low to medium range molar mass polymers. Molecular weights between 1,200 and 3,000 are

used as surfactants, antifoaming agents, also as solvents, and used in personal care products, detergents, and soaps. PPG is an indirect food additive for use only as a component of adhesives. Toxicity of PPG increases as molecular weight decreases. PPGs with molecular weights of 2,000 or greater are of low toxicity, with oral LD₅₀ values from 2 to >15 g/kg and acute dermal LD₅₀ values >10 g/kg. Toxicity to aquatic organisms is also low. Lower weight PPGs (molecular weights of 200 to 1,200) are of higher toxicity and also can cause central nervous system stimulation.

The siloxane polyalkyleneoxide copolymer is likely referring to an ethoxylated polydimethylsiloxane. The generic name does not allow for a determination of the number of dimethylsiloxane molecules or the degree of ethoxylation present. Ethoxylated siloxanes are added to adjuvants as nonionic superspreaders/wetters or as defoamers. They are also used in cosmetics (as antifoamer and skin conditioner), paints and other products. In this case there is a hydrophobic siloxane backbone and a hydrophilic ethylene oxide chain. Similar to the alcohol ethoxylates, toxicity appears to be related to the number of ethoxylate groups, with more ethoxylate groups representing lower toxicity.

Glycerol (also called glycerine or glycerin) is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. Due to having antimicrobial and antiviral properties it is widely used in FDA-approved wound and burn treatments. It is also widely used as a sweetener in the food industry and as a humectant in pharmaceutical formulations. Glycerol is miscible with water and is hygroscopic in nature. Glycerol is used in medical, pharmaceutical and personal care preparations, often as a means of improving smoothness, providing lubrication, and as a humectant. Glycerol is endogenous in the human body. It has no signal word due to low hazard. Glycerol can be irritating to the eyes, but without injury. It has very low toxicity when ingested. The oral LD₅₀ in rats ranges from 5.6 – 12.6 g/kg; in the mouse 4.1 g/kg. It has a dermal LD₅₀ in the rabbit of >10 g/kg. It is of low aquatic toxicity. Biodegradation is an important environmental fate process in water and soil.

The large percentage of inert ingredients (70.47%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Water Conditioning Agents

Bronc[®] Max Water Conditioning Agent (Wilbur-Ellis Company)

CA Reg. # 2935-50174; WA Reg. # 2935-03005

Active Ingredients – 39.08%, noted as NPE-free

Ammonium sulfate, CAS 7783-20-2, 30-<40%, 3.68 pounds/gallon

Sodium alkyl sulfobenzene salt, not further identified, likely anionic surfactant

2-hydroxy-1,2,3-propanetricarboxylic acid (a synonym for citric acid) CAS 77-92-9, 1-<3%

Bronc[®] Max has a Warning signal word, with a note that it can be harmful if inhaled and a warning to avoid breathing the mist or spray. Direct contact with eyes may cause temporary irritation. Prolonged skin contact may cause temporary irritation. There is a conflict between the PPE required by the label (none) and the PPE required by the SDS (chemical-resistant gloves,

chemical respirator with full facepiece). There is no conflict between the label and SDS as regards the signal word.

There are no mammalian acute toxicity data in the SDS for the formulation, only for two of the component ingredients. There are mammalian acute toxicity data for the formulation in Table 1. Bronc[®] Max is considered practically non-toxic via oral exposure and slightly toxic via dermal or inhalation exposure. It is not considered a skin sensitizer.

There are aquatic toxicity data in the SDS (refer to Table 2). There is a 96-hour LC₅₀ for an unspecified fish species of >100 mg/L with a corresponding NOEC of 50 mg/L. The species is likely trout based on WSDA 2018 and Glatzhofer 2020. The SDS also listed a 48-hour EC₅₀ for daphnia of 100 mg/L, however this value is questionable since the SDS also lists a corresponding NOEC of >100 mg/L. The NOEC being higher than the EC₅₀ brings into question both values, however this paper assumes the values were erroneously reversed and considers the EC₅₀ value to be >100 mg/L. There are acute toxicity values for rainbow trout and daphnia listed in a Washington State document (WSDA 2018), which are also shown in Table 2. These values indicate this product is practically nontoxic to fish and daphnia. This product is approved for aquatic use by the state of Washington.

Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Sodium alkyl sulfobenzene salt may be referring to sodium dodecylbenzene sulfonates. The exact compound included here is unknown. This ingredient is likely added as a surfactant although some forms can also mitigate hard water. While commercial linear alkyl benzenesulfonates (LAS) consists of more than 20 individual components, the ratio of the various homologs and isomers, representing different alkyl chain lengths and aromatic ring positions along the linear alkyl chain, is relatively constant in currently produced products, with the weighted average carbon number of the alkyl chain based on production volume per region between 11.7-11.8. Because the mean carbon chain length is approximately 12, dodecylbenzene sulfonate is considered representative of the entire class of compounds. It has a signal word of danger due to serious eye damage. It is a skin irritant. It is toxic to aquatic life, although rapidly biodegrades.

Citric acid is also present, likely added to provide the acidifier quality of this formulation. Citric acid is a weak organic acid occurring naturally in citrus fruits. It is very soluble in water. Citric acid is GRAS as it has many uses in foods and food products, medicines, household and personal care products. EPA has completed several comprehensive reviews of citric acid. Citric acid

carries a signal word of Warning due to the risk of serious eye damage or irritation. It can also cause skin irritation. It is slightly toxic to practically non-toxic via oral exposure to rats and mice ($LD_{50} >3$ g/kg). Dermal $LD_{50} >5$ g/kg (slightly toxic), although it is not a skin sensitizer. Citric acid is of low toxicity to freshwater fish (bluegill 96-hour LC_{50} is 1,516 mg/L) and aquatic invertebrates (waterflea 72-hour EC_{50} is 240 mg/L).

The large percentage of inert ingredients (60.92%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Quest[®] (CA) Water Conditioning Agent – California Label (Helena Agri-Enterprises, LLC)

CA Reg. # 5905-50076

Active Ingredients – 49.76%

Hydroxy carboxylic acid, not further identified (citric acid?)

Phosphoric acids, not further identified

Ammonium sulfate, not further identified (CAS 7783-20-2)

Polyacrylic acid, 1%, CAS 9003-01-4

Quest[®] (CA) has a Warning signal word, mainly as a result of its ability to be a skin irritant and sensitizer. It can cause eye irritation. Quest[®] (CA) may be harmful if swallowed or inhaled. There is a discrepancy between the label-required PPE (gloves and eye protection) and the PPE required by the SDS (which also includes impervious apron and footwear). There is no discrepancy between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation. This product is considered slightly toxic via dermal, inhalation, and oral exposure. It may cause an allergic skin reaction in sensitive individuals.

There are no aquatic toxicity data in the SDS.

The term hydroxy carboxylic acid could represent any of several compounds, including glycolic, citric, and lactic acid. It is unknown what specific compound is being referred to in this case, although citric acid is a common ingredient found in adjuvants. If this is referring to citric acid, it is likely added to provide the acidifier quality of this formulation. Citric acid is a weak organic acid occurring naturally in citrus fruits. It is very soluble in water. Citric acid is GRAS as it has many uses in foods and food products, medicines, household and personal care products. EPA has completed several comprehensive reviews of citric acid. Citric acid carries a GHS signal word of Warning due to the risk of serious eye damage or irritation. It can also cause skin irritation. It is slightly toxic to practically non-toxic via oral exposure to rats and mice ($LD_{50} >3$ g/kg). Dermal $LD_{50} >5$ g/kg (slightly toxic), although it is not a skin sensitizer. Citric acid is of low toxicity to freshwater fish (bluegill 96-hour LC_{50} is 1,516 mg/L) and aquatic invertebrates (waterflea 72-hour EC_{50} is 240 mg/L).

Phosphoric acid is a colorless, odorless phosphorus-containing inorganic acid. In low concentrations, it is safe on skin and even for consumption (it is used in food, cosmetics and dental products). However, at very high concentrations, it is corrosive and can cause skin burns and eye damage. It has a Danger signal word. Phosphoric acid is a sequestering agent which binds many metal cations. It is likely added to this formulation as an acidifier. The 96-hour oral

LD₅₀ in rats is 1,530 mg/kg. The dermal LD₅₀ in rabbits is 2,740 mg/kg. A 1-hour inhalation LC₅₀ is >0.85 mg/L.

Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Polyacrylic acid is a synthetic high-molecular weight polymer of acrylic acid. Polyacrylic acids have the ability to absorb and retain water and swell to many times their original volume. They are used as thickening, dispersing, suspending, and emulsifying agents in pharmaceuticals, cosmetics, and paints. From a search of online SDSs polyacrylic acid appears to have no signal word due to low hazard. The oral LD₅₀ in rats is 2,500 mg/kg. Polyacrylic acid is not a skin or eye irritant. Aquatic toxicity is low with the 96-hour LC₅₀ in bluegill of 580 mg/L and the 96-hour EC₅₀ in *Daphnia* of 168 mg/L.

The large percentage of inert ingredients (50.24%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Quest® (WA) Water Conditioning Agent – Washington Label (Helena Agri-Enterprises, LLC)

WA Reg. # 5905-11003

Active Ingredients – 56%

Ammonium sulfate, not further identified (CAS 7783-20-2)

Phosphoric acid, not further identified

Carbamide, not further identified (aka urea, CAS 57-13-6)

Quest® (WA) has a Warning signal word. Skin exposure may be harmful and lead to irritation and a possible allergic skin reaction. It may cause eye irritation and may be harmful if inhaled or swallowed. There is a discrepancy between the label-required PPE (gloves and eye protection) and the PPE required by the SDS (which also includes impervious apron and footwear). There is no discrepancy between the label and SDS as regards the Warning signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation. This product is considered slightly toxic via dermal, inhalation, and oral exposure. It may cause an allergic skin reaction in sensitive individuals.

There are no aquatic toxicity data in the SDS.

Ammonium sulfate is used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. As an adjuvant it functions to bind iron and calcium cations that are

present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4-D (amine), glyphosate, and glufosinate herbicides. Ammonium sulfate is GRAS as it is used as an acidity regulator in flours and breads. It has a signal word of Warning due to skin and eye irritation, although it is of relatively low acute toxicity (oral LD₅₀ in rats ranges from 2,000 – 4,250 mg/kg; dermal LD₅₀ in rat is >2 g/kg). Slightly toxic to aquatic organisms (a 96-hour LC₅₀ in rainbow trout ranged from 35 – 44 mg/L while a 48-hour EC₅₀ in the water flea (*Ceriodaphnia dubia*) ranged from 52-67 mg/L). A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOAEC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Phosphoric acid is a colorless, odorless phosphorus-containing inorganic acid. In low concentrations, it is safe on skin and even for consumption (it is used in food, cosmetics and dental products). However, at very high concentrations, it is corrosive and can cause skin burns and eye damage. It has a Danger signal word. Phosphoric acid is a sequestering agent which binds many metal cations. It is likely added to this formulation as an acidifier. The 96-hour oral LD₅₀ in rats is 1,530 mg/kg. The dermal LD₅₀ in rabbits is 2,740 mg/kg. A 1-hour inhalation LC₅₀ is >0.85 mg/L.

Carbamide, also known as urea, is the main nitrogen-containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water, and practically non-toxic (the oral LD₅₀ for rats is 8 - 15 g/kg). Dissolved in water, it is neither acidic nor alkaline. Urea is widely used in fertilizers as a source of nitrogen and is an important raw material for the chemical industry. Urea is GRAS. It does not carry a signal word because it is not considered hazardous. It may irritate the eyes, skin, and respiratory tract. Repeated or prolonged contact with skin can cause dermatitis. It is practically non-toxic to aquatic organisms and is rapidly hydrolyzed to ammonia and carbon dioxide. It is not expected to bioconcentrate.

The large percentage of inert ingredients (44%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

h. Dyes and Colorants

Hi-Light[®] Blue and Hi-Light[®] Blue WSP[®] (BASF)

With the exception of the following ingredients listed on the 2015 SDS, no further ingredients have been identified:

SDS for the WSP includes benzenemethanaminium, CAS 3844-45-9 (C.I. Acid Blue 9, disodium salt)

Hi-Light[®] Blue dye is not required to be registered as a pesticide; therefore, they have no label signal word. The SDSs includes notations that no signal word is needed due to low hazard. Prolonged or repeated contact may be mildly irritating to the skin, eyes, and respiratory tract. Ingestion may cause gastrointestinal disturbance. The SDSs require gloves and eye protection.

There are mammalian acute toxicity data in the SDS (refer to Table 1) for the product formulation. This product is considered slightly toxic via dermal and inhalation exposure. It is

considered practically nontoxic via oral exposure. The SDSs state that, based on the properties of the individual components, chronic exposure should not result in any specific organ toxicity, genotoxicity, carcinogenicity, reproductive toxicity or teratogenicity. However, the SDS for the WSP formulation states that it contains a chemical known to the state of California to cause cancer and birth defects or other reproductive harm, although what specific chemical this is referring to is unknown. It does not appear to be the dye.

There are no aquatic toxicity data in the SDS.

Hi-Light[®] Blue is a liquid while Hi-Light[®] Blue WSP is a dry flowable. Both are water-soluble dyes that contain no listed hazardous substances. They are considered to be virtually non-toxic to humans. The effect on non-target terrestrial and aquatic species is unknown, however use has not resulted in any known problems. The dye used in Hi-Light[®] Blue is commonly used in toilet bowl cleaners and as a colorant for lakes and ponds (SERA 1997b).

The SDS for the WSP formulation lists a specific dye as being present, benzenemethanaminium, also known as C.I Acid Blue 9, disodium salt. Whether this is the same dye found in the liquid formulation is unknown. This dye is used as a coloring in food, drugs, and cosmetics. There is a human acceptable daily intake of 0.6 mg/kg/day based on a NOAEL of 631 mg/kg/day in a chronic rat exposure study. It has no signal word due to low hazard. The 96-hour oral LD₅₀ in rat is >2 g/kg. The 96-hour LC₅₀ in bluegill is >96 mg/L and in rainbow trout is 96 mg/L. The 48-hour EC₅₀ in Daphnia is >97 mg/L.

Colorfast[™] Purple (BASF)

From the 2014 SDS, these ingredients have been identified:

Glacial Acetic Acid (CAS 64-19-7) 25-50% by weight

C.I. Basic Violet 1 (CAS 8004-87-3) 25-50% by weight

Proprietary ingredients 65-84% by weight

Colorfast[™] Purple dye is not required to be registered, therefore it has no label signal word. However, the SDS does have the Danger signal word. It contains a very concentrated acetic acid. It is irritating to the skin, and repeated contact may cause dermatitis and burns. It can be severely irritating to the eyes, and can cause burns and permanent damage. There is a conflict between the label required PPE (organic acid-resistant gloves and goggles) and the SDS required PPE (which also recommends coveralls and an apron).

There are mammalian acute toxicity data in the SDS (refer to Table 1). Colorfast[™] Purple is slightly toxic via oral and dermal exposure and practically nontoxic via inhalation exposure (all acute toxicity estimates). Severe inhalation exposure may cause pulmonary edema, irritation of the respiratory tract, and inflammation of the lungs. Ingestion may cause moderate to severe gastric irritation. Ulceration or perforation of the gastro-intestinal tract may also occur. Exposure may provoke an asthmatic response in persons with asthma who are sensitive to airway irritants.

There are no aquatic toxicity data in the SDS. A statement in the SDS indicates a high probability that it is not acutely harmful to aquatic organisms.

Acetic acid is the ingredient in household vinegar, although vinegars are normally 4% acetic acid, whereas Colorfast™ Purple contains approximately 30% by weight. Concentrated acetic acid is a very strong eye and skin irritant, and eye exposure can be very hazardous, with permanent damage a possibility. It carries a Danger signal word. Beyond its health effects, concentrated acetic acid is the active ingredient found in several organic herbicide formulations. Aquatic toxicity is low with a 96-hour LC₅₀ in rainbow trout of >1,000 mg/L.

The colorant in Colorfast™ Purple is identified in the SDS as C.I. Basic Violet 1, or methyl violet 2B. Older SDS and MSDS documents identified it as gentian violet, so it appears to have recently undergone a formulation change. Gentian violet is closely related chemically to methyl violet 2B. From a search of on-line SDSs, methyl violet 2B has either a signal word of Danger or Warning. It is corrosive, with serious eye damage possible and skin irritation and possible dermatitis. The 96-hour oral LD₅₀ in rats is 413 to 460 mg/kg; in mice 105 mg/kg. It is very toxic to aquatic life with a 96-hour LC₅₀ in fathead minnow of 0.047 mg/L. The Colorfast™ Purple SDS includes statements that this colorant may be a possible carcinogen, although it is not listed under California's Proposition 65 list.

The large percentage of non-specified proprietary ingredients (65-84%) in this product is troublesome.

Colorfast™ Red (BASF)

From the 2014 SDS, these ingredients have been identified:

Lactic acid, CAS 50-21-5, 25-35% by weight

C.I. Basic Violet 10, CAS 81-88-9, 25-40% by weight (Rhodamine B)

Non-disclosed proprietary ingredients 25-50% by weight

Colorfast™ Red dye is not required to be registered, therefore it has no label signal word. However, the SDS does have the Danger signal word. It is irritating to the skin. It can cause serious eye damage. There is a conflict between the label required PPE (organic acid-resistant gloves and goggles) and the SDS required PPE (which also recommends coveralls and an apron).

There are no mammalian acute toxicity data in the SDS. Based on an assessment of the individual ingredients, the manufacturer asserts that Colorfast™ Red should be virtually nontoxic via inhalation or after a single skin exposure. Single oral exposure should be of moderate toxicity. Similarly, assessment of components resulted in no statements of concern for chronic exposures, although the basic violet 10 dye is a potential human carcinogen and is listed as such under California's Proposition 65.

There are no aquatic toxicity data in the SDS. A statement in the SDS indicates that it is acutely harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

Lactic acid is an organic acid that is miscible in water and is hygroscopic (absorbs water). Lactic acid is found primarily in sour milk products, such as yogurt. It is also responsible for the sour flavor of sourdough bread. It is used as a flavoring agent and acidifying agent in foods. Lactic acid is GRAS when added to food. Lactic acid is a normal metabolic compound produced by most mammalian cells. In Colorfast™ Red, it is probably added as a solvent for the dye. It has a Danger signal word due to risk of serious eye damage. It is caustic in concentrated solutions and

can cause skin irritation. It has a 96-hour LD₅₀ value in rats of 3.5 g/kg. The dermal LD₅₀ in rabbit is >2 g/kg. In the environment, it is expected to move quickly through the soil, but also to quickly biodegrade. The 18-hour LC₅₀ in rainbow trout is 100 mg/L.

