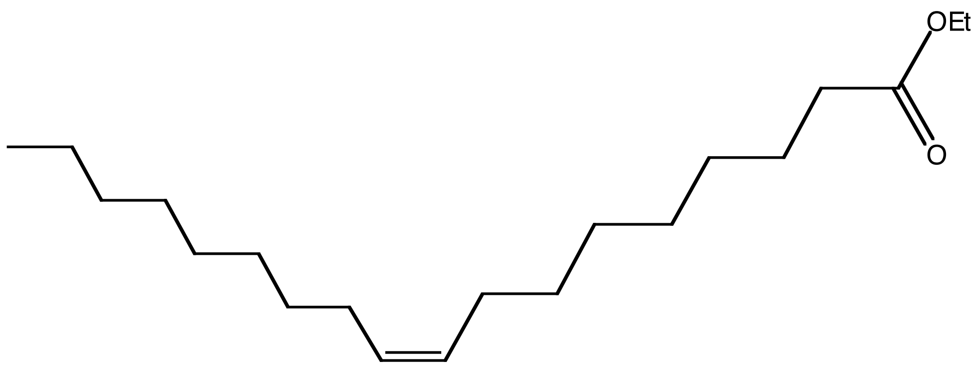
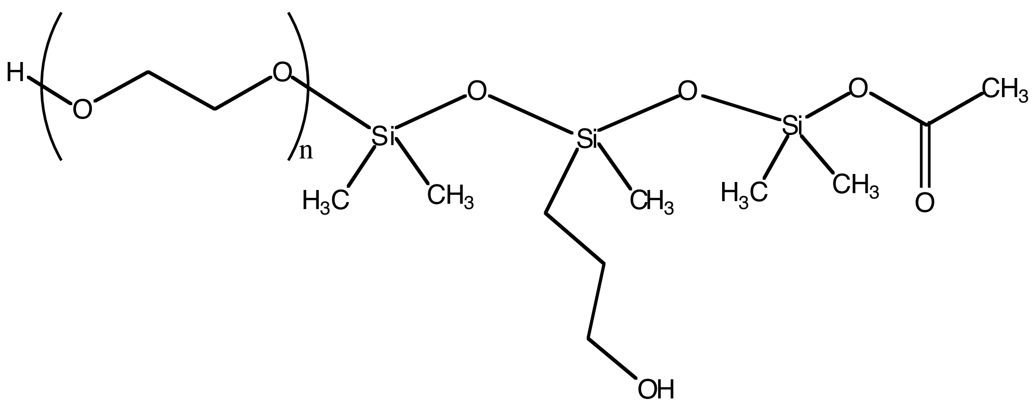
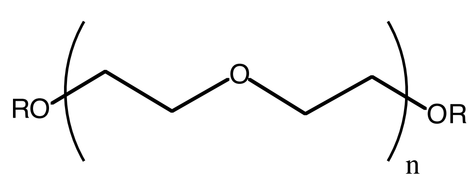
Chapter 8—Surfactants and Dyes



Ethyl oleate



Ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane



Dialkyl polyethylene glycol

8 Table of Contents — Surfactants and Dyes

8.1 Introduction

Two surfactants—Competitor and Sylgard 309—and one dye—Blazon Blue dye—are being considered for use in the MMWD vegetation management project. Surfactants are materials added to active herbicidal ingredients to improve performance. Surfactants facilitate herbicidal activity by improving herbicide dispersal, absorption, spread, adherence and/or penetration to foliage. Water droplets containing a surfactant will spread in a thin layer over a waxy leaf surface and penetrate the waxy leaf cuticle more easily. Surfactants are also used to control spray drift by altering the surface tension of the solution so small droplets cannot form. The purpose of the dye is to mark areas that have been treated with herbicides to ensure full coverage and avoid duplicative treatments. The dye also serves to notify workers and the general public of the location of treated areas.

The EPA does not register surfactants or dyes, nor does the Agency review their labels. No toxicity information is required to be submitted for the individual ingredients in surfactant mixtures or for the mixtures themselves. However, EPA has categorized approximately 1,200 "inert" ingredients into four lists, and some of the surfactant ingredients are on these lists.[1] Lists 1 and 2 contain inert ingredients of toxicological concern. List 4 contains nontoxic substances such as vegetable oils and water. List 3 includes substances for which the EPA has insufficient information to classify as either hazardous (Lists 1 and 2) or nontoxic (List 4). This chapter also provides information on the EPA inerts list for the known surfactant ingredients, where this information is available.