The C.I Basic Violet 10 dye in Colorfast™ Red has several other names including rhodamine B and D&C Red No. 19. D&C Red No. 19 is listed on California's Proposition 65 as a potential carcinogen. This dye has a signal word of Danger due to risk of serious eye damage. It can be harmful if swallowed. The oral LD₅₀ in mice is 887 mg/kg and in rats is 2,000 mg/kg. In a chronic toxicity test with mice, there was a significant increase in hepatocellular carcinomas in high-dose females. Adverse reproductive and mutagenic effects have also been seen in test animals. For a more complete review of the carcinogenicity of this dye (SERA 1997b). Rhodamine dye is harmful to aquatic life with long-lasting effects. The 96-hour LC₅₀ in sheepshead minnow is 83.9 mg/L; it is less toxic in bluegill and rainbow trout. The 48-hour EC₅₀ in *Daphnia magna* is 22.9 mg/L. The 72-hour EC₁₀ for the freshwater green algae *Scenedesmus subspicatus* is 12 mg/L. It is not considered to be rapidly biodegradable.

The large percentage of non-specified proprietary ingredients (25-50%) in this product is troublesome.

Bas-Oil® Blue (BASF)

From the 2013 SDS, these ingredients have been identified:

Solvent naphtha, CAS 64742-94-5, 1 - 5%

Proprietary Ingredients, 90-100%

Bas-Oil® Blue is not required to be registered; therefore, it has no label signal word. Even though signal words are required on the SDS, the available SDS does not contain a signal word, nor does it give a reason for not including it. It may cause mild eye and skin irritation. Prolonged or repeated exposure may cause respiratory tract irritation. Ingestion may cause gastrointestinal disturbances. There is a conflict between the label required PPE (none) and the SDS required PPE (protective gloves, safety glasses, and recommends coveralls and an apron).

There are no mammalian acute toxicity data in the SDS. The SDS includes a statement that this product contains a chemical listed as a carcinogen under California's Proposition 65.

There are no aquatic toxicity data in the SDS. A statement in the SDS indicates that it is acutely harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

The heavy aromatic solvent naphtha is a complex combination of hydrocarbons obtained from distillation of aromatic streams. It consists predominantly of aromatic hydrocarbons having 9 to 16 carbon atom chains. It is used here as a solvent. It is of low acute toxicity in mammals. The primary effect of naphtha and petroleum solvents involves central nervous system depression and other signs of neurotoxicity. Naphthas may also contain naphthalene. Naphthalene contents >1% are described as harmful to health and suspected of causing cancer. It is unknown what level of naphthalene is present here, although the SDS does not specifically break out naphthalene for identification. Whether the possible presence of naphthalene is the reason for the Proposition 65 cancer warning in the SDS is unclear. For a discussion of risks, refer to Forest Service human

health and ecological risk assessments on sethoxydim (SERA 2001) and clethodim (SERA 2014).

The large percentage of non-specified proprietary ingredients (90-100%) in this product is troublesome. The identity of the colorant or dye would be helpful. It is unknown whether this dye is still the same compound, anthraquinone dye, identified under the 2007 MSDS.

Bas-Oil[®] Red (BASF)

From the 2014 SDS, these ingredients have been identified:

Hydrotreated heavy naphthenic distillates (petroleum), CAS 64742-52-5, 25-45% by weight

Hydrotreated light naphthenic distillates (petroleum), CAS 64742-53-6, 25-45% by weight

Ethylbenzene, CAS 100-41-4, 0.1-1% by weight

Proprietary Ingredients, 10-50%

Bas-Oil[®] Red is not required to be registered; therefore, it has no label signal word. The SDS does not have a signal word due to low hazard. Prolonged or repeated contact may cause minor eye and skin irritation. Prolonged or excessive exposure may cause respiratory tract irritation. Ingestion may cause gastrointestinal disturbances. There is a conflict between the label required PPE (none) and the SDS required PPE (protective gloves, safety glasses, and recommends coveralls and an apron).

There are estimates of mammalian acute toxicity data in the SDS (refer to Table 1). It is practically nontoxic due to oral and inhalation exposure. It is slightly toxic via dermal exposure. The SDS includes a statement that this product contains a chemical listed as a carcinogen under California's Proposition 65.

There are no aquatic toxicity data in the SDS. A statement in the SDS indicates that there is a high probability that the product is not acutely harmful to aquatic organisms.

The hydrotreated light and heavy naphthenic distillates are complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists predominantly of aromatic hydrocarbons having carbon numbers predominantly in the range of C₁₅ through C₃₀ (light) and C₂₀ through C₅₀ (heavy). They are used here as solvents. Both are of low acute toxicity in mammals. The primary effect of these naphthas and petroleum solvents involves central nervous system depression and other signs of neurotoxicity. Naphthas may also contain naphthalene. Naphthalene contents >1% are described as harmful to health and suspected of causing cancer. It is unknown what level of naphthalene is present here, although the SDS does not specifically break out naphthalene for identification. Whether the possible presence of naphthalene is the reason for the Proposition 65 cancer warning in the SDS is unclear. For a discussion of risks, refer to Forest Service human health and ecological risk assessments on sethoxydim (SERA 2001) and clethodim (SERA 2014).

Ethylbenzene is a highly flammable liquid with the smell of gasoline. Ethylbenzene is often found in other manufactured products, including pesticides, cellulose acetate, synthetic rubber, paints, and inks. The acute toxicity of ethylbenzene is low unless aspirated into lungs where it

may result in chemical pneumonitis. The most sensitive target of ethylbenzene toxicity in laboratory animals is the inner ear. Repeated exposure to low vapor levels or high oral doses causes irreversible damage and hearing loss. The longer-term toxicity and carcinogenicity are ambiguous. Ethylbenzene is classified as a possible carcinogen by the International Agency for Research on Cancer (IARC) and under California's Proposition 65, however, the EPA has not determined ethylbenzene to be a carcinogen.

The large percentage of non-specified proprietary ingredients (10-50%) in this product is troublesome. The identity of the colorant or dye would be helpful.

Mark-It Blue[®] Spray Solution Colorant (Lawn and Garden Products, Inc.)

No information on ingredients is available.

Mark-It Blue[®] has a Caution signal word. Direct contact with eyes may cause temporary eye irritation. Prolonged contact with the skin may cause temporary irritation. It is expected to be a low ingestion hazard. There is no conflict between the label required PPE (protective gloves, safety glasses) and the SDS required PPE. There is a conflict between the label signal word (Caution) and the SDS signal word (none).

There are limited (estimated) mammalian acute toxicity data in the SDS (refer to Table 1). It is practically nontoxic via oral exposure.

There are limited (estimated) aquatic toxicity data in the SDS (refer to Table 2). A 96-hour LC₅₀ in fish is estimated at 9,890 mg/L. A statement in the SDS indicates that this product is not classified as environmentally hazardous. The acute toxicity value would indicate this product as practically nontoxic to fish.

There are no available ingredients listed on the label, the SDS, or product literature.

Blazon[®] Blue (Milliken Chemical)

From the 2015 SDS, these ingredients have been identified:

Sodium hydroxide, CAS 1310-73-2

Urea, CAS 57-13-6

Blazon[®] Blue is not required to be registered; therefore, it has no label signal word. The SDS does not have a signal word due to low hazard. Exposure may cause temporary skin and eye irritation. There is a conflict between the label required PPE (none) and the SDS required PPE (protective gloves, safety glasses, and coveralls).

There are limited (estimated) mammalian acute toxicity data in the SDS (refer to Table 1). It is practically nontoxic via oral exposure.

There are no aquatic toxicity data in the SDS.

Section 15 of the SDS lists urea and sodium hydroxide as potential air or water contaminants from the use of Blazon[®] Blue. But it is not known how much of the formulation is made up of these two ingredients.

Urea is the main nitrogen-containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water, and practically non-toxic (the oral LD₅₀ for rats is 8 - 15 g/kg). Dissolved in water, it is neither acidic nor alkaline. Urea is widely used in fertilizers as a source of nitrogen and is an important raw material for the chemical industry. Urea is GRAS. It does not carry a signal word because it is not considered hazardous. It may irritate the eyes, skin, and respiratory tract. Repeated or prolonged contact with skin can cause dermatitis. It is practically non-toxic to aquatic organisms and is rapidly hydrolyzed to ammonia and carbon dioxide. It is not expected to bioconcentrate.

Sodium hydroxide (also known as lye) is a caustic material that can decompose proteins and lipids in living tissues resulting in chemical burns. It has a signal word of Danger due to its corrosiveness to skin and eyes. It can also be corrosive to metals. As a liquid it is clear, colorless, and odorless. Inhalation, ingestion, skin contact can all be damaging to those tissues.

Dynamark® U.V. (Winfield Solutions, LLC)

No information on ingredients is available.

Dynamark® U.V. has a Caution signal word. Direct contact may cause mild but reversible eye and skin irritation. Inhalation may cause minor irritation of the respiratory tract. It is expected to be a low ingestion hazard. There is a conflict between the label required PPE (none) and the SDS required PPE (recommends protective gloves and safety glasses). There is no conflict between the label and the SDS as regards the signal word.

There are mammalian acute toxicity data in the SDS (refer to Table 1). It is slightly toxic via dermal and inhalation exposure and practically nontoxic via oral exposure.

There are no aquatic toxicity data in the SDS. There is a statement in the SDS that this product is anticipated to be harmful to aquatic life with long lasting effects. This is a troublesome statement.

There are no available ingredients listed on the label, the SDS, or product literature.

i. Table 1 – Standard Mammalian Acute Toxicity Testing Results⁵

Name	Oral LD ₅₀	Dermal LD ₅₀	Inhalation LC ₅₀
Alkylphenol ethoxylate-based surfactants			
R-11 [®]	1.75 g/kg (Glatzhofer 2020)	>5 g/kg (Glatzhofer 2020)	>0.55 mg/L (Glatzhofer 2020)
Activator 90	3.87 to 5.0 g/kg	>2 g/kg	>1.42 mg/L
Pro-Spreader Activator	1.7 g/kg	>2.02 g/kg	NA
Pro-90	1.7 g/kg	>2.02 mg/kg	NA
Ad-Wet 90 CA	NA	NA	NA
Ad-Wet 90	NA	NA	NA
Induce [®] WA label	>4 g/kg	>2 g/kg	2.02 mg/L
Induce [®] CA label	>4 g/kg	>2 g/kg	2.02 mg/L
Alcohol ethoxylate-based surfactants			
Denali EA [™]	>5 g/kg (Glatzhofer 2020)	>5 g/kg (Glatzhofer 2020)	>2.07 mg/L (Glatzhofer 2020)
Wetcit	>2 g/kg	>2 g/kg	>2.13 mg/L
Rainier-EA [™]	NA	NA	NA
Liberate [®]	>5 g/kg	>2 g/kg	2.1 mg/L
Silicone-based wetter/spreaders			
Freeway ^{®6}	<5 g/kg	>2 g/kg	>0.01 mg/L
Silwet L-77 [®]	2.33 g/kg	2.64 g/kg	NA
Kinetic [®] CA label	>2.89 g/kg	>2.02 g/kg	>0.754 mg/L 2015 SDS
Kinetic [®] WA label	>2.89 g/kg	>2.02 g/kg	NA
Silwet [®] Eco Spreader	>2 g/kg	>2 g/kg	2 mg/L
Hi-Wett [®]	>2 g/kg	>2 g/kg	2 mg/L
Cationic Surfactants – Ethoxylated Fatty Amines			
Entry [™] II, POEA	1.3 g/kg Toximul TA-5 SDS	>1.26 g/kg Toximul TA-5 SDS	NA
Sticker/Spreaders			
Bond [®]	>5 g/kg 2010 MSDS	>2 g/kg 2010 MSDS	4.73 mg/L 2010 MSDS
Bond Max [®]	>2 g/kg	>2 g/kg	4.73 mg/L
Tactic [™]	>5 g/kg	>2 g/kg	>2.33 mg/L

⁵ Source of data is recent SDS (refer to Section 6) unless otherwise noted. NA indicates toxicity data for the formulation was not available.

⁶ Oral and Inhalation toxicity values for Freeway[®] are suspected of being in error but are the values in most recent SDS.

Name	Oral LD ₅₀	Dermal LD ₅₀	Inhalation LC ₅₀
Cohere [®]	>5 g/kg	>5 g/kg	NA
Surfix [®] -P	>5.05 g/kg	>5.05 g/kg	NA
Sustain [®]	>5.05 g/kg	>5.05 g/kg	>5.26 mg/L
Vegetable-Based Oils			
Competitor [®]	>5 g/kg 2005 MSDS	>5 g/kg 2005 MSDS	>2.02 mg/L (Glatzhofer 2020)
MSO [®] Con'c	5 g/kg	>4 g/kg	>2.01 mg/L
Hasten-EA [™]	>5 g/kg 2014 SDS	>5 g/kg 2014 SDS	>2.08 mg/L 2014 SDS
Pathfinder [®] II	4.183 g/kg	>2g/kg	>4.7 mg/L
Improved JLB Oil Plus	>5 g/kg 2000 MSDS	>3.16 g/kg 2000 MSDS	NA
M.O.C	>3.989 g/kg	>4.950 g/kg	NA
MSO [®] with Leci-Tech	>2 g/kg	>4 g/kg	>2.01 mg/L
Renegade-EA [®]	>5 g/kg (Glatzhofer 2020)	>5 g/kg (Glatzhofer 2020)	>2.14 mg/L (Glatzhofer 2020)
Super Spread [®] MSO	>5 g/kg (Glatzhofer 2020)	>5 g/kg (Glatzhofer 2020)	>2.09 mg/L (Glatzhofer 2020)
MES-100 [™]	>5 g/kg	>5 g/kg	NA
Spraytech Oil [™]	>5 g/kg 1996 MSDS	>3.16 g/kg 1996 MSDS	NA
Blends of vegetable oils and silicone-based surfactants			
Syl-Tac-EA [™]	>5 g/kg 2014 SDS	>5 g/kg 2014 SDS	>2.07 ml/L 2014 SDS
Phase [®]	>5 g/kg	>2 g/kg	0.91 mg/L
Dyne-Amic [®]	>5.05 g/kg	>2.02 g/kg	>5.07 mg/L
Crop Oils and Crop Oil Concentrates			
Agri-Dex [®]	>5 g/kg	>5.05 g/kg	>2.17 mg/L
Mor-Act [®] (CA)	>2 g/kg (Glatzhofer 2020)	>2 g/kg (Glatzhofer 2020)	NA
Mor-Act [®] (WA)	>5 g/kg (Glatzhofer 2020)	>2 g/kg (Glatzhofer 2020)	>2.02 mg/L (Glatzhofer 2020)
Herbimax [®]	>5 g/kg	>2 g/kg	1.42 mg/L
Grounded [®] -CA	>5 g/kg	>5.05 g/kg	>2.17 mg/L
Grounded [®] -WA	>5 g/kg	>5.05 g/kg	>2.17 mg/L
Inlet [®]	>5 g/kg	>5 g/kg	>2.10 mg/L
W.E.B. Oil	NA	NA	NA
OMRI-Certified Wetter/Spreaders/Stickers			
Freeway ^{®7}	<5 g/kg	>2 g/kg	>0.01 mg/L

⁷ Oral and Inhalation toxicity values for Freeway[®] are suspected of being in error but are the values in most recent SDS.

Name	Oral LD₅₀	Dermal LD₅₀	Inhalation LC₅₀
Kinetic [®] CA label	>2.89 g/kg	>2.02 g/kg	>0.754 mg/L 2015 SDS
Kinetic [®] WA label	>2.89 g/kg	>2.02 g/kg	NA
Organic BioLink [®]	NA	NA	NA
Miller Nu Film P [®]	>5.05 g/kg	>5.05 g/kg	>5.26 mg/L
Sustain [®]	>5.05 g/kg	>5.05 g/kg	>5.26 mg/L
Activators - Fertilizer/Surfactant Mixtures			
Brandt [®] Magnify	>5 g/kg	>5 g/kg	888 mg/L
Class Act [®] NG [®]	>5 g/kg	>5 g/kg	NA
Bronc [®] Plus Dry-EDT	NA	NA	NA
Cayuse [®] Plus	>2 g/kg (Glatzhofer 2020)	>2 g/kg (Glatzhofer 2020)	>2.14 mg/L (Glatzhofer 2020)
pht [®] Kicker CA	NA	NA	NA
Acidifiers			
LI 700 [®]	>5 g/kg	>5 g/kg	>6.04 mg/L
Tri-Fol [®]	>5 g/kg (Glatzhofer 2020)	NA	NA
Drift Reduction Agents			
In-Place [®]	>5 g/kg (Glatzhofer 2020)	>5 g/kg (Glatzhofer 2020)	>5.07 mg/L (Glatzhofer 2020)
Strike Zone [®] DF	>5 g/kg	>5 g/kg	>2.12 mg/L
InterLock [®]	>5 g/kg	>5.05 g/kg	>5 mg/L
Defoamers			
Foaminator [®] Dry	NA	NA	NA
FTF [™] Defoamer	NA	NA	NA
Water Conditioning Agents			
Bronc [®] Max	>5 g/kg (Glatzhofer 2020)	>5 g/kg (Glatzhofer 2020)	>2.13 mg/L (Glatzhofer 2020)
Quest [®] CA label	5 g/kg	>2 g/kg	>5.01 mg/L
Quest [®] WA label	5 g/kg	>2 g/kg	>5.01 mg/L
Dyes and Colorants			
Hi-Light [®] Blue and Hi-	>5 g/kg	>5 g/kg	>20 mg/L for vapor; >5 mg/L for mist

Name	Oral LD₅₀	Dermal LD₅₀	Inhalation LC₅₀
Light [®] Blue WSP			
Colorfast [™] Purple	1.23 g/kg	>5 g/kg	>20 mg/L for vapor; >5 mg/L for mist
Colorfast [™] Red	NA	NA	NA
Bas-Oil [®] Blue	NA	NA	NA
Bas-Oil [®] Red	>5 g/kg	>5 g/kg	>20 mg/L for vapor; >5 mg/L for mist
Mark-It Blue [®]	10 g/kg	NA	NA
Blazon [®] Blue	>5 g/kg	NA	NA
Dynamark [®] U.V.	>5 g/kg	>5 g/kg	>20 mg/L for vapor; >5 mg/L for mist

j. Table 2 – Standard Acute Aquatic Species Toxicity Testing Results⁸

Name	Rainbow Trout 96-hour LC ₅₀	Bluegill or other fish species 96-hour LC ₅₀	Daphnia spp. 48-hour EC ₅₀	Other Species
Alkylphenol ethoxylate-based surfactants				
R-11 [®]	3.8 mg/L (SERA 2011a); 6.0 mg/L (Smith et al 2004)	4.2 mg/L (SERA 2011a)	19 mg/L (SERA 2011a); 13.2 mg/L (LC ₅₀) (Stark and Walthall 2003); 9.24 mg/L (LC ₅₀) (Chen et al 2010); 5.7 mg/L (Siemering et al 2008)	Fathead minnow 1.1 mg/L; delta smelt 0.7 mg/L; Sacramento splittail 3.9 mg/L (Siemering et al 2008)
Activator 90	2.0 mg/L (SERA 2011a)	1.4 mg/L (SERA 2011a)	5.2 mg/L (24 hour); NOEC 1.0 mg/L (24 hour); 2.0 mg/L (48 hour) (SERA 2011a)	Freshwater guppy (<i>Poecilia reticulata</i>) 12.7 mg/L; NOEC 5.8 mg/L
Pro-Spreader Activator	NA	Unspecified fish species 7.1 mg/L (estimated)	49,701 mg/L (estimated)	NA
Pro-90	NA	Unspecified fish species 7.1 mg/L (estimated)	49,701 mg/L (estimated)	NA
Ad-Wet 90 CA	NA	NA	NA	NA
Ad-Wet 90	NA	NA	NA	NA
Induce [®] WA label	7.5 mg/L (SERA 2011a)	9.0 mg/L (Haller and Stocker 2003)	18.0 mg/L (SERA 2011a)	NA
Induce [®] CA label	7.5 mg/L (SERA 2011a)	9.0 mg/L (Haller and Stocker 2003)	18.0 mg/L (SERA 2011a)	NA
Alcohol ethoxylate-based surfactants				
Denali EA [™]	11.25 mg/L (WSDA 2018) NOEC 7.5 mg/L (Glatzhofer 2020)	NA	9.7 mg/L (WSDA 2018); NOEC 4 mg/L (Glatzhofer 2020)	NA
Wetcit	NA	Zebrafish (<i>Danio rerio</i>) 18.7 mg/L	11 mg/L	Freshwater green algae 72 hr NOEC 2.3 mg/L

⁸ Source of data is recent SDS (refer to Section 6) unless otherwise noted. NA indicates toxicity data for the formulation was not available. The mg/L refers to milligrams per liter (or parts per million).

Name	Rainbow Trout 96-hour LC ₅₀	Bluegill or other fish species 96-hour LC ₅₀	Daphnia spp. 48-hour EC ₅₀	Other Species
Rainier-EA™	82.6 mg/L (WSDA 2018)	NA	218.8 mg/L (WSDA 2018)	NA
Liberate®	17.6 mg/L; NOEC 12.5 mg/L	NA	9.3 mg/L; NOEC 7.5 mg/L	NA
Silicone-based wetter/spreaders				
Freeway®	NA	29.7 mg/L (Haller and Stocker 2003)	NA	NA
Silwet L-77®	NA	Zebrafish 2.75 mg/L; NOEC 0.56 mg/L (2001 MSDS)	22.6 mg/L; NOEC 10 mg/L (2001 MSDS); 23.4 (LC ₅₀) (Stark and Walthall 2003)	Green algae 96 hr EC ₅₀ 5.5 mg/L; NOEC 1 mg/L (2001 MSDS)
Kinetic® CA label	NA	19.8 mg/L (Haller and Stocker 2003)	111 mg/L (LC ₅₀) (Stark and Walthall 2003)	NA
Kinetic® WA label	13.9 mg/L (WSDA 2018)	19.8 mg/L (Haller and Stocker 2003)	111 mg/L (LC ₅₀) (Stark and Walthall 2003); 60.7 mg/L (LC ₅₀) (WSDA 2018)	NA
Silwet® Eco Spreader	2.1 mg/L; NOEC 1 mg/L	NA	NA	NA
Hi-Wett®	4.5 mg/L	NA	NA	NA
Cationic Surfactants – Ethoxylated Fatty Amines				
Entry™ II, POEA	4.2 mg/L	1.3 mg/L	2.0 mg/L	Green algae (<i>Selenastrum capricornutum</i>) 96-hr EC ₅₀ 3.7 – 4.5 mg/L (SERA 2011a)
Sticker/Spreaders				
Bond®	190 mg/L (WSDA 2018)	NA	614 mg/L (LC ₅₀) (Stock and Walthall 2003)	NA
Bond Max®	NA	360 mg/L; NOEC 220 mg/L	NA	NA
Tactic™	>100 mg/L (WSDA 2018)	Freshwater guppy 160.0 mg/L	99.1 mg/L (24 hour); 310 mg/L (WSDA 2018)	NA
Cohere®	NA	NA	NA	NA
Surfix®-P	NA	NA	NA	NA
Sustain®	NA	NA	NA	NA
Vegetable-Based Oils				

Name	Rainbow Trout 96-hour LC ₅₀	Bluegill or other fish species 96-hour LC ₅₀	Daphnia spp. 48-hour EC ₅₀	Other Species
Competitor [®]	>50 mg/L (Glatzhofer 2020); NOEC 50 mg/L (Glatzhofer 2020)	NA	>50 mg/L (Glatzhofer 2020); NOEC 50 mg/L (Glatzhofer 2020)	NA
MSO [®] Con'c	35 mg/L (WSDA 2018)	NA	18 mg/L (WSDA 2018)	NA
Hasten-EA [™]	375 mg/L (WSDA 2018); NOEC 250 mg/L (2014 SDS)	NA	84.615 mg/L (WSDA 2018); NOEC 50 mg/L (2014 SDS)	NA
Pathfinder [®] II	NA	NA	NA	NA
Improved JLB Oil Plus	NA	NA	NA	NA
M.O.C.	NA	NA	NA	NA
MSO [®] with Leci-Tech	35 mg/L (WSDA 2018)	NA	17 mg/L (WSDA 2018)	NA
Renegade-EA [®]	42.0 mg/L (WSDA 2018); NOEC 25 mg/L (Glatzhofer 2020)	NA	25 mg/L (WSDA 2018); NOEC 12.5 mg/L (Glatzhofer 2020)	NA
Super Spread [®] MSO	NA	NA	NA	NA
MES-100 [™]	NA	NA	NA	NA
Spraytech Oil [™]	NA	NA	NA	NA
Blends of vegetable oils and silicone-based surfactants				
Syl-Tac-EA [™]	45 mg/L (WSDA 2018); NOEC 30 mg/L (2014 SDS)	NA	137.5 mg/L (WSDA 2018); NOEC 50 mg/L (2014 SDS)	NA
Phase [®]	85 mg/L (WSDA 2018)	NA	>100 mg/L (WSDA 2018)	NA
Dyne-Amic [®]	23.2 mg/L (WSDA 2018)	NA	60 mg/L (LC ₅₀) (WSDA 2018)	NA
Crop Oils and Crop Oil Concentrates				
Agri-Dex [®]	1000 mg/L (1996 Tech Data Sheet); 271 mg/L (Smith et al 2004)	1000 mg/L (1996 Tech Data Sheet)	1000 mg/L (1996 Tech Data Sheet)	NA
Mor-Act [®] (CA and WA)	NA	NA	NA	NA

Name	Rainbow Trout 96-hour LC ₅₀	Bluegill or other fish species 96- hour LC ₅₀	Daphnia spp. 48- hour EC ₅₀	Other Species
Herbimax [®]	NA	2.2 mg/L	NA	Marine segmented worm 24 hr EC ₅₀ 4,720 mg/L
Grounded [®] -CA	NA	NA	NA	NA
Grounded [®] -WA	NA	NA	NA	NA
Inlet [®]	NA	NA	NA	NA
W.E.B. Oil	NA	NA	NA	NA
OMRI-Certified Wetter/Spreaders/Stickers				
Freeway [®]	NA	29.7 mg/L (Haller and Stocker 2003)	NA	NA
Kinetic [®] CA label	NA	19.8 mg/L (Haller and Stocker 2003)	111 mg/L (LC ₅₀) (Stark and Walthall 2003)	NA
Kinetic [®] WA label	13.9 mg/L (WSDA 2018)	19.8 mg/L (Haller and Stocker 2003)	111 mg/L (LC ₅₀) (Stark and Walthall 2003); 60.7 mg/L (LC ₅₀) (WSDA 2018)	NA
Organic BioLink [®]	NA	NA	NA	NA
Miller Nu Film P [®]	NA	NA	NA	NA
Sustain [®]	NA	NA	NA	NA
Activators - Fertilizer/Surfactant Mixtures				
Brandt [®] Magnify	>100 mg/L	NA	7.7 mg/L	NA
Class Act [®] NG [®]	447 mg/L; NOEC 40 mg/L; LOEC 200 mg/L	NA	377 mg/L; NOEC 40 mg/L; LOEC 200 mg/L	NA
Bronc [®] Plus Dry-EDT	382.9 mg/L (WSDA 2018)	43.5 mg/L (minnows); NOEC 25 mg/L (minnows) (Glatzhofer 2020)	223.6 mg/L (WSDA 2018); NOEC 100 mg/L (Glatzhofer 2020)	NA
Cayuse [®] Plus	NA	NA	NA	NA
ph [®] Kicker CA	NA	NA	NA	NA
Acidifiers				

Name	Rainbow Trout 96-hour LC ₅₀	Bluegill or other fish species 96-hour LC ₅₀	Daphnia spp. 48-hour EC ₅₀	Other Species
LI 700 [®]	130 mg/L; NOEC <100 mg/L (2015 SDS); 17 mg/L (Smith et al 2004)	210 mg/L; NOEC 100 mg/L (2015 SDS); 60.8 mg/L (Haller and Stocker 2003)	190 mg/L; NOEC 100 mg/L (2015 SDS)	NA
Tri-Fol [®]	NA	NA	NA	NA
Drift Reduction Agents				
In-Place [®]	>162 mg/L; NOEC >50 mg/L (both Glatzhofer 2020)	NA	40.12 mg/L; NOEC 2.25 mg/L (both Glatzhofer 2020)	NA
Strike Zone [®] DF	NA	NA	NA	NA
InterLock [®]	>100 mg/L (WSDA 2018)	NA	>100 mg/L (WSDA 2018)	NA
Defoamers				
Foaminator [®] Dry	NA	NA	NA	NA
FTF [™] Defoamer	NA	NA	NA	NA
Water Conditioning Agents				
Bronc [®] Max	≥100 mg/L (WSDA 2018); NOEC 50 mg/L (Glatzhofer 2020)	NA	>100 mg/L (WSDA 2018); NOEC 100 mg/L (Glatzhofer 2020)	NA
Quest [®] CA label	NA	NA	NA	NA
Quest [®] WA label	NA	NA	NA	NA
Dyes and Colorants				
Hi-Light [®] Blue and Hi-Light [®] Blue WSP	NA	NA	NA	NA
Colorfast [™] Purple	NA	NA	NA	NA
Colorfast [™] Red	NA	NA	NA	NA
Bas-Oil [®] Blue	NA	NA	NA	NA
Bas-Oil [®] Red	NA	NA	NA	NA

Name	Rainbow Trout 96-hour LC₅₀	Bluegill or other fish species 96- hour LC₅₀	Daphnia spp. 48- hour EC₅₀	Other Species
Mark-It Blue [®]	NA	Unspecified fish species 9,890 mg/L (estimated)	NA	NA
Blazon [®] Blue	NA	NA	NA	NA
Dynamark [®] U.V.	NA	NA	NA	NA

4. Issue Discussions Dealing With Adjuvants

- a. Can surfactants cause pesticides to move more readily in the soil, or resolubilize, hence causing an increased risk of pesticide movement offsite into water? Can they cause effects to soil systems so that environmental decomposition of pesticides is affected?**

Based on the following studies, it appears that the ability of a surfactant to increase the mobility of pesticides throughout the soil profile is a function of the type of surfactant (anionic, cationic, or non-ionic), the concentration of the surfactant in the soil solution (especially as related to the critical micelle concentration (CMC) of the surfactant), the type of soil, and the cation exchange capacity (CEC) and organic matter of the soil (Locke et al 2002; Wang and Keller, 2008; Michel et al 2016; Sanchez-Camazano et al 2000) as well as the chemistry of the pesticide. Surfactants have been used as tools for site amelioration of soil pollution, through their ability to solubilize hydrophobic compounds, so a concern about moving pesticides has merit. It is important to keep in mind that most pollutants that have been treated with this method are hydrophobic materials that strongly sorb to soils, which is unlike most of the herbicides used in forestry.

As can be seen in many of the study summaries that follow, although the potential exists for surfactants to affect the movement of pesticides through soil and the environmental fate of herbicides in soil, most effects would be unlikely under normal conditions because of the relatively low concentration of surfactants in the soil/water matrix and the solubility of many of the herbicides used in forestry. Localized effects could be seen if a spill occurred on soil resulting in very high concentrations of surfactant but these effects would be limited in space.

Desorption of pesticides is related to the CMC of the surfactant and the solubility of the pesticide. The CMC is the point of concentration of a surfactant at which individual molecules of surfactants (or monomers) gather to form micelles, or grouped formations of surfactant molecules (Volkering et al 1997). Below the CMC, surfactants exist in solution as individual monomers. These monomers can remain in solution or can attach to soil particles and organic matter. Pesticides can bind to these monomers, or can be 'out-competed' for binding sites, essentially increasing their concentration in soil water. In most studies, this effect increases as concentration of the surfactant reaches and exceeds CMC (Edwards et al 1991; Garcia et al 2001; Haigh 1996; Laha and Luthy 1991, 1992; Quintero et al 2005; Rodriguez-Cruz et al 2004; Sanchez-Camazano et al 1995). The formed micelles can act to attract hydrophobic compounds like oils, which are attracted to the hydrophobic cores of the micelles. CMC values can vary substantially depending upon the matrix the surfactant is in, such as water or a soil/water mixture. CMC values in water are generally much lower than the corresponding CMC levels in a soil/water matrix, hence the need for high levels of surfactants in soils prior to solubilizing of hydrophobic compounds. There are some examples of solubilization of hydrophobic compounds occurring at surfactant concentrations below the CMC (Deshpande et al 1999), but this is not common in the reviewed literature.

Surfactants (and herbicides) applied to the soil, as part of a pesticide application, or in subsequent applications, would remain on the soil surface until decomposed, unless driven down by water, thereby also diluting the surfactant in the soil/water system. Surfactants tend to bind to

soil particles and organic matter, resulting in a loss of surfactants in soil solution and reduced ability for solubilizing other compounds. As a result of surfactant binding to soils, pesticides that can bind to the surfactant molecules will tend to remain in the soil and not move out (Locke et al 2002). In order to increase the soil water concentration of surfactants above the CMC additional loading of surfactants must occur. Based on the studies that follow, for desorption of pesticides or other pollutants to occur, concentrations of surfactants must be above the CMC, which varies by surfactant, in the range of 10 - 4,000 mg/liter (ppm) or more. This level is unlikely to be reached in normal applications (Huggenberger et al 1973).

As an example, if a surfactant were at 2.5% dilution in an herbicide mixture applied at 40 gallons per acre, it would be applied to the soil at a rate of 0.0935 mg/cm² (assuming 100% application to the soil, and no foliar or litter interception):

$$\frac{40 \text{ gallons}}{\text{acre}} \times 0.025 \times \frac{1 \text{ acre}}{43560 \text{ ft}^2} \times \frac{3.785 \text{ liters}}{\text{gallon}} \times \frac{1000 \text{ cm}^3}{\text{liter}} \times \frac{1 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ ft}^2}{929 \text{ cm}^2} \times \frac{1000 \text{ mg}}{\text{g}} = \frac{0.0935 \text{ mg}}{\text{cm}^2}$$

If there were about 1 inch of rainfall (2.54 cm) to move this material into the soil, the surfactant would be diluted to about 37 mg/liter (ppm):

$$(0.0935 \text{ mg/cm}^2) / 2.54 \text{ cm} \times 1000 \text{ cm}^3/\text{liter} = 36.8 \text{ mg/liter}$$

Assuming that the herbicide is bound to the soil, if concentrations were high enough to move pesticides through the soil (possible with some surfactants, but unlikely outside of a spill), when the mixture reached soil ground water, the surfactant would become diluted once more resulting in dispersion of the micelles and the binding of both the surfactant and herbicide onto soil particles (Grant et al 2011).

It appears that biodegradation of pesticides can be affected by surfactants in the soil, however this too is concentration dependent similar to desorption effects and may be dependent on the type of surfactant (Valoras et al 1976; Volkering et al 1998). It appears that effects to pesticide biodegradation may be the result of preferential degradation of the surfactant rather than through a toxic action on microorganisms, although this question remains (Mata-Sandoval et al 2001; Tiehm et al 1997). Surfactants at low levels can also cause pesticides to be more absorbed to soil particles thereby increasing retention time in soil and not allowing for soil microbes in the upper levels of soil to break these compounds down. Once mobilized, these pesticides would be more readily available for breakdown as long as the surfactant itself is not biologically toxic to soil bacteria.

References:

Abu-Zrieg, M., R. Rudra, W. Dickinson. 2000. Influence of surfactants on leaching of atrazine through soil columns. *Toxicological and Environmental Chemistry*. Vol. 75:1-16.

This study involves the application of two non-ionic surfactants (Rexol 25/7 and Rexonic N25-7, not further identified) and one anionic surfactant (Sulphonic Acid LS, not further identified) to soil columns with subsequent measurement of movement of atrazine. This study used approximately 3-inch soil columns, saturated with surfactant at 200, 1000, 3000

mg/L. Sulphonic Acid LS decreased atrazine movement. The two non-ionic surfactants increased movement of atrazine except for lower dose of Rexonic in a loam soil.

Banks, M.L., A.C. Kennedy, R.J. Kremer, F. Eivazi. 2014. Soil microbial community response to surfactants and herbicides in two soils. *Applied Soil Ecology*. 74:12-20.

Applied three herbicides singly and three surfactants singly and herbicide/surfactant combinations (glyphosate/Activator 90, bentazon/Thrust, atrazine/Agri-Dex[®]) to a silt loam and a silty clay loam soil in pots to determine the effects on soil microbial communities. Most of the herbicides and surfactants did not affect soil processes, although there were some changes noted in some biological markers. The authors could not determine the biological significance of these changes. There were less impacts in silty clay loam than the silt loam, possibly due to higher absorption of the compounds to the soil. The changes seen from addition of these three surfactants to herbicides were minimal.

Beigel, C., E. Barriuso, R. Calvet. 1998. Sorption of low levels of nonionic and anionic surfactants on soil: effects on sorption of triticonazole fungicide. *Pesticide Science*. 54:52-60.

Low levels (<1000 mg/L or ppm) of nonionic NPE-based surfactants caused little or no decrease in sorption of a fungicide. At 10,000 mg/L, an increase in sorption was seen. The authors state that reported desorption of contaminants are a result of exceptionally high surfactant application rates (one study referenced here used 100,000-200,000 mg/L). Increase in sorption postulated two ways: 1) an increase in soil organic carbon content as a result of surfactant addition created increased affinity for bonding; 2) at low levels, the surfactant sorbs to soil through hydrophobic interactions, leaving the hydrophilic heads to extend into soil solution, increasing desorption. As more surfactant is added, a bilayer of surfactant is created on soil, with hydrophobic tails of second layer sticking into solution, creating an affinity for additional sorption.

Bramwell, D.P., S. Laha. 2000. Effects of surfactant addition on the biomineralization and microbial toxicity of phenanthrene. *Biodegradation*. 11(4):263-277.

This study looks at biomineralization and toxic effects of the polycyclic aromatic hydrocarbon (PAH) phenanthrene as affected by the presence of four surfactants in aqueous and soil-water systems. The four surfactants are the nonionic surfactant Tween 20 (polyoxyethylene sorbitan monolaurate); sodium dodecyl sulfonate, an anionic surfactant; TTAB, a cationic surfactant; and Citrikleen (a commercial emulsifier). High doses of Tween 20 applied to soil are needed to inhibit mineralization of phenanthrene (≥ 5000 mg/L). Doses above 5,000 mg/L of Tween 20, TTAB, and Citrikleen, and doses above 8,000 mg/L of sodium dodecyl sulfonate are needed to solubilize phenanthrene in soil-water systems. It may be that mineralization is affected due to preferential mineralization of the surfactant.

The authors report on another study where Triton X-100 (an octylphenol polyethoxylate, with 9-10 ethoxylates) at 12 mg/L neither enhanced nor inhibited the biodegradation rate of naphthalene by bacteria, whereas a concentration of 12,000 mg/L enhanced biodegradation (Milhelcic et al 1995). Other studies show inhibition or improvement of degradation of PAHs.

Deshpande, S., B.J. Shiau, D. Wade, D.A. Sabatini, J.H. Harwell. 1999. Surfactant Selection for Enhancing *Ex Situ* Soil Washing. *Water Research*. 33(2):351-360.

Evaluation of eight surfactants (anionic and nonionic) for moving petroleum products through soil. CMCs of the eight surfactants ranged from 13 to 4,040 mg/L. Some of the nonionic surfactants were able to increase movement of contaminants at 0.25X the CMC. Authors surmise that the surfactant monomers gather at the soil/contaminant and soil/water interfaces and cause a decrease in the contact between the contaminant and the soil. The anionic surfactants could only cause movement at levels of 4 – 25X the CMC.

Edwards, D.A., R.G. Luthy, Z. Liu. 1991. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions. *Environmental Science and Technology*. 25(1):127-133.

Experimental data are presented on the enhanced apparent solubilities of four PAHs resulting from solubilization in aqueous solutions of four nonionic surfactants. Solubilization of each PAH compound commenced at the surfactant CMC and was proportional to the concentration of surfactant in micelle form.

Garcia, J.M., L.Y. Wick, H. Harms. 2001. Influence of the nonionic surfactant Brij 35 on the bioavailability of solid and sorbed dibenzofuran. *Environ. Sci. Technol.* 35:2033-2039.

Used a nonionic linear alcohol ethoxylate surfactant. CMC in water determined as >0.17 g/L (>170 ppm). To elicit solubilization of the test material, density of surfactant had to be greater than CMC. Test then used 10X the CMC (1,700 ppm). Consistent with other studies showing need to utilize high rates of surfactants before movement is seen. At concentrations below the CMC, this surfactant had no effect on the dissolution kinetics, indicating that surfactant micelles rather than individual surfactant molecules play a crucial role in dibenzofuran dissolution.

Grant, S., M. Mortimer, G. Stevenson, D. Malcolm, C. Gaus. 2011. Facilitated transport of dioxins in soil following unintentional release of pesticide-surfactant formulations. *Environmental Science and Technology*. 45:406-411.

Analysis of movement of dioxins through soil after a pesticide storage facility fire. Appears that surfactants, also stored in the facility were the cause of movement; analysis of possible volume of surfactants came up with an estimate approaching 10,000 ppm of surfactant in soil. Dioxins were found near groundwater levels; authors thought this was due to surfactants becoming diluted in ground water, breaking up micelles. Any compounds being moved by surfactants would then sorb to soil particles.

Haigh, S.D. 1996. A review of the interaction of surfactants with organic contaminants in soil. *The Science of the Total Environment*. 185:161-170.

Absorption of surfactants to soil removes much of any surfactant from pore water. Therefore, higher amounts of surfactant are needed to reach the CMC in pore water as compared to water in a test tube. As an example, the CMC of a linear alkylbenzene sulphonate surfactant with a CMC in pore water of 1,640 mg/kg as compared to 82 mg/L in pure water. Surfactants

at low concentrations (below CMC) can increase adsorption of pollutants in soils. Once the CMC is reached these same pollutants can be remobilized.

Hernandez-Soriano, C., D. Mingorance, A. Peña. 2009. Dissipation of insecticides in a Mediterranean soil in the presence of wastewater and surfactant solutions. A kinetic model approach. *Water Research*. 43(2009):2481-2492.

A non-ionic surfactant at rates 2X the CMC (708 ppm) caused a dissipation reduction with one insecticide because the pesticides more strongly sorbed to soil and were not available for microbial degradation. With several other insecticides there was some increase in dissipation. There were no effects seen at a surfactant concentration of 0.75 mg/L. In terms of soil processes, the authors used dehydrogenase activity (DHA) as a measure of soil microbial activity. Surfactants at 0.75 mg/L showed no effect on DHA, but at 2X CMC, DHA levels decreased. The authors surmise this is due to effects on the soil microbes.

Huggenberger, F., J. Letey, W.J. Farmer. 1973. Effect of two nonionic surfactants on adsorption and mobility of selected pesticides in a soil system. In, *Proceedings, Soil Science Society of America*. 37(1973): 215-219.

Two surfactants (alkylpolyoxyethylene ethanol, a linear alcohol ethoxylate (Soil Penetrant 3685) and a mixture of a polyoxyethylene ester and a polyoxyethylene ether (Aqua Gro)) were applied to soil to test movement of lindane, diuron, and atrazine. Low rates (~50 ppm) had no effect on sorption or mobility; moderate rates (500-2,000 ppm) resulted in an increase in sorption (i.e., less movement), high rates (2,000-10,000 ppm) increased mobility with lindane and diuron. There were no effects to atrazine at any dose.

It is important to remember that surfactants applied to the soil as part of a pesticide application would remain on the soil surface unless driven down by water. This would have the effect of greatly diluting the surfactant in the soil/water system. Hence these authors conclude that at the high dilution rates commonly used for surfactants (~1%) when applied to soil would not result in risk of desorption of pesticides.

Ke-Bin, L.I., J-T. Cheng, X-F. Wang, Y. Zhou, W-P. Liu. 2008. Degradation of herbicides atrazine and bentazone applied alone and in combination in soils. *Pedosphere*. 18(2):265-272.

Application of the two herbicides atrazine and bentazone with Tween-20 surfactant. Addition of the Tween-20 at 1.1 g/kg slightly slowed the degradation of atrazine in soil (but not significantly), while bentazone degradation was not affected. Authors could not determine why the Tween-20 slowed degradation, but likely due to increased soil sorption.

Krogh, K.A., B. Halling-Sørensen, B.B. Mogensen, K.V. Verjup. 2003. Environmental properties and effects of nonionic surfactant adjuvants in pesticides: a review. *Chemosphere*. 50:871-901.

Review of data from studies looking at alcohol ethoxylate surfactants (AEO) and alkylamine ethoxylate surfactants. AEOs absorb to clay, and those with longer ethoxylate chains bind more tightly to soils. AEOs tend to bind and not move down through the soil column. Most

of these surfactants are absorbed or broken down, with half-lives in soil of 20-40 days; few have been found in groundwater.

Kucharski, M., J. Sadowski. 2011. Behaviour of metazachlor applied with additives in soil: laboratory and field studies. *Journal of Food, Agriculture & Environment*. 9(3&4):723-726.

Three different surfactants (MSO, silicone, and one other) were applied at normal (field) rates along with metazachlor herbicide. Both the MSO and silicone surfactants caused increased levels of the herbicide in the soil profile as compared to the herbicide applied alone, however only at shallow depths (0-15 cm). At deeper levels (up to 50 cm) amount of herbicide was less when surfactants were used as compared to the herbicide alone. The speed of leaching through the soil profile was less when surfactants were added.

Laha, S., R.G. Luthy. 1991. Inhibition of phenanthrene mineralization by nonionic surfactants in soil-water systems. *Environmental Science and Technology*. 25(11):1920-1930.

In the presence of surfactants (alcohol ethoxylate (C12AE4), OP9.5E, and NP10.5E) at concentrations above 1,000 ppm in soil water system, phenanthrene is solubilized. At rates below that solubilization was not significantly different than simple aqueous solubility. Rates of surfactants that resulted in micelle formulation in soil/water system completely inhibited the mineralization of phenanthrene. The inhibition was reversible when the surfactant solutions were diluted below the CMC.

Laha, S., R.G. Luthy. 1992. Effects of nonionic surfactants on the solubilization and mineralization of phenanthrene in soil-water systems. *Biotechnology and Bioengineering*. 40(11):1367-1380.

In the presence of surfactants (four linear alcohol ethoxylates (C12AE4, C12AE23, C12-15AE3, C12-15AE4), OP9.5E, NP10.5E, polysorbate 20 and 80, and two high CMC surfactants (CHAPS, and octylglucoside)) at concentrations that resulted in micelle formulation, solubilization of phenanthrene commenced. Surfactants didn't increase rate of mineralization. Authors also established CMC in soil-water systems for these surfactants (only reported the following: 850 ppm for C12AE4; 560 ppm for OP9.5E). Results supported findings of earlier study (Laha & Luthy 1991) with these additional surfactants.

Locke, M.A., K.N. Reddy, L.A. Gaston, R.M. Zablotowicz. 2002. Adjuvant modification of herbicide interactions in aqueous soil suspensions. *Soil Science*. July 2002, 167(7):444-452.

The effects of adjuvant on the sorption and desorption of three herbicides (cyanazine, atrazine, and norflurazon) in several soils were studied for the potential of adjuvant use in remediating herbicide-contaminated soils. Adjuvants used were classified as nonionic, cationic, and anionic, with CMCs ranging from 80 to 2,200 mg/liter. Adjuvants were added to soil at rates of 2,500 or 10,000 mg/liter. Adjuvant effects on sorption and desorption are herbicide and soil-type specific. Higher soil CEC and organic matter reduce the effects of surfactants. Nonionic herbicides, like norflurazon, will tend to bind to soil more in the presence of a surfactant than water alone because of an increase in binding sites. The authors conclude that from an agronomic standpoint, an aspect for further study might be that greater

solubility and reduced sorption of soil-applied herbicides co-applied with adjuvants may increase the bioavailability of these herbicides for weed control.

Mata-Sandoval, J.C., J. Karns, A. Torrents. 2001. Influence of rhamnolipids and Triton X-100 on the biodegradation of three pesticides in aqueous phase and soil slurries. *Journal of Agriculture and Food Chemistry*. 49:3296-3303.

Looked at the effects of adding a surfactant to soils contaminated with trifluralin, atrazine, or coumaphos, focusing on the degradation of these pesticides. Shows the inhibitory effects of nonionic Triton X-100 surfactant (an octylphenol ethoxylate with 9-10 ethoxylate units) on atrazine and coumaphos degradation at high concentrations (2,000 and 4,000 mg/L) in aqueous suspensions in soil. Effect appears dose-dependent, with lower doses (100, 500 mg/L) showing no inhibitory effect. Decrease in degradation assumed to be the result of preferential degradation of surfactant utilizing resources, rather than any toxic effect. Triton X-100 had a positive effect on degradation of trifluralin. Authors state that previous studies have shown that Triton X-100 can sorb to soils, increasing their hydrophobicity, and enhance sorption of pesticides, which means solubilization of the pesticides may be promoted only at very high surfactant concentrations.

Michel, A., C. Dietschweiler, M. Böni, M. Burkhardt, H-J. Brauch, E. Worch, F.T. Lange. 2016. Mobility of a polyether trisiloxane surfactant in soil: soil/water distribution coefficients and leaching in a soil column. *Water, Air, and Soil Pollution*. 227:66.

Measurement of the leaching of a trisiloxane surfactant (e.g., Silwet L-77[®]) in loam and sandy loam soils determined that it could be considered a slightly mobile compound. Higher organic matter and clay in the soil will lower movement. Even in a pure sand experiment, simulating heavy rainfall after application, this trisiloxane didn't leach below 15 cm. It was determined that the trisiloxane moved 38 times slower than water through this sand matrix. Authors determined the low likelihood of trisiloxane surfactant to reach groundwater.

Paveglio, F.L., K.M. Kilbride, C.E. Grue, C.A. Simenstad, K.L. Fresh. 1996. Use of Rodeo and X-77 spreader to control smooth cordgrass (*Spartina alterniflora*) in a southwestern Washington estuary: I. Environmental fate. *Environmental Toxicology and Chemistry*. 15(6):961-968.

Aerial application of the Rodeo formulation of glyphosate and X-77, a nonylphenol ethoxylate (NPE) surfactant, over tidal wetlands at rate of 4.7 liters/hectare (2 quarts/acre) Rodeo and 0.9 liters/hectare (1% or 0.1 gallons/acre) X-77 in 93.5 liters/hectare (10 gallons/acre) total volume. Application occurred at low tide, allowing 5 hours prior to inundation. Deposition was measured and sediment samples were taken, both prior to inundation. Seawater samples with the first high tide (1 cm depth) were taken above the plots. Seawater samples were taken when tide had reached 1 meter in depth after treatment. *Spartina* samples were taken.

69 to 77% of applied glyphosate was detected in sediment. NPE was sampled at 65 to 85% of applied in sediment. NPE concentration declined within 14 days post-treatment, likely from microbial degradation, but then stabilized (likely due to partitioning to sediment (hence unavailable for biodegradation) and lower temperatures). NPE was detected in seawater at 3

to 16 µg/l. NPE was not detected in deeper seawater (while glyphosate was). NPE was not detected in spartina.

Quintero, J.C., M.T. Moreira, G. Feijoo, J.M. Lema. 2005. Effects of surfactants on the soil desorption of hexachlorocyclohexane (HCH) isomers and their anaerobic biodegradation. *Journal of Chemical Technology and Biotechnology*. 80:1005-1015.

Investigation of three surfactants (two NIS and one anionic) and the effect each had on the desorption and biodegradation of the insecticide lindane. Rates of application were at 5 times the CMC and for one of the NIS also at 20 times the CMC. Results were diverse. One of the NIS at 5 times the CMC showed considerable ability to increase desorption of lindane, but also resulted in slower degradation of lindane, possibly due to effects to microbial processes. The other NIS needed to be at 20 times the CMC concentration to see similar results, but at that rate lindane degradation was also increased.

Rodríguez-Cruz, M.S., M.J. Sanchez-Martín, M. Sanchez-Camazano. 2004. Enhanced desorption of herbicides sorbed on soils by addition of Triton X-100. *Journal of Environmental Quality*. 33:920-929

A non-ionic OPE surfactant (Triton X-100) and atrazine and linuron herbicides were applied to several different soil types and compared to the herbicides applied in conjunction with water. Atrazine did not desorb from soil at rates different from water until the surfactant was at a concentration of 50X the CMC (7,500 mg/L) – the amount of surfactant had to greatly exceed the amount bound to soil. Organic matter and clay tend to bind these herbicides and surfactant. With linuron, desorption was seen at surfactant levels much lower than atrazine (0.75X CMC (112 mg/L)).

Sanchez-Camazano, M., M. Arienzo, M.J. Sanchez-Martin, T. Crisanto. 1995. Effect of different surfactants on the mobility of selected non-ionic pesticides in soil. *Chemosphere*. 31(8):3793-3801.

Three surfactants (cationic (TDTMA); anionic (lauryl sulphate); and non-ionic (tween 80, a polyoxyethylene sorbitan monooleate)) were either added to soil prior to adding four pesticides (diazinon, atrazine, metolachlor, acephate), or used as a rinse on soil already contaminated with these same pesticides to see how these pesticides would react (increase or decrease mobility). Application rates ranged from critical micelle concentration (CMC) to 50 g/kg (50,000 ppm) in the application test, and at 5 and 50 g/L (5,000 and 50,000 ppm) in the rinse test.

The cationic surfactant, when added to the soil, decreased the mobility of all 4 pesticides at 0.1, 5 and 50 g/kg. The anionic surfactant, when added to the soil, increased sorption of all four pesticides at 2.38 g/kg, but caused the mobility of diazinon and atrazine to increase at 5 g/kg, and metolachlor to increase at 50 g/kg. Tween 80 added to soil decreased mobility of hydrophobic pesticides (diazinon, atrazine) at levels up to 50 g/kg, but increased the mobility of metolachlor at 5 g/kg (but not at 0.04 g/kg).

The cationic surfactant applied as a rinse had little or no effect at 5 g/L, while at 50 g/L metolachlor sorption was decreased. The anionic surfactant and Tween 80 added in high

concentrations (50 g/L) as a rinse, increased mobility of these pesticides, while at 5 g/L both had little or no effect.

Sanchez-Camazano, M., M.J. Sanchez-Martin, M.S. Rodriguez-Cruz. 2000. Sodium dodecyl sulphate-enhanced desorption of atrazine: Effect of surfactant concentration and of organic matter content of soils. *Chemosphere*. 41:1301-1305.

Anionic surfactant (sodium dodecyl sulphate) showed increasing desorption of atrazine with increasing soil organic matter and increasing concentration of surfactant. Tested rates are fairly high (1.7 to 23.8 g/L (1,700 to 23,800 ppm) of surfactant) and reflect rates above the critical micellar concentration (except for lowest rates, at 0.75 of CMC). Results show desorption of atrazine greatly increases above the CMC, owing to the affinity of atrazine, as a hydrophobic compound, for the hydrophobic cores of the surfactant micelles. Soils with low organic matter cause sorption to increase at concentrations below the CMC.

Singh, R.P., S.A. Nabi, S. Singh. 2009. Evaluation of the effect of surfactants on the adsorption and movement of carbaryl in soils of divergent texture. *Adsorption Science and Technology*. 27(10):921-935.

Comparison of three surfactants (cationic, nonionic, and anionic) applied at 0.1, 1.0, 10.0 times the CMC into four soils, measuring their ability to aid in movement of the insecticide carbaryl out of soil. The cationic surfactant at all concentrations reduced the movement of carbaryl, as the surfactant strongly adsorbed to the soils, increasing soil surface hydrophobicity and increasing adsorption of carbaryl. The nonionic surfactant caused increased carbaryl desorption in two soils, opposite in two. Soils high in organic matter adsorbed less surfactant, therefore adsorbed less carbaryl; soils high in clay adsorbed more. Anionic surfactant caused desorption of carbaryl to decrease in all four soils but only at 10 times the CMC.

Swarcewicz, M.K., A. Gregorczyk. 2013. Atrazine degradation in soil: effects of adjuvants and a comparison of three mathematical models. *Pest Management Science*. 69:1346-1350.

Comparison of three surfactants (a methylated seed oil (MSO), a crop oil concentrate (COC) and a trisiloxane) applied with atrazine herbicide on the degradation of atrazine. The addition of the MSO or trisiloxane did not change the soil half-life of atrazine whereas the COC extended the half-life 2-3X. The authors conclude this will increase atrazine's effectiveness against target plants (it is in the root zone longer) but also delays its disappearance from the environment.

Tiehm, A., M. Stieber, P. Werner, F.H. Frimmel. 1997. Surfactant-enhanced mobilization and biodegradation of polycyclic aromatic hydrocarbons in manufactured gas plant soil. *Environmental Science and Technology*. 31(9):2570-2576.

Two surfactants (an NP30E, Arkopal N-300; and a 12-carbon alkylphenol with 30 ethoxylate groups, Sapogenat T-300) enhanced the mass transfer rate of sorbed PAHs into the aqueous phase due to solubilization when added to soil above the CMC. These solubilized PAHs were then available for biodegradation. The rapid degradation of the NP30EO caused a lack of oxygen in soil, resulting in a decrease in biodegradation of the PAHs, however the slower

degradation of the 12-carbon surfactant resulted in an increased rate of PAH biodegradation as compared to a mineral medium alone.

Valoras, N., J. Letey, J.P. Martin, J. Osborn. 1976. Degradation of a nonionic surfactant in soils and peat. *Soil Science Society of America Journal*. 40: 60-63.

Investigation of the effects of different soils and moisture regimes on the degradation of a linear alcohol ethoxylate surfactant. One interesting observation was that soil microbial activity appeared to not be affected at surfactant rates in the soil as high as 2,000 ppm. Shows that potential impacts on soil processes can occur but only at very high rates of surfactant loading.

Volkering, F., A.M. Breure, W.H. Rulkens. 1997. Microbiological aspects of surfactant use for biological soil remediation. *Biodegradation*. 8(6):401-417.

A review of the use of surfactants in soil remediation focusing on soil microbiology. The most important effect of surfactants on the interactions among soil and pollutant is stimulation of mass transport of the pollutant from the soil to the aqueous phase. This can be caused by three different mechanisms: emulsification of the liquid pollutant, micellar solubilization, and facilitated transport. The complexity of the effect of surfactants on pollutant bioavailability is reflected by the results in the literature, which range from stimulation to inhibition of desorption and biodegradation of polluting compounds. No general trends can be found in these results.

Wang, P., A. A. Keller. 2008. Partitioning of hydrophobic organic compounds within soil-water-surfactant systems. *Water Research*. 42:2093-2101.

Two herbicides (atrazine and diuron) applied with two surfactants (Triton-100 a non-ionic APE, and benzalkonium chloride, a cationic surfactant). At surfactant concentrations below the CMC there was no interaction between the surfactant monomers and the pesticides (no enhancement of solubility). The authors' review of the literature finds that only extremely hydrophobic compounds are known to be associated with the monomers of surfactants. Surfactants when sorbed to soils particles result in a loss of surfactants and reduced rates of solubilization of other compounds. These surfactants can also increase the OM of soil when sorbed, thereby further tying up more hydrophobic organic compounds. Higher CEC levels in soil increases the amount of sorbed surfactants.

b. Do adjuvants represent a unique risk to terrestrial or aquatic invertebrates?

Based on a review of the current research, it would appear that adjuvants have the potential to affect terrestrial insects. However, as is true with many toxicity issues, it would appear that any effect is dose related. The research does indicate that the silicone-based surfactants, because of their very effective spreading ability, may represent a risk of lethality through the physical effect of drowning, rather than through any toxicological effects although sensitive life stages (such as early instar nymphs) can be at risk. Silicone surfactants can also increase the toxicity of insecticides to invertebrates over the insecticide alone, likely through their ability to increase the

amount of contact between the insecticide and the insect. Silicone surfactants are typically used at relatively low rates and are not applied at high spray volumes because they are very effective surfactants. Hence it is unlikely that insects would be exposed to rates of application that could cause the effects noted in these studies. Other adjuvants, which are less effective at reducing surface tension, can also cause the drowning effect. Horticultural oils are used as insecticides and can also smother insects, so it is likely that oil-based adjuvants might also act in that same fashion. As with silicone type materials, exposures have to be high, to the point of being unrealistically high, for such effects.

When considering the need for relatively high doses for a direct lethal effect, combined with the fact that individuals, not colonies or nests of invertebrates, may be affected, there is little chance that the adjuvants could cause widespread effects to terrestrial invertebrates under normal operating conditions. Spills or accidents could result in concentrations sufficiently high to cause effects, depending upon the adjuvant.

A few recent studies have pointed to potential impacts to bee social learning or behaviors. In the study by Ciarlo et al 2012, juvenile honeybees were exposed to silicone surfactants, nonionic surfactants, and crop oil concentrates both orally and on their antennae. Effects to the proboscis extension reflex (olfactory learning) were seen with silicone-based adjuvants, and to some extent with nonionic surfactants. The authors are unsure of the cause of the observed effect, or whether the doses represent what could be expected from nectar found in flowers in treated fields. In a follow-up study (Chen and Mullin 2013) detected components of silicone adjuvants in the beeswax and pollen of sampled commercial beehives indicating field exposure to this class of adjuvants. Silicone-based adjuvants may represent some risk to honeybees if used while honeybees are actively foraging. Artz and Pitts-Singer 2015 found some impacts to nest recognition after exposure to a nonionic surfactant that had been sprayed on foraged plants.

References:

Artz, D.R., T.L. Pitts-Singer. 2015. Effects of fungicide and adjuvant sprays on nesting behavior in two managed solitary bees, *Osmia lignaria* and *Megachile rotundata*. *Plos One*. 10(8):e0135688

Exposure of solitary bees to two fungicides and an NPE surfactant within a sprayed and vegetated enclosure to assess effects on nest recognition abilities. The study had serious flaws with lack of replicates. Results did show that exposure to vegetation sprayed with the NPE surfactant caused some impairment of nest recognition in female bees.

Chen, J., C.A. Mullin. 2013. Quantitative determination of trisiloxane surfactants in beehive environments based on liquid chromatography coupled to mass spectrometry. *Environmental Science and Technology*. 47(16):9317-9323.

An analysis of honey, beeswax, and pollen collected from beehives in several locations in the United States, looking for three trisiloxane compounds that are ingredients of silicone adjuvants. All ten samples of beeswax contained some level of one or more of these compounds, ranging from 12 to 390 nanograms per gram (0.0000012% to 0.000039%). Six of ten samples of pollen contained one or more of these compounds, although at lower levels than beeswax (8 to 39 nanograms/gram). None of the five honey samples contained any

detectable amounts. The presence of these trisiloxane compounds in beehives may lead to impacts on developing bees.

Chen, L., Q. Yan, J. Zhang, S. Yuan, X. Liu. 2019. Joint toxicity of acetamiprid and co-applied pesticide adjuvants on honeybees under semifield and laboratory conditions. *Environmental Toxicology and Chemistry*. 38(9):1940-1946.

Exposure of honeybees to the noenicitinoid insecticide acetamiprid alone and in conjunction with a solvent (NMP), a silicone adjuvant (Silwet L-77[®]), and an octylphenol ethoxylate surfactant (Triton X-100). The honeybee LD₅₀ for Triton X-100 is 1,436 µg/bee and for Silwet L-77[®] is 357 µg/bee, although the combinations of acetamiprid and these two adjuvants were not appreciably different in terms of their LC₅₀ values.

Ciarlo, T. J., C.A. Mullin, J.L. Frazier, D.R. Schmehl. 2012. Learning impairment in honey bees caused by agricultural spray adjuvants. *Plos One*. 7(7):e40848.

Juvenile honeybees exposed to organosilicone adjuvants (Dyne-Amic[®], Syl-tac, Sylgard 309), NIS (Activator 90, R-11[®], Induce[®]), and COCs (Penetrator, Crop Oil Concentrate, Agri-Dex[®]) through 1% adjuvant in sucrose solutions. Exposure was either orally for 2 seconds or placed on antenna (using only Dyne-Amic[®], Activator 90, and Penetrator), or both (using all adjuvants). Controls of sucrose were used. The tested response was the proboscis extension reflex (PER) assay, which may also lead to effects to other behaviors, such as orientation performance. Test solutions of 1% were based on range-finding test with the most sensitive adjuvant, Dyne-Amic[®], which elicited no significant effects at 0.1 or 0.5% solution, but did at 1%. None of the three adjuvants caused a negative effect after antennae contact alone. Only the silicone Dyne-Amic[®] caused a significant effect after oral exposure alone. All of the silicones caused significant effects after both oral exposure and antenna contact; while only one of the NIS, and none of the COCs did. The measured dose per bee averaged out to 20 µg/bee for the silicones and NIS and 17.5 µg/bee for the COCs. The authors recognize two limitations to this study: whether nectar in flowers in treated fields would contain any adjuvant at the levels tested here; and, whether effects to individual bees tested here would translate to effects at the colony level in the field.

Cowles, R.S., E.A. Cowles, A.M. McDermott, D. Ramotaur. 2000. "Inert" formulation ingredients with activity: Toxicity of trisiloxane surfactant solutions to twospotted spider mites (Acari:Tetranychidae). *Journal of Economic Entomology*. 93(2):180-188.

Testing of Silwet L-77[®] and several other organosilicone surfactants as miticides. Mites were exposed by dipping leaf surface for 3 seconds into solutions of 0, 4, 9, 20, 45, and 100 ppm of Silwet L-77[®]; results of LC₅₀ of 8.61 ppm; LC₉₀ of 55.6 ppm. Two other trisiloxanes had similar results. Leaf species made a difference (higher values for LC_{50/90} on strawberry vs bean leaves). Authors propose that these materials perform like extremely active soaps, permitting interaction of water with insect and mite cuticles at a small fraction of the concentration required for conventional insecticidal soaps. Effects probably caused by drowning by permitting water to infiltrate mites' respiratory apparatus. Authors admit that leaf dip is an exaggeration of likely exposures, and would be expected when using high-volume spray techniques, possibly only with high humidity. Important to note that trisiloxane

surfactants would not normally be used with high volume applications as the risk of surface runoff and loss of effect is high.

Donoven, B.J., G.S.Elliott. 2001. Honey bee response to high concentrations of some new spray adjuvants. In *54th Conference Proceedings of the New Zealand Plant Protection Conference*. Accessed on-line at http://www.hortnet.co.nz/publications/nzpps/proceedings/01/01_51.pdf on February 19, 2002. 5 pages.

Tested four adjuvants, including two surfactants (Du-Wett, a silicone-based surfactant at 0.1, 0.25, 0.5% and LI-700 at 0.25, 0.5, 1.0%) and two deposition agents (Bond, a carboxylated latex sticker at 0.125, 0.25, 0.5%, and Bond Xtra, a blend of silicones and latex at 0.2, 0.5, 1.0%) both orally and topically against bees. All concentrations of all adjuvants tested topically and orally were non-toxic to bees at doses well above those used in the field. Topical applications were done by applying 1 µl of test solution to each bee (Du-Wett and Bond up to 0.005 mg/bee; LI-700 and Bond Xtra up to 0.01 mg/bee). Observations were made after 4, 24, and 48 hours.

Goodwin, R.M., H.M. McBrydie. 1999. Effects of surfactants used with fungicides, herbicides, and insecticides on honey bee mortality. Confidential report to the National Beekeeper's Association. Accessed on-line at <http://www.nba.org.nz/surfactants.html> on February 19, 2002. 16 pages.

This study showed toxic effects to honey bees when exposed to some of the eleven surfactants tested. These eleven surfactants included two silicone-based surfactants (Pulse and Boost), two APE-based surfactants (Citowett and Multifilm), two petroleum oil-based surfactants (Peptoil and Sunspray) and a tallow-amine surfactant (Ethokem). Exposure involved anesthetizing the bees, placing them in petri dishes, and spraying them as they lay in the dish (mortality may have been caused by drowning). Spray volume rates were high given the concentrations (utilizing low-volume recommended concentrations but applying at high volume rates). Four of tested surfactants were toxic to bees (Citowett, Pulse, Boost, and Ethokem).

Because of the treatment method, this study must be carefully interpreted. The application method does not represent normal spray applications, since avoidance responses would be expected in nature, while anesthetized bees cannot avoid the activity. Also, the rates of application for several of these surfactants were very high in relation to expected field application rates (lowest rate of application was the equivalent of approximately 155 gallons per acre; highest was 280 gallons per acre).

Henry, C.J., K.F. Higgins, K.J. Buhl. 1994. Acute toxicity and hazard assessment of Rodeo, X-77 Spreader, and Chem-Trol to aquatic invertebrates. *Environmental Contamination and Toxicology*. 27(3):392-399.

X-77, a nonylphenol ethoxylate surfactant mixed with the Rodeo formulation of glyphosate and applied to wetlands as well as in lab acute tox tests. 48- and 96 hour-LC₅₀ values for X-77 ranged from 2.0 to 14.1 mg/L for 4 species of aquatic invertebrates. This was about 2 orders of magnitude greater acute toxicity than the Rodeo formulation of glyphosate. Mortality patterns in treated and untreated wetlands were similar, indicating a lack of acute

toxicity from application of tank mix. Based on application rates applied, and assuming X-77 would be detected at same rate as applied, margin of safety would indicate no acute risk. Little known about chronic effects to aquatic organisms.

Imai, T., S. Tsuchiya, T. Fujimori. 1995. Aphicidal effect of Silwet L-77, organosilicone nonionic surfactant. *Applied Entomology and Zoology*. 30(2):380-382.

A solution of 0.1% Silwet L-77[®] was applied to aphids on leaves until leaves were dripping wet. Silwet by itself did not produce a substantial effect under low humidity conditions, but controlled aphids almost completely under high humidity conditions. The authors make the conclusion that the use of silicone surfactants as insecticides would only be effective on aquatic insects and small insects such as aphids, whiteflies and mites. With larger insects it would be difficult to expose them to a large enough dose for suffocation to occur (a criticism of the future Goodwyn and McBrydie study on bees).

Liu, T-X., P.H. Stansly. 2000. Insecticidal activity of surfactants and oils against silverleaf whitefly (*Bemisia argentifolii*) nymphs (Homoptera: Aleyrodidae) on collards and tomato. *Pest Management Science*. 56:861-866

Testing of three surfactants (Silwet 77 (silicone), APSA-80 (APE), and Cide-Kick (limonene)) as well as horticultural soaps and oils against nymphs of whiteflies. All surfactants had effects on 2nd and 3rd instar nymphs, with Silwet being the most toxic. Surfactants were applied at rates from 250 to 1,000 mg/L.

Both this study and the one by Srinivasan et al 2008 note the importance of considering the location where these nymphs exist, which is typically on the underside of leaves. To affect the whiteflies, these surfactants would need to be applied to the undersides of leaves, not typically done when applying herbicides. This study also made the point that these surfactants are only lethal to nymphs when the surfactant is still in liquid form; once dried the risk of toxicity is eliminated.

Mascarin, G.M., N.N. Kobori, E.D. Quintela, S.P. Arthurs, Í.D. Júnior. 2014. Toxicity of non-ionic surfactants with fungal entomopathogens towards *Bemisia tabaci* biotype B. *BioControl*. 59:111-123.

Found that the use of silicone-based surfactants increased the mortality of whiteflies when combined with pathogenic fungi (biocontrol). Used Agral (an APE), an oil (Solub'oil), and two silicone-based surfactants (L-77, Breakthru S240). All these surfactants could kill early nymphs; late nymphs needed more exposure to see same level of mortality. When sublethal levels of surfactant were added to fungi, the mortality rates to whiteflies were higher than with the fungi alone. All effects were dose dependent, with LC₅₀ values of the surfactants alone ranging from 120 ppm (early nymphs Silwet) to 1,225 ppm (early nymphs Agral).

Purcell, M.F., W.J.Schroeder. 1996. Effect of Silwet L-77 and diazinon on three tephritid fruit flies (Diptera: Tephritidae) and associated endoparasitoids. *Horticultural Entomology*. 89(6):1566-1570.

Demonstrated toxicity of silicone-based surfactant to fruit flies and fruit fly parasitoids. LC_{50} for puparia exposed to Silwet L-77[®] ranged from 0.098 to 0.145% active ingredient (AI) At 0.5% AI significant decrease in emergence of parasitoid wasps. Indicates that silicone-based surfactants could be considered as an effective alternative to conventional insecticides in treatment of fruit flies in soil. Other studies referenced discuss effects of Silwet L-77[®] on aphids and thrips. Hypothesis is that because of its very low surface tension, silicone-based surfactants spread rapidly over the insect's body, infiltrating the tracheal system, and the insect dies by drowning.

Roberts, J.F., S.J. Marshall, D.W. Roberts. 2007. Aquatic toxicity of ethoxylated and propoxylated alcohols to *Daphnia magna*. *Environmental Toxicology and Chemistry*. 26(1):68-72.

Experimental results indicate that alcohol ethoxylates with similar carbon-chain lengths will show decreasing toxicity to *Daphnia magna* with increasing ethoxylate length.

Simenstad, C.A., J.R. Cordell, L. Tear, L.A. Weitkamp, F.L. Paveglio, K.M Kilbride, K.L Fresh, C.E. Grue. 1996. Use of Rodeo and X-77 spreader to control smooth cordgrass (*Spartina alterniflora*) in a southwestern Washington estuary: 2. Effects on benthic microflora and invertebrates. *Environmental Toxicology and Chemistry*. 15(6):969-978.

This associated study with Paveglio et al 1996 looked at effects on benthic invertebrates and found no differences between control and treated areas 119 days after treatment. The authors could not detect either short- or long-term responses by any component of the mudflat community attributable to the application of Rodeo and X-77, including indirect effects from habitat modifications.

Srinivasan, R., M.A. Hoy, R. Singh, M. E. Rogers. 2008. Laboratory and field evaluations of Silwet L-77 and Kinetic alone and in combination with imidacloprid and abamectin for the management of the Asian citrus psyllid, *Diaphorina citri* (Hemiptera: Psyllidae). *Florida Entomologist*. 91(1):87-100.

Asian citrus psyllid nymphs in lab studies were shown to be killed by an application of L-77 surfactant with an LC_{50} of 7.3 ppm. At approximately 50 ppm, L-77 resulted in almost 100% mortality of nymphs. Adult psyllids were not as sensitive; and eggs were not particularly sensitive. Similar results with the surfactant Kinetic[®].

c. Do mixtures of herbicides and adjuvants represent a greatly increased risk over the individual compounds alone (i.e. synergism)?

Adjuvants are intended to improve the efficacy, application, or mixing of a pesticide. This is not synergism, but more accurately is a reflection of the herbicide active ingredient getting into the plant or to the target.

Although there is not much data in the technical literature, the references included in this paper indicate a lack of synergistic effects, or at most only a slight synergism between adjuvants and pesticides.

Also refer to the Forest Service risk assessment on glyphosate (SERA 2011a), specifically section 3.1.4.3.2 *Joint actions of glyphosate and surfactant*.

References:

Abdelghani, A.A., P.B. Tchounwou, A.C. Anderson, H. Sujono, L.R. Heyer, A. Monkiedje. 1997. Toxicity evaluation of single and chemical mixtures of Roundup, Garlon 3A, 2,4-D, and Syndets surfactant to channel catfish (*Ictalurus punctatus*), bluegill sunfish (*Lepomis microchirus*), and crawfish (*Procambarus spp.*). *Environmental Toxicology and Water Quality*. 12:237-243.

This study used an anionic surfactant (Syndets, an ethoxylated alcohol). 96-hour LC₅₀ values (static) were determined for bluegill, crawfish, and catfish for the individual herbicides and surfactant plus mixtures. Results indicate additive rather than synergistic effects between these chemicals in mixtures. This study also shows that this surfactant is more toxic than the individual formulated herbicides.

Henry, C.J., K.F. Higgins, K.J. Buhl. 1994. Acute toxicity and hazard assessment of Rodeo, X-77 Spreader, and Chem-Trol to aquatic invertebrates. *Environmental Contamination and Toxicology*. 27(3):392-399.

This study looked at the effects of X-77 spreader (a nonylphenol ethoxylate-based surfactant) mixed with Rodeo and Chemtrol (drift reducer) and applied to wetlands as well as in lab acute toxicity tests. Mixtures of the three materials, including binary mixtures, indicated additive effects to lethality as tested against five invertebrate wetland species.

Krogh, K.A., B. Halling-Sørensen, B.B. Mogensen, K.V. Verjup. 2003. Environmental properties and effects of nonionic surfactant adjuvants in pesticides: a review. *Chemosphere*. 50:871-901.

Review of data from studies looking at alcohol ethoxylate surfactants (AEO) and alkylamine ethoxylate surfactants. AEOs absorb to clay, and those with longer ethoxylate chains bind more tightly to soils. AEOs tend to bind and not move down through the soil column. Most of these surfactants are absorbed or broken down, with half-lives in soil of 20-40 days; few have been found in groundwater.

In terms of toxicity to several classes of animals, linear AEOs are more toxic than branched AEOs, and those with longer ethoxylate chains are less toxic. Based on a few studies considered, mixtures of surfactants and surfactants and pesticides should follow an additive model of effects, not multiplicative.

Lewis, M.A. 1992. The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. *Water Research*. 6(8):1013-1023.

This review paper looked at 58 reports, most dealing with the anionic surfactant linear alkylbenzene sulfonate. Effects of mixtures and water quality parameters is compound specific; difficult to relate individual studies to untested mixtures. One study that is referenced (Wong 1985) looked at mixtures of the octylphenol ethoxylate surfactant Triton X-100, in combination with several organic compounds (including an unidentified algicide and the herbicide 2,4-D) and two metals, and the effects these combinations had on the growth rate of a freshwater algae. The study showed antagonistic effects of the organic compounds and Triton X-100, while showing synergistic effects with the metals.

Oakes, D.J., J.K. Pollak. 1999. Effects of a herbicide formulation, Tordon 75D, and its individual components on the oxidative functions of mitochondria. *Toxicology*. 136(1):41-52.

Tordon 75D contains two herbicides (2,4-D and picloram), a proprietary surfactant (polyglycol 26-2) as well as several other inert ingredients. The authors examined the effects of the components of Tordon 75D (individually and in various combinations) on rat liver mitochondria. Toxic effects of Tordon 75D were not due to any additive or synergistic actions of a mixture of its active and other components, but rather were caused solely by the proprietary surfactant.

Oakes, D.J., J.K. Pollak. 2000. The in vitro evaluation of the toxicities of three related herbicide formulations containing ester derivatives of 2,4,5-T and 2,4-D using sub-mitochondrial particles. *Toxicology*. 151:1-9.

The authors conclude that it is important to look at formulations. The study looked at combined effects of the two herbicides and diesel fuel, as well as with two surfactants (Alkanate CS, anionic, and Teric N12, a nonionic nonylphenol polyethoxylate). The results of this study support additive toxicities of surfactants with active ingredients as well as between active ingredients, rather than any synergistic effects. The method of exposure in this study is not indicative of effects to the whole body, as it doesn't utilize the body's detoxification abilities.

Tatum, V.L., D.L. Borton, W.R. Streblov, J. Louch, J.P. Shephard. 2011. Acute toxicity of commonly used forestry herbicide mixtures to *Ceriodaphnia dubia* and *Pimephales promelas*. *Environmental Toxicology*. 27(12):671-684.

Exposure of various mixtures of eight herbicides and four adjuvants to daphnia and fathead minnows modeling a direct overspray of a shallow pond. Calculation of LC₅₀ values were then used to ascertain the effects of the various tank mixes. There did not appear to be any pattern of increased toxicity associated with the presence of surfactants. The herbicide formulations, at exposure concentrations considerably higher than those reported in the field following operational forestry applications, were not associated with appreciable acute toxicity to fathead minnows or daphnia when used alone or in mixtures with each other or with adjuvants. Herbicide mixtures exhibited primarily antagonistic or simple additive toxicity. In the few cases where synergistic toxicity was observed, the degree of synergism was slight, never exceeding about twice the effect based on additive toxicity.

d. Do adjuvants represent a unique risk to aquatic organisms?

For a comprehensive review of the effect of nonylphenol ethoxylate-based surfactants to aquatic organisms, refer to USDA 2003.

There is little information in the scientific literature on effects of seed oils and silicone-based surfactants on aquatic organisms. There is more information on linear alcohol ethoxylates (LAE) and alkylphenol ethoxylates, such as NPE and OPE as these have more commercial uses in soaps and detergents, so environmental studies of water treatment plants have generated more data.

The interest in the NPE and OPE surfactants is largely driven by findings of estrogenic effects in fish and other aquatic organisms. From USDA 2003, based on various studies, it can be said that the threshold for estrogenic effects is generally above the threshold for other effects; hence protective levels of NPE exposure would encompass any concerns for estrogenic effects.

With linear alcohol ethoxylates, it appears that toxicity to aquatic organisms increases in relation to increased carbon chain length, but like the NPE-based surfactants, toxicity decreases with increasing ethoxylate length. It does appear that aquatic plants and most aquatic invertebrates are relatively insensitive to alcohol ethoxylates, although some specific invertebrate taxon may be identified as being more sensitive.

One study (Yahnke et al 2017) demonstrated that a 96-hour exposure of northern red-legged frog (*Rana aurora*) metamorphs to a triclopyr amine and vegetable-oil-based adjuvant (Competitor[®]) tank mix resulted in no long-term effects to growth or metamorphic condition after a 90-day post-exposure observation period. Another study (Vincent and Davidson 2015), calculated 24- and 48-hour LC₅₀ values for tank mixes of glyphosate and Competitor[®] adjuvant as well as glyphosate and Agri-Dex[®] adjuvant. Both tank mixes were more toxic to western toad tadpoles (*Anaxyrus boreas*) than the glyphosate alone.

Effects on aquatic organisms are driven by the same dose-response principles as any other group of organisms (i.e., dosage thresholds can be determined for various effects). There are interspecies differences, as well as differences within species depending upon age, however the results of studies on the same surfactants are consistent with each other. It does appear that in general, the surfactants used in forestry can affect aquatic organisms at lower doses than for terrestrial organisms.

Both the states of California and Washington require toxicity research and data of any products with aquatic sites listed in their label. The research and data collection that is required by manufacturers ensures that these products meet toxicity requirements for the aquatic environment.

Also refer to the Forest Service risk assessment on glyphosate (SERA 2011a), specifically section 4.1.3.1.2.2 *Glyphosate formulations*, where the risk assessment discusses the toxic effects of the POEA surfactant found in some commercial glyphosate formulations.

References:

Buhl, K. J., N.L. Faerber. 1989. Acute toxicity of selected herbicides and surfactants to larvae of the midge *Chironomus riparius*. *Archives of Environmental Contamination and Toxicology*. 18:530-536.

Testing of Rodeo herbicide (glyphosate), Activator NF (linear alcohol ethoxylate), and X-77 (a nonylphenol polyethoxylate) against the midge to determine 24- and 48-hour EC₅₀ values (based on lack of movement). Rodeo toxicity tests resulted in 24-hour EC₅₀ of 5,900 mg/L and a 48-hour EC₅₀ of 5,600 mg/kg. The NOEC value for Rodeo was 3,200 mg/L. For X-77 both the 24- and 48-hour EC₅₀ equaled 8.6 mg/L. For Activator NF the 24-hour EC₅₀ was 10.1 mg/L while the 48-hour EC₅₀ was 8.9 mg/L.

Cardellini, P., L. Ometto. 2001. Teratogenic and toxic effects of alcohol ethoxylate and alcohol ethoxy sulfate surfactants on *Xenopus laevis* embryos and tadpoles. *Ecotoxicology and Environmental Safety*. 48:170-177.

This study involved testing a linear alcohol ethoxylate (C12-14, AE-7) at rates of 0, 1, 2, 4, 4.5, 5, 5.5, 6, and 8 mg/L for 72 hours against the common frog test species *Xenopus laevis*. Tested both stage 8 blastulas and stage 46 embryos. 72-hour LC₅₀ for the linear alcohol ethoxylate for embryos is 4.59 mg/L (ppm). Effects on heart rate and motility at 4.5 mg/L. Teratogenic effects were observed at doses near LC₅₀. The authors conclude that the embryonic stage is most susceptible to teratogenic effects, when epithelia and gill cartilage in particular suffer malformations. Oxygen consumption was reduced at 3.5 mg/L, the authors assume this is caused by surfactant toxicity to mitochondria. There was rapid recovery from effects after suspension of exposure, indicating an ability to restore function and structure.

Dorn, P.B., J.H. Rodgers, S.T. Dubey, W.B. Gillespie, Jr., A.R. Figueroa. 1996. Assessing the effects of a C14-15 linear alcohol ethoxylate surfactant in stream mesocosms. *Ecotoxicology and Environmental Safety*. 34(2):196-204.

This study involved exposure of organisms in a southeast U.S. stream mesocosm to C14-15AE7 (a linear alcohol ethoxylate) at rates from 80 to 550 ppb. Two 30-day periods of exposure between April and August (330 ppb highest dose in first period; 550 ppb highest dose in second period). No effects on periphyton or vascular plants at highest doses. Macroinvertebrates were relatively insensitive (no significant differences between controls and surfactant in terms of number of taxa or abundance) with the exception of Simuliidae (blackflies) (density, which was affected at 160 ppb (NOEC of 80 ppb). Fathead minnow reproduction was significantly reduced at >280 ppb, and larval survival was reduced at 330 ppb. Growth and mortality of bluegill sunfish were not affected at highest exposure of 330 ppb. Lab testing of bluegill showed 96-hour LC₅₀ of 700 ppb, 10-day LC₅₀ of 600 ppb. Lab testing of fathead minnow showed 96-hour LC₅₀ of 800 ppb and 10-day LC₅₀ of 700 ppb. The authors compared the results of mesocosm study with the scientific literature chronic NOECs for these same fish and found comparable results.

Gardner, S.C, C.E. Grue. 1996. Effects of Rodeo and Garlon 3A on nontarget wetland species in central Washington. *Environmental Toxicology and Chemistry*. 15(4):441-451.

This study involved the application of Garlon 3A and Rodeo along with LI 700[®] surfactant to an aquatic weed. Garlon 3A (6% by vol), LI 700[®] (0.5% by vol) and water applied at rate of 0.54 gpa Garlon 3A (approximately 11 gpa mix). Rodeo (1% by vol), LI 700[®] (0.5% by vol) and water applied at rate of 0.1 gpa Rodeo (approximately 10 gpa mix). In both applications, LI 700[®] was applied at rate of approximately 0.05 gpa. Although nothing specifically mentioned about LI 700[®] monitoring or toxicity in this study, this amount of LI 700[®] and Garlon 3A or Rodeo did not affect trout, Daphnia, or duckweed survival.

Gillespie, W.B., Jr., J.H. Rodgers, Jr., P.B. Dorn. 1998. Responses of aquatic invertebrates to a linear alcohol ethoxylate surfactant in stream mesocosms. *Ecotoxicology and Environmental Safety*. 41(3):215-221.

This study involved exposure of organisms in a southeast U.S. stream mesocosm to C12-13AE6.5 (a linear alcohol ethoxylate) at rates from 320 to 5,150 ppb. Significant effects were seen to population densities of simuliids, copepods, and cladocerans during 30-day exposures. 30-day Lowest Observable Effect Concentration (LOEC) is thus 320 ppb for aquatic invertebrates (NOEC <320 ppb). No significant differences in drift at any dose, although trends were seen at highest dose. After 2-week post-treatment period, no differences between control and treatment streams. The authors compared this study with two previous mesocosm experiments (including Dorn et al 1996) and determined that toxicity to linear alcohol ethoxylates is positively correlated with the carbon chain length. One of the previous studies involved a C9-11AE6 linear alcohol ethoxylate, with a 30-day LOEC of 4,350 ppb (Gillespie et al 1997).

Howe, C.M., M. Berrill, B.D. Pauli, C.C. Helbing, K. Werry, N. Veldhoen. 2004. Toxicity of glyphosate-based pesticides to four North American frog species. *Environmental Toxicology and Chemistry*. 23(8):1928-1938.

Acute and chronic exposure tests to four species in which various formulations of glyphosate, as well as the POEA surfactant were tested. In all cases, POEA was more toxic to all four species than glyphosate formulations. In green frog tadpoles, the 96-hour LC₅₀ was 1.1 mg/L for POEA. The authors determined that POEA was the major contributor to Roundup formulation toxicity in these tests.

Jumel, A., M.A. Coutellec, J.P. Cravedi, L. Lagadic. 2002. Nonylphenol polyethoxylate adjuvant mitigates the reproductive toxicity of fomesafen on the freshwater snail *Lymnaea stagnalis* in outdoor experimental ponds. *Environmental Toxicology and Chemistry*. 21(9):1876-1888.

An outdoor mesocosm study using an NPE-based surfactant (Agral 90), made up of 91-93% NPE and 7-9% isobutanol. Although this study doesn't deal specifically with aquatic toxicity, it does show that adding Agral 90 to the herbicide fomesafen mitigates the reproductive toxicity of the herbicide to an aquatic snail. The authors assume that the surfactant attached to plants and mesocosm walls, making the herbicide unavailable to the snails.

Kline, E.R., R.A. Figueroa, J.H. Rodgers, Jr., P. Dorn. 1996. Effects of a nonionic surfactant (C14-15 AE-7) on fish survival, growth, and reproduction in the laboratory and in outdoor stream mesocosms. *Environmental Toxicology and Chemistry*. 15(6):997-1002.

A linear ethoxylated alcohol surfactant was tested for 1-10 days against bluegills and fathead minnows at 0, 50, 150, 500, 1,000, and 2,000 µg/L. 96-hour LC₅₀ values were 650 and 770 µg/L. 10-day LC₅₀ were 560 and 690 µg/L. Exposure data resulted in a NOEC of 160 µg/L for both species for both survival and swimming ability. In 30-day mesocosm experiments, there were no effects to growth or survival below 330 µg/L. No effects on abundance of zooplankton at any dose.

Lewis, M.A. 1991. Chronic and sublethal toxicities of surfactants to aquatic animals: a review and risk assessment. *Water Research*. 25(1):101-113.

This paper references older studies for NP10EO on sublethal responses (behavioral) (Table 4). In Swedmark et al 1976, swimming activity and avoidance were affected at 2-4 mg/L in cod and mussels. In Swedmark et al 1971, effects to mussels, cockles, and barnacles were seen at 2-5 mg/L; effects to locomotion of a decapod, hermit crab and shore crab were seen at 20-40 mg/L. In Høglund 1976, avoidance behavior to NP10EO in cod was seen at a much lower concentration (0.002 mg/L).

Several studies dealt with linear alcohol ethoxylates (LAE) and invertebrates, with 21-day NOEC for *Daphnia magna* of 0.24 mg/L, and LOEL levels of 0.17 mg/L (7-day for *Ceriodaphnia dubia* with effects on reproduction) to 1.75 mg/L (14-day for a clam species, affecting larval growth and development). One study in fish, showed a 28-day NOEC value of 0.18 to 0.32 mg/L with fathead minnows using LAE surfactants (Maki 1979a).

As for sublethal effects in fish, two studies dealing with nonionic surfactants are mentioned. One (Maki 1979b) showed LOEL values of 0.54 mg/L (C14-15 AE6) and >1.56 mg/L (C12-13 AE) for respiration in bluegills. Another (Sutterlin et al 1971) doesn't describe the exact nature of the tested surfactants but found no effects to Atlantic salmon olfactory responses at doses up to 10 mg/L. Swedmark et al 1976 showed effects to swimming activity in cod with an NPE-based surfactant at levels greater than 1 mg/L.

Lewis, M.A. 1992. The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. *Water Research*. 26(8):1013-1023.

This review paper looked at 58 reports, most dealing with the anionic surfactant linear alkylbenzene sulfonate. Effects of mixtures and water quality parameters is compound specific; difficult to relate individual studies to untested mixtures.

One study involving NPE surfactants and copper exposure to rainbow trout showed an antagonistic effect on 14-day survival (Calamari and Marchetti 1973). Another study of NPE surfactants and cadmium exposure to rainbow trout indicated a lack of synergism on 1-hour metal transfer in gills, but a synergistic effect on gill viability (Part et al 1985). Wong 1985 showed a synergistic effect of an OPE surfactant in combination with copper or cadmium on freshwater algae 14-day growth rate, but antagonism with an algicide and the herbicide 2,4-D.

Lizotte, R.E., Jr., D.C.L. Wong, P.B. Dorn, J.H. Rodgers, Jr. 1999. Effects of a homologous series of linear alcohol ethoxylate surfactants on fathead minnow early life stages. *Archives of Environmental Contamination and Toxicology*. 37:536-541.

28-day flow-through testing with fathead minnows, using three linear alcohol ethoxylates (C9-11AE6, C12-13AE6.5, C14-15AE7) at nominal concentrations of 0, 1, 3, 5, 7, 10 mg/L for first two surfactants and 0, 0.5, 1, 1.5, 2, 2.5 mg/L for the last. 48-hour exposures at any tested dose had no effect on embryo survival. 48-hour NOEC (survival) were 10.27, 8.06, and 2.19 mg/L respectively (highest dose tested). 28-day LC₅₀ values were 4.87, 2.39, and 1.02 ppm respectively. Corresponding NOECs for survival were 1.01, 1.76, and 0.74 ppm. 28-day survival decreased with increasing alkyl chain length (carbon chain); polyethoxylate chain length, although not specifically considered, appeared to have no effect. The authors compared their results with previously established data from 96-hour, 10-day, 28-day lab tests, and 30-day stream mesocosm data and found a close similarity between the endpoints from the different exposures. The authors conclude it may be possible to use either lab test to predict safe environmental concentrations of these surfactants for fish and that the use of safety factors applied to acute toxicity tests may be conservative.

Mann, R.M., J.R. Bidwell. 2001. The acute toxicity of agricultural surfactants to the tadpoles of four Australian and two exotic frogs. *Environmental Pollution*. 114:195-205.

Testing of both NPE (Agral 600 and Teric GN8) and a C12-15 linear alcohol ethoxylate (LAE)(BS1000). Narcosis of Gosner-stage 25 tadpoles was the measured endpoint. 48-hour EC₅₀ values for LAE ranged from 5.3 mg/L (ppm) for mild narcosis to 25.4 mg/L for full narcosis. Low oxygen conditions increased toxic effect from exposure to NPE surfactant.

Rodriguez-Gil, J.L., L. Lissemore, K. Solomon, M. Hanson. 2016. Dissipation of a commercial mixture of polyoxyethylene amine surfactants in aquatic outdoor microcosms: effect of water depth and sediment organic carbon. *Science of the Total Environment*. 550:449-458.

A mesocosm experiment using the POEA surfactant found in some Roundup formulations. It was found that POEA binds very strongly to sediments, to point of not being bio-available. Its life in the water column is short (half-life of 3.2 to 5.3 hours); in sediment more persistent (5.9-71.2 days). Two phase degradation in sediments: a rapid initial decrease followed by a much slower dissipation or even a plateau. Rapid movement of POEA through the water column would result in low bioavailability. Lab studies without sediment may over-estimate effects for these reasons.

Smith, G.R. 2001. Effects of acute exposure to a commercial formulation of glyphosate on the tadpoles of two species of Anurans. *Bulletin of Environmental Contamination and Toxicology*. 67:483-488.

Testing of a 0.75% ready-to-use formulation of glyphosate (Kleeraway) with a POEA surfactant. This study involved exposure to western chorus frog and plains leopard frog larvae (Gosner stage 25 or 26-30) for 24 hours. Surviving tadpoles were then transferred to clean water for 2 weeks and measured for development stage and weight. Exposure levels for glyphosate not clearly stated, but could be approximately 0.75 to 750 ppm. Surfactant exposure not determined. LC₅₀ values not calculated, there was high variability in mortality at low exposure levels. 100% mortality in both species at levels at or above 7.5 ppm. No differences in subsequent growth and development. This study had similar results to Berrill (1997) and Mann and Bidwell (1999). This study didn't separate out the surfactant or test with just glyphosate, so no comparisons can be made directly.

Turner, A.H., F.S.Abram, V.M.Brown, H.A.Painter. 1985. The biodegradability of two primary alcohol ethoxylate nonionic surfactants under practical conditions, and the toxicity of the biodegradation products to rainbow trout. *Water Research*. 19(1):45-51.

This study involved the testing of two linear alcohol ethoxylate (C14-15, AE7 and 11) surfactants to see whether they were effectively broken down when filtered through a biological filter (a model of what might be seen in sewage treatment). The resultant outflow from the filter was then tested against juvenile rainbow trout in a continuous flow test. First a 96-hour LC₅₀ was determined for the surfactants themselves – range from 0.75 mg/L (for shorter chain surfactant) to 1.10 mg/L (for longer-chain surfactant). after biodegradation of the surfactants (up to 35 ppm input), no effects were seen to fish exposed to the flow-through water containing any metabolites over a 7-day period. The authors refer to two other studies showing similar results with fathead minnows (Maki et al 1979), mosquito larvae, guppies (no species stated), and a species of water snail (not specified) (van Emden et al 1974). Conclusion is that the environmental metabolites of these alcohol ethoxylates are of very low short-term toxicity to trout.

Vincent, K., C. Davidson. 2015. The toxicity of glyphosate and glyphosate-surfactant mixtures to western toad (*Anaxyrus boreas*) tadpoles. *Environmental Toxicology and Chemistry*. 34(12):2791-2795.

Calculation of 48- and 96-hour LC₅₀ values for wild-caught western toad (*Anaxyrus boreas*) tadpoles (Gosner stage 35 to 38) from an exposure to glyphosate herbicide (Aquamaster) alone and to two tank mixes of the herbicide and Competitor[®] adjuvant or Agri-Dex[®] adjuvant. Both tank mixes were mixed at a rate of two parts herbicide and one part adjuvant by volume. Results indicated that both tank mixes were more toxic than the herbicide alone, with 48-hour LC₅₀ values of 6,392 mg/L for the herbicide alone, 4,254 mg/L for the Agri-Dex[®] tank mix and 711 mg/L for the Competitor[®] tank mix. The higher toxicity of Competitor[®] adjuvant as compared to Agri-Dex[®] is consistent with the LC₅₀ values in trout shown in Table 2.

Yahnke, A.E., C.E. Grue, M.P. Hayes, S. Pearman-Gillman. 2017. Effects of the herbicide triclopyr on metamorphic northern red-legged frogs. *Environmental Toxicology and Chemistry*. 36(9):2316-2326.

Northern red legged frogs (*Rana aurora*) reared from eggs were tested at Gosner stage 41 (metamorphic climax – first forelimb emergence). Exposed to Renovate 3 herbicide (triclopyr amine) at 47.1 mg/L a.i., Competitor[®] adjuvant at 41.3 mg/L, Hi-Light[®] Blue at 12.9 mg/L for 96 hours (with solution renewal every 24 hours to demonstrate worst case). The frogs were then transferred to clean water and observed for two months. Some lethargy was observed during exposure, and completion of metamorphosis was delayed on average one day over control frogs. Behavior and body condition of exposed individuals suggested some level of stress during the exposure period. Recovery in activity levels was observed after placement in clean water. By completion of metamorphosis, no difference existed in body condition between tank-mix and control frogs and there were no differences in survival.

e. Do adjuvants represent a unique risk to mammals?

For a comprehensive review of the effect of nonylphenol ethoxylate-based surfactants to mammals, refer to USDA 2003.

There is little information in the scientific literature on effects of seed oils and silicone-based surfactants on mammals beyond some basic acute testing results as displayed in Table 1. A general statement that can be made about adjuvants is that eye and skin irritation will be the most common effects seen from exposure to any of the adjuvants described in this paper, and this risk is highest to those actually involved in the application itself, especially the mixing of tankmixes.

There is more information on the toxicity of alkylphenol ethoxylates, such as NPE. The interest in the alkylphenol ethoxylates surfactants is largely driven by findings of estrogenic effects (USDA 2003). From USDA 2003, based on various studies, it can be said that the threshold for estrogenic effects is generally above the threshold for other effects; hence protective levels of NPE exposure would encompass any concerns for estrogenic effects.

References

Calvin, G., L.F. Chasseaud, W.H. Down, S.A. Ballard, D.R. Hawkins. 1983. Absorption and elimination of a branched-chain alkylpolyethoxylate surfactant in rats. *Toxicology Letters (Amst)*. 18(3):351-357.

This study involved oral and dermal exposures to rats of a branched-chain alcohol ethoxylate surfactant (C12AE6). Extensive oral absorption and excretion, daily excretion essentially matched daily exposures (< 0.3% of oral dose remained 5 days after 7 daily doses (100 mg/kg per day). Extensively metabolized, <15% excreted in urine remained unchanged. Excretion in both urine and feces (in equal amounts). Cutaneous application (8 mg, ~40 mg/kg) resulted in 25% of dermal dose absorbed over 4 days, mainly during first 12 hours. Authors conclude that alcohol ethoxylates can be extensively absorbed orally, and to a lesser degree dermally, by mammalian species. There was no evidence of bioaccumulation. Metabolites appear to be more polar than parent compound and produced through oxidation.

Drotman, R.B. 1980. The absorption, distribution, and excretion of alkylpolyethoxylates by rats and humans. *Toxicology and Applied Pharmacology*. 52(1):38-44.

This study looked at radiolabeled linear alcohol ethoxylates (C12AE6, C13AE6, C14AE7, C15AE7) either applied to skin of rats and humans (*in vivo*) or dosed orally to rats and humans. With rats, oral doses absorbed quickly and extensively, while cutaneous doses absorbed slowly and incompletely (40-50% remained at application site after 72 hours). About half of C12AE6 and C13AE6 excreted in urine (promptly); smaller amounts in feces or exhaled in CO₂; while with C15AE7, over half excreted through CO₂. Increasing alkyl chain length from 12 to 15 caused less to be found in urine/feces, more in CO₂. Human oral absorption/excretion similar to rat, while cutaneous absorption much lower (~75-88% remained at application site after 8 hours). It appears that the carbon chain is largely metabolized to CO₂, while the ethoxylate chain is excreted unchanged. There was little indication of bioaccumulation.

Farmer, D.R., T.A. Kaempfe, W.F. Heydens, W.R. Kelce. 2000. Developmental toxicity studies with glyphosate and selected surfactants in rats. Abstract. *Teratology*. 2000, June; 61(6):446.

Testing of glyphosate, POEA, and phosphate ester neutralized POEA. Female rats were administered glyphosate at 0, 300, 1,000, or 3,500 mg/kg/day on days 6–19 of gestation by gavage. POEA was administered at 0, 15, 100 and 300 mg/kg/day and the phosphate ester neutralized POEA at 0, 15, 50, and 150 mg/kg/day, both on days 6-15 of gestation. The glyphosate NOEL for maternal and developmental toxicity was 1,000 mg/kg/day. Maternal NOEL for POEA was 15 mg/kg/day and for the phosphate ester neutralized POEA, the maternal NOEL was 150 mg/kg/day. There was no developmental toxicity as a result of exposure from the surfactants (NOEL >300 and 150 mg/kg respectively).

Garry, V.F., B. Burroughs, R. Tarone, J.S. Kesner. 1999. Herbicides and adjuvants: an evolving view. *Toxicology and Industrial Health*. 15:159-167.

X-77, an NPE surfactant, showed dose dependent positive results in assay of genotoxicity using an *in vitro* assay of human lymphocytes. Garlon 4 (triclopyr) and Roundup and Accord (both glyphosate) did not result in genotoxic effects. The authors mention that ethylene oxide is a known human mutagen and that some glycol derivatives can also be mutagenic. They assume that these materials could be in X-77, in biologically active amounts. Ethylene oxide could be a contaminant in ethoxylated surfactants.

Lin, N., V.F. Garry. 2000. *In vitro* studies of cellular and molecular developmental toxicity of adjuvants, herbicides, and fungicides commonly used in Red River Valley, Minnesota. *Journal of Toxicology and Environmental Health, Part A*. 60:423-439.

Among other chemicals, looked at two alkylphenol-based surfactants (X-77 and Activate Plus). Both induced MCF-7 proliferation at rates of 0.01 to 1 µg/ml, significantly higher than controls, indicating an estrogenic response. Both surfactants are 3 orders of magnitude less sensitive than estradiol or estrogen. Roundup and glyphosate did not show estrogenic effects, indicating the POEA surfactant is not estrogenic.

Munley, S.M., T. Martin, A.M. Hoberman, M.E. Hurtt, R.E. Staples. 1996. Developmental toxicity of Exell, a surfactant mixture, in rats and rabbits. *Drug and Chemical Toxicology*. 19(4):279-300.

Exell, a surfactant mixture that is made up of ethoxylated tallow amine (64%), NPEO (14%), and a solvent (EGBE) (22%), was administered by gavage to pregnant rats and rabbits for 10-12 days, at levels of 0, 3, 8, 20, or 50 mg/kg/day (rats), and 0, 12, 35, or 100 mg/kg/day (rabbits). In rats, the maternal NOEL was 8 mg/kg/day; no developmental effects were seen at any dose (developmental NOEL >50 mg/kg/day). In rabbits, the maternal NOEL was 12 mg/kg/day. Reduced fetal weight gain at 35 mg/kg/day yields a developmental NOEL in rabbits of 12 mg/kg/day. No effects on fetal morphology (teratogenic effects) were seen in either species. Authors conclude that Exell is not uniquely toxic to either the rat or rabbit conceptus.

f. Do adjuvants affect the absorption rate of herbicides through the skin?

Various adjuvants are used in products applied to the skin, including pharmaceuticals. There is little research on the non-ionic surfactants that are commonly used in pesticide applications. The exception is the alkylphenol ethoxylates, since this class of surfactants is also used in consumer products, such as hair dyes and cosmetics.

What research there is show that for an adjuvant to increase the absorption of another compound, the adjuvant must affect the upper layer of the skin (Eagle et al 1992). Without some physical effect to the skin, there will be no change in absorption as compared to the other compound alone. In the study by Baynes and Riviere 1998, the use of an anionic surfactant caused an increased absorption of the insecticide carbaryl through pig skin. The particular surfactant, sodium lauryl sulfate, is known to be a skin irritant. Anionic surfactants seem to have a more consistent effect on absorption, followed by cationic surfactants, and then non-ionic surfactants (Ashton et al 1986).

The studies discussed below indicate that in general non-ionic surfactants have less of an effect on the skin, and hence absorption, than anionic or cationic surfactants. Compound specific studies indicate that the alkylphenol ethoxylates generally have little or no effect on absorption of other compounds. In several studies, the addition of a surfactant actually decreased the absorption through the skin (Boman et al 1989; Chowhan and Pritchard 1978; Dalvi and Zatz 1981). It would appear that, given the data available here, there is little support for the contention that the addition of surfactants to herbicide mixtures would increase the absorption through the skin of these herbicides.

References:

Ashton, P., J. Hadgraft, KA Walters. 1986. Effects of surfactants in percutaneous absorption. *Pharm. Acta Helv.* 61(8):228-234.

This is a general essay on the topic of surfactants and absorption. Surfactants can act to either increase or decrease absorption. Increases are usually due to physical effects to the skin surface. Generally, they describe anionic>cationic>non-ionic surfactants in terms of their ability to accelerate absorption. Most of surfactants specifically discussed in this study (Brij, Tween, Atlas, Laureth) are pharmaceutical surfactants, designed to assist in movement of materials into skin.

Baynes, R.E., J.E. Riviere. 1998. Influence of inert ingredients in pesticide formulations on dermal absorption of carbaryl. *American Journal of Veterinary Research.* 59:168-175.

Tested an anionic surfactant, sodium lauryl sulfate, at 1% and 5%, in combination with other compounds, on the absorption of the insecticide carbaryl through pig skin. The addition of this surfactant caused an increased absorption of the insecticide carbaryl through pig skin. The particular surfactant, sodium lauryl sulfate, is known to be a skin irritant. It is also used to enhance absorption of transdermal drugs. It was noted in the study that a 1% solution of the surfactant increased absorption, whereas a 5% solution did not, likely due to micelles forming on the skin surface, making less carbaryl available to absorb.

Boman, A., I. Blute, P. Fernstrom, J. Carlfors, L. Rydhag. 1989. Percutaneous absorption of 4 organic solvents in the guinea pig. II. Effect of surfactants. *Contact Dermatitis*. 21(2):92-104.

Tested several surfactants, including OP4.5E (5, 10%), OP10E (5, 10, 20, 30%). They also tested Berol 065, described as a nonionic surfactant and an ethoxylated fatty alcohol (ethoxylated linear alcohol). Adding nonionic surfactant reduced absorption of an alcohol (butanol) and three organic solvents thru *in vivo* guinea pig skin, as compared to solvents alone. Longer chain ethoxylate OPE had more of an inhibitory effect than the shorter chain OPE. The anionic surfactant, sodium dodecyl sulfate, increased absorption. Authors conclude that cleaning products should incorporate non-ionic surfactants as opposed to anionic surfactants, which in this experiment increased absorption. They state that nonionic surfactants do not denature keratin or solubilize lipids as effectively as anionic surfactants; hence there is no hydration of the stratum corneum.

Chowhan, Z.T., R. Pritchard. 1978. Effects of surfactants on percutaneous absorption of naproxen I: Comparisons of rabbit, rat, and human excised skin. *Journal of Pharmaceutical Sciences*. 67(9):1272-1274.

The authors tested several surfactants, including an octylphenol ethoxylate (OP5E), on their ability to affect the absorption of naproxen through excised human skin. The OP5E was tested at 2% (above the CMC). The anionic surfactants (sodium laurate and sodium lauryl sulfate) increased absorption. Effects of nonionic and cationic surfactants on absorption were either to decrease it or result in no change over controls. The OP5E resulted in a decrease in absorption.

Dalvi, U.G., J.L. Zatz. 1981. Effects of nonionic surfactants on penetration of dissolved benzocaine through hairless mouse skin. *Journal of the Society of Cosmetic Chemists*. 32(March-April 1981):87-94.

The authors tested a series of NPEs on *in vitro* hairless mouse skin (NP9E, NP15E, NP30E, NP50E). The presence of NPE reduced skin penetration of benzocaine as compared to aqueous solutions alone. As NPE increases in concentration, benzocaine absorption decreases. As the number of ethoxylate groups in the NPE surfactant increases, absorption of benzocaine decreases. The authors conclude that a portion of the benzocaine is associated with surfactant micelles resulting in a reduction of the number of free benzocaine molecules. The authors conclude that the concentration of benzocaine is the primary driver for absorption.

Eagle, S.C., B.W. Barry, R.C. Scott. 1992. Differential scanning calorimetry and permeation studies to examine surfactant damage to human skin. *Journal of Toxicology. Cutaneous and Ocular Toxicology*. 11(1):77-92.

Anionic surfactants caused an increase in skin permeability (human skin, 12-hour exposure at 10%, measured as water permeation) while nonionic surfactants (NPEO, 8, 10, 13, 15, 20, 30) produced few or no changes as compared to hydration alone. When mixtures of anionic and nonionic surfactants were used, the nonionic surfactant protected the skin from the anionic with reduced permeation as compared to anionic alone. Protection increased with

increasing EO units. Authors state that NPEO in the range tested do not disrupt the intercellular lipid and intracellular keratin structure of the stratum corneum enough to influence skin physiology. Protection of skin from anionic surfactants is through hindering penetration through micellization or preventing entry into the inter- and intracellular region.

Nielsen, J.B. 2000. Effects of four detergents on the in-vitro barrier function of human skin. *International Journal of Occupational and Environmental Health*. 6:143-147

Four different surfactants were tested on their ability to affect the transfer of water through human skin. NP12E, ethanol, sodium lauryl sulfate, and lutensol AP10 all increased water movement. Ethanol and NP12E caused increases (to 160% of controls) in absorption that did not change over time, but were lower than the other two.

Nielsen, J.B., H.R. Andersen. 2001. Dermal in vitro penetration of methiocarb, paclobutrazol, and primicarb: Effect of nonylphenolethoxylate and protective gloves. *Environmental Health Perspectives*. 109(2):129-132.

The authors tested nonylphenol ethoxylate (NPE, as NP12E) on in vitro human skin. The presence of NPE decreased the dermal penetration of these three compounds over 24, 48, and 72 hours, although not significantly in most compound/time combinations. Increasing the amount of NPE relative to primicarb decreased the penetration.

Nielsen, G.D., J.B. Nielsen, K.E. Andersen, P. Grandjean. 2000. Effects of industrial detergents on the barrier function of human skin. *International Journal of Occupational and Environmental Health*. 6:138-142.

Several different types of detergents were tested in their ability to affect the transfer of water or nickel through human skin. Three of the detergents were nonylphenol polyethoxylates (NP9E, NP10E, NP12E). Of these three, one increased the movement of water compared to controls, while none increased the movement of nickel.

Sarpotdar, P.P., J.L. Zatz. 1986. Evaluation of penetration enhancement of lidocaine by nonionic surfactants through hairless mouse skin *in vitro*. *Journal of Pharmaceutical Sciences*. 75(Feb):176-181.

When in combination with propylene glycol, polysorbates 20 and 60 (polyethylene glycol sorbitan monolaurate) increased absorption of lidocaine. This effect increased with increasing levels of propylene glycol as propylene glycol is an excellent solubilizer of lidocaine, resulting in less absorption on its own.

Van der Merwe, D., J.E. Riviere. 2005. Effect of vehicles and sodium lauryl sulphate on xenobiotic permeability and stratum corneum partitioning in porcine skin. *Toxicology*. 206:325-335.

The authors tested sodium lauryl sulphate (SLS) on in vitro pig skin using three carriers (water, ethanol, propylene glycol) and ten compounds, including several pesticides. Generally, the addition of SLS to water and the tested compounds reduced the partitioning into the stratum corneum and reduced permeability. Some studies have shown that

sunscreens and topical insect repellants can increase the dermal penetration of pesticides, but these studies show that this is a function of the active ingredients in these products, rather than the inert ingredients.

Walters, K.A., W. Bialik, K. R. Brain. 1993. The effects of surfactants on penetration across the skin. *International Journal of Cosmetic Science*. 15:260-270.

General review of studies showing effects to permeation of skin caused by surfactants. In order for surfactants to interact directly with the skin, they must first partition into it. Anionic surfactants can penetrate and interact strongly with the skin, producing large alterations in barrier properties. It appears this is due to their ability to interact and bind with epidermal proteins. Although not studied as much, cationic surfactants have demonstrated a propensity for enhancement activity. Non-ionic surfactants are recognized as those with the least potential for irritancy, however there is conflicting data on skin penetration, because of the wide variation in structure within this broad class.

One study (Walters et al 1988) indicated that OP10E had a small decrease in the absorption of methyl nicotinate across hairless mouse skin (*in vitro*) (-7%), while NP10E resulted in a small increase over 8 hours (+5%).

Walters, K.A., A.C. Watkinson, K.R. Brain. 1998. *In vitro* skin permeation evaluation: the only realistic option. *International Journal of Cosmetic Science*. 20:307-316.

Reports on previous studies involving NPEs. Using *in vitro* human skin, exposure to 10% solutions in isopropyl alcohol of NP2E, NP4E, or NP9E, absorption was low (about 0.5% after 48 hours - $\sim 5 \mu\text{g}/\text{cm}^2$). Each nonoxynol mixture permeated to same extent. Within mixtures of NPEs, the shorter chain oligomers permeated slightly more, resulting in a shift in mixture percentages within skin as opposed to what is placed on the skin.

Whitworth, C.W., E.R. Carter. 1969. Effect of certain nonionic surfactants on the absorption of salicylic acid from solutions by the frog, *Rana pipiens*. *Journal of Pharmaceutical Sciences*. 58(Oct):1285-1287.

Polysorbates 20, 40, 60, 80 (polyethylene glycol sorbitan monolaurate; Tween 20, 40, 60, 80) were added to a solution of salicylic acid at concentrations of 0.001, 0.005, or 0.1%. Frogs were statically exposed to this solution while the amount of salicylic acid remaining in solution was measured over two hours. The lower concentration (0.001%) of Polysorbate 20 and 40 increased absorption while the higher concentrations did not. For Polysorbate 60 and 80, the high concentration increased absorption while the lower ones did not. Absorption appeared to be through first order kinetics. It appears that the surfactants did not affect the skin of the frog, since pre-immersion in surfactant followed by immersion in salicylic acid didn't increase absorption of salicylic acid over those frogs not pre-immersed.

5. Toxicity Categories

Hazard Indicators	Toxicity Categories			
	I	II	III	IV
Oral LD ₅₀	Up to and including 50 mg/kg	From 50 thru 500 mg/kg	From 500 thru 5000 mg/kg	Greater than 5000 mg/kg
Inhalation LC ₅₀	Up to and including 0.2 mg/L	From 0.2 to 2 mg/L	From 2. to 20 mg/L	Greater than 20 mg/L
Dermal LD ₅₀	Up to and including 200 mg/kg	From 200 thru 2000 mg/kg	From 2000 thru 20,000 mg/L	Greater than 20,000 mg/kg
Eye Effects	Corrosive; corneal opacity not reversible within 7 days	Corneal opacity reversible within 7 days; irritation persisting for 7 days	No corneal opacity; irritation reversible within 7 days	No irritation.
Skin Effects	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irritation at 72 hours

Source: 40 CFR 156.62

Toxicity category I = Highly toxic; Severely irritating

Toxicity category II = Moderately toxic; Moderately irritating

Toxicity category III = Slightly toxic; Slightly irritating

Toxicity category IV = Practically non-toxic; not an irritant

To assign a signal word, use the highest hazard shown by any of the indicators for the product:

- Danger – Category I. In addition, if the product is in Category I because of its oral LD₅₀, inhalation LC₅₀, or dermal LD₅₀, the word “Poison” along with skull and crossbones will be on the label.
- Warning – Category II.
- Caution – Category III or IV.

EPA Categories of Toxicity for Aquatic Organisms

LC50 (ppm or mg/L)	Toxicity Category
<0.1	Very highly toxic
>0.1 – 1	Highly toxic
>1 – 10	Moderately toxic
>10 – 100	Slightly toxic
>100	Practically nontoxic

Washington State pesticide registration regulations require no more than slightly toxic to rainbow trout and no more than moderately toxic to *Daphnia* spp. in order to obtain aquatic registration.





Toxicity categories for adjuvants, fertilizers, and other agricultural-related products (including pesticide SDSs but NOT pesticide labels) underwent an overhaul. The Globally Harmonized System (GHS) of Classification and Labeling of Chemicals was initiated to promote standard criteria for classifying chemicals according to their health, physical and environmental hazards. The goal of the GHS is to identify the intrinsic hazards of chemical substances and mixtures and to convey hazard information about these hazards.

The standardized label elements included in the GHS are:

Symbols (hazard pictograms): Convey health, physical and environmental hazard information, assigned to a GHS hazard class and category.

Signal Words: “Danger” or “Warning” are used to emphasize hazards and indicate the relative level of severity of the hazard, assigned to a GHS hazard class and category.

Hazard Statements: Standard phrases assigned to a hazard class and category that describe the nature of the hazard.

GHS - Acute Oral Toxicity					
	Category 1	Category 2	Category 3	Category 4	Category 5
LD₅₀	≤ 5 mg/kg	> 5 < 50 mg/kg	≥ 50 < 300 mg/kg	≥ 300 < 2000 mg/kg	≥ 2000 < 5000 mg/kg
Pictogram					No symbol
Signal Word	Danger	Danger	Danger	Warning	Warning
Hazard Statement	Fatal if swallowed	Fatal if swallowed	Toxic if swallowed	Harmful if swallowed	May be harmful if swallowed

6. List of Source Labels and SDSs

The following are the product label identifiers and issuance dates of SDS documents used in this paper. All are available electronically in accompanying files.

Product	Label ID	SDS Date
Activator 90	G0814	5/20/19
Ad-Wet 90	GHS R6-24-2015	6/24/15
Ad-Wet 90 CA	GHS R4-22-2015	1/2/20
Agri-Dex [®]	SN-020114	3/29/15
Bas-Oil [®] Blue	1/08	7/9/13
Bas-Oil [®] Red	2019 02	9/24/14
BioLink [®]	150820	10/23/13
Blazon [®] Blue	undated	6/8/15
Bond [®]	G0814	7/8/10 (MSDS)
Bond Max [®]	G0814	7/31/14
Brandt [®] Magnify	6/18	1/28/16
Bronc [®] Max	F-060816	9/26/17
Bronc [®] Plus Dry-EDT	F-012716	9/26/17
Cayuse [®] Plus	F-070918	11/13/19
Class Act [®] NG [®]	1/0216/5	8/7/18
Cohere [®]	CASN 020114	2/8/16
Colorfast [™] Purple	10-11	5/27/14
Colorfast [™] Red	10/11	7/25/14
Competitor [®]	F-080417	10/26/20
Denali EA [™]	F-012716	1/10/19
Dynamark [®] UV	1/0105/5	8/7/18
Dyne-Amic [®]	SN 020114	7/13/17
Entry [™] II	43011V2-2/CG	1/5/00
Foaminator [®] Dry	1/0117/7	8/8/18
Freeway [®]	1GL G0814	2/20/19
FTF [™] Defoamer	F-012716	9/26/17
Grounded [®] -CA	SN 020114	2/13/17
Grounded [®] -W	SN032515	4/8/15
Hasten-EA [™]	F-071916	9/26/17
Herbimax [®]	J0316	11/2/18
Hi-Light [®] Blue	2019 06	9/7/14
Hi-Light [®] Blue WSP	7/23/09	5/31/15
Hi-Wett [®]	G0814	2/26/19
Improved JLB Plus	undated	10/16/15
Induce [®] (CA)	CASN 020114	8/4/15
Induce [®] (WA)	WASN 033115	5/12/15
Inlet [®]	SN 033115	3/17/15
In-Place [®]	F-012716	9/26/17
InterLock [®]	1/0509/2	10/17/19

Product	Label ID	SDS Date
Kinetic [®] (CA)	SN 020114	6/15/16
Kinetic [®] (WA)	WASN 040115/0616	8/11/17
LI 700 [®]	C0618	5/22/18
Liberate [®]	G0814	9/7/16
M.O.C.	SN 011215	5/25/15
Mark-It Blue [®]	01032016	1/12/16
MES-100 [™]	01/15	2/12/20
Miller Nu Film P [®]	20150311	9/12/16
Miller Sustain [®]	2017	9/19/16
Mor-Act [®] (CA)	F-051519	5/6/19
Mor-Act [®] (WA)	F-021517	9/26/17
MSO [®] Con'c w/ LeciTech	I0916	3/27/17
MSO [®] Concentrate	I0916	1/2/14
Pathfinder [®] II	1/9/18	5/22/15
Phase [®]	A2517	2/24/15
ph [®] Kicker CA	GHS R4-22-2015	4/28/15
Pro-90	2019-01	2/25/16
Pro-Spreader	2017-10 (GHS)	4/4/16
Quest [®] (CA)	CASN 020114	5/20/15
Quest [®] (WA)	WSN 040115	7/7/15
R-11 [®]	F-092818	1/9/20
Rainier-EA [™]	F-012716	9/26/17
Renegade-EA [®]	F-070918	6/5/17
Silwet [®] EcoSpreader	2015	1/2/18
Silwet L-77 [®]	SN 033115	4/14/15
Spraytech Oil [™]	undated	4/1/96 (MSDS)
Strike Zone [®] DF	SN 033115	4/9/15
Super Spread [®] MSO	F-070918	9/26/17
Surfix [®] -P	SN 042916G	8/7/17
Sustain [®]	undated	9/19/16
Syl-Tac-EA [™]	F-071916	9/26/17
Tactic [™]	G0814	5/9/17
Tri-Fol [®]	F-012716	9/26/17
W.E.B. Oil	F-102017	9/26/17
Wetcit	V20170606	12/7/17

7. Acronyms and Abbreviations Used

µg – microgram

µl – microliter

APE – alkylphenol polyethoxylate

APG – alkyl polyglycoside

BCF – bioconcentration factor

CA Reg. # - California State Pesticide Registration Number

CAS – Chemical Abstracts Service Registry

CEC – cation exchange capacity

CFR - Code of Federal Regulations

cm - centimeter

CMC – critical micelle concentration

COC – crop oil concentrate

DEA – diethanolamide

EC₅₀ – Concentration that affects 50% of the test population

EPA – United States Environmental Protection Agency

FDA – United States Food and Drug Administration

FIFRA - Federal Insecticide, Fungicide, and Rodenticide Act

g/kg – grams per kilogram

GHS - United Nations' Globally Harmonized System of Classification and Labelling of Chemicals

gpa – gallons per acre

GRAS – generally regarded as safe, a designation by the US FDA

HLB – hydrophilic/lipophilic balance

LC₅₀ – A concentration that kills 50% of the test population, used as an acute toxicity measure

LD₅₀ – A dose that kills 50% of the test population, used as an acute toxicity measure

LOAEL – lowest observable adverse effect level

LOEC – lowest observable effect concentration

LOEL – lowest observable effect level

mg/kg/day – milligrams per kilogram of body weight per day

mg/L – milligrams per liter, a metric measure of concentration, equivalent to parts per million

MSDS – Material Safety Data Sheet

MSO – methylated seed oil

NIS – Nonionic Surfactant

NOAEC – No observable adverse effect concentration

NOAEL – No observable adverse effect level

NOEC – No Observable Effect Concentration

NPE – nonylphenol polyethoxylate-based surfactants

OM – organic matter

OMRI – Organic Materials Review Institute

OPE – octylphenol polyethoxylate

OSHA – United States Department of Labor, Occupational Safety and Health Administration

PAH – polycyclic aromatic hydrocarbon

pH – referring to scale used to specify how acidic or basic something is

POEA – polyoxyethyleneamine, also known as ethoxylated tallow amine

PPE – Personal protective equipment

PPG – polypropylene glycol

ppm – parts per million, equivalent to mg/L

ppb – parts per billion, equivalent to $\mu\text{g/L}$

SDS, SDSs – Safety Data Sheet(s)

UAN – urea and ammonium nitrate

USDA – United States Department of Agriculture

v/v – volume per volume, meant to be used as a mixing amount

WA Reg. # - Washington State Pesticide Registration Number

8. References

- Chen, X.D., E. Culbert, V. Herbert, J.D. Stark. 2010. Mixture effects of the nonylphenol polyethoxylate, R-11 and the insecticide imidacloprid on population growth rate and other parameters of the crustacean, *Ceriodaphnia dubia*. *Ecotoxicology and Environmental Safety*. 73(2):132-137
- Damiano, J. 2021. Personal communication. February 12, 2021. J. Damiano is the Branch Chief of Enforcement Headquarters at the California Department of Pesticide Regulation within the California Environmental Protection Agency.
- Gadhawe, A. 2014. Determination of hydrophilic-lipophilic balance value. *International Journal of Science and Research*. 3(4):573-575
- Glatzhofer, J. 2020. Personal Communication. July 2, 2020. J. Glatzhofer is the senior formulations chemist at Wilbur-Ellis Company.
- Green, J.M. 1999. Effect of nonylphenol ethoxylation on the biological activity of three herbicides with different water solubilities. *Weed Technology*. 13(4):840-842
- Haller, W.T., R.K. Stocker. 2003. Toxicity of 19 adjuvants to juvenile *Lepomis macrochirus* (bluegill sunfish). *Environmental Toxicology and Chemistry*. 22(3):615-619
- Nebeker, A.V., G.S. Schuytema. 2000. Effects of ammonium sulfate on growth of larval northwestern salamanders, red-legged and Pacific treefrog tadpoles, and juvenile fathead minnows. *Bulletin of Environmental Contamination and Toxicology*. 64(2):271-278
- Organic Materials Review Institute (OMRI). 2019. OMRI List of Products, by Category. Accessed on-line at <https://www.omri.org/omri-lists/download> on February 7, 2019
- Penner, D. 2000. Activator adjuvants. *Weed Technology*. 14(4):785-791
- Schuytema G.S., A.V. Nebeker. 1999. Effects of ammonium nitrate, sodium nitrate, and urea on red-legged frogs, Pacific treefrogs, and African clawed frogs. *Bulletin of Environmental Contamination and Toxicology*. 63(3):357-364
- SERA (Syracuse Environmental Research Associates, Inc.) 1997a. Effects of surfactants on the toxicity of glyphosate, with specific reference to Rodeo. February 6, 1997. SERA TR 97-206-1b. 32 pages
- SERA (Syracuse Environmental Research Associates, Inc.) 1997b. Use and assessment of marker dyes used with herbicides. December 21, 1997. SERA TR 96-21-07-03b. 47 pages
- SERA (Syracuse Environmental Research Associates, Inc.) 2001. Sethoxydim [Poast] - Human Health and Ecological Risk Assessment – Final Report. October 31, 2001. SERA TR 01-43-01-01c. 182 pages

SERA (Syracuse Environmental Research Associates, Inc.) 2011a. Glyphosate – Human Health and Ecological Risk Assessment – Final Report. March 25, 2011. SERA TR-052-22-03b. 336 pages

SERA (Syracuse Environmental Research Associates, Inc.) 2011b. Triclopyr – Revised Human Health and Ecological Risk Assessment – Final Report. May 24, 2011. SERA TR-052-25-03a. 267 pages

SERA (Syracuse Environmental Research Associates, Inc.) 2014. Scoping/Screening Level Risk Assessment on Clethodim: Final Report. October 30, 2014. SERA TR 056-08-02b. 246 pages

Siemering, G.S., J.D. Hayworth, B.K. Greenfield. 2008. Assessment of potential aquatic herbicide impacts to California aquatic ecosystems. *Archives of Environmental Contamination and Toxicology*. 55:415-431.

Smith, B.C., C.A. Curran, K.W. Brown, J.L. Cabarrus, J.B. Gowan, J.K. McIntyre, E.E., Moreland, V.L. Wong, J.M. Grassley, C.E. Grue. 2004. Toxicity of four surfactants to juvenile rainbow trout: Implications for use over water. *Bulletin of Environmental Contamination and Toxicology*. 72(3):647-654

Stark, J.D., W.K. Walthall. 2003. Agricultural adjuvants: Acute mortality and effects on population growth rate of *Daphnia pulex* after chronic exposure. *Environmental Toxicology and Chemistry*. 22(12):3056-3061

USDA Forest Service, 2003. Human and ecological risk assessment of nonylphenol polyethoxylate-based (NPE) surfactants in Forest Service herbicide applications. Unpublished report, written by David Bakke, Pacific Southwest Region Pesticide-Use Specialist. May 2003. 182 pages

United States Environmental Protection Agency (EPA), 2013. Memorandum to Amend the Current Exemption from the Requirement of a Tolerance for D-Glucoyanose, oligomeric, decyl octyl glycoside (CAS Reg. No. 68515-73-1), when used as Inert Ingredients in Pesticide Formulations, to include 40 CFR 180.940(a). Accessed on-line on January 20, 2020 at <https://www.regulations.gov/docket?D=EPA-HQ-OPP-2013-0165>

Washington State Department of Agriculture (WSDA), 2018. Spray Adjuvants Registered for Use on Aquatic Sites in Washington (Revised August 29, 2018).

Washington State Department of Agriculture (WSDA), 2019. Partial List of Spray Adjuvant Ingredients – 8/30/2019. Washington State Department of Agriculture. Accessed on-line on September 6, 2019 at <https://agr.wa.gov/departments/pesticides-and-fertilizers/pesticides/spray-adjuvants>