In 2006 after most of the pesticide re-registrations were complete, EPA dropped this listing scheme for "inert" ingredients, although other organizations continue to use the classifications, as noted by EPA.[1]

> *"**Note**: The List Category policy, created in 1987, has now served its purpose as a tool for prioritizing the evaluation of chemicals. Now that reassessment of food tolerances/tolerance exemptions under the Food Quality Protection Act (FQPA) is complete, there are no longer inerts classified as List 1, 2, or 3. All-food use inert ingredient tolerances and tolerance exemptions are considered to be safe when used according to the conditions set forth in the CFR's text and tables. As noted above, the "4A" category is still being used for the purposes of FIFRA Section 25(b), and USDA is still utilizing "List 4" for their National Organic Program. For non-food inert ingredients, the 1987 List Category policy remains pertinent (including labeling) for those identified as "List 1" (toxicological concern). For informational purposes you can still access EPA's old inert list categories."*

Risk assessments can only be conducted for chemicals for which toxicity data and physical properties that describe the persistence and mobility of the chemical are available. For the MMWD project, sufficient data were not available to conduct a risk assessment for the two surfactants—Competitor and Sylgard 309—and Blazon dye. The available toxicity and environmental fate data are summarized in this chapter.

Information on the surfactants and dye were obtained from several sources, including the labels and MSDSs, the Loveland Products web site,[2] the USFS documents on surfactants,[3] a risk assessment developed for the San Francisco cordgrass project[4] and the USFS Plumas County risk assessment.[5] Additional work from the National Toxicology Program and the peer-reviewed literature was also included and is discussed below.

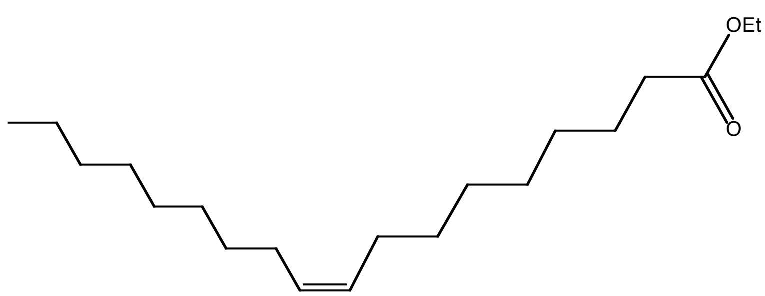
8.2 Surfactant Composition and Background Information

Surfactants are typically mixtures of ingredients, some of them polymers of varying chain length, and are difficult to characterize and analyze in the environment. In this section, the known ingredients in Competitor and Sylgard 309 are described. The actual percentages of each component are not precisely known.

8.2.1 Competitor

Competitor is a nonionic surfactant, with 98% of the product comprised of a mixture of the ethyl ester of oleic acid (ethyl oleate, CAS number 111-62-6), sorbitan alkylpolyethoxylate, and dialkyl polyoxyethylene glycol (PEG).[6] Competitor was designed specifically for use in water and contains an alkyl ethoxylate instead of nonyl phenol ethoxylate (NPE), which is associated with endocrine disrupting effects in aquatic ecosystems.[3,7]

Ethyl oleate: Ethyl oleate is a fatty acid ester prepared by reacting oleic acid derived from seed oils (*e.g.* corn, soybean, sunflower, canola) with ethanol (the same alcohol in beer, wine and liquor).



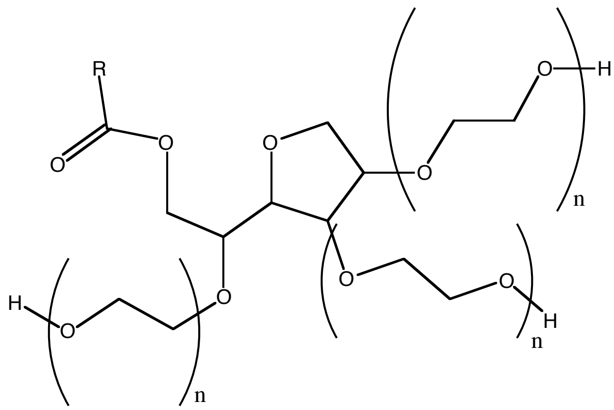
Ethyl oleate

Ethyl oleate is both metabolized and synthesized by the human body. Metabolism of ethyl oleate occurs rapidly to produce ethanol and oleic acid, with a half-life in rats of less than 24 hours.[8] Both ethanol and oleic acid are metabolized further to produce energy for the organism, just as if the two separate ingredients had been ingested in the diet. In the presence of high concentrations of ethanol in the body, e.g., when alcohol is consumed, enzymes in the mammalian system produce ethyl oleate.[8]

The FDA has approved the use of ethyl oleate as a food additive.[9] The methyl, ethyl, propyl and butyl esters of oleic acid are used as emollients in cosmetics and other personal care products and as lubricants.[10]

Sorbitan alkylpolyethoxylate: The class of chemicals known as the alcohol ethoxylates (AEs) are among the highest production volume chemicals in the US. These nonionic surfactants are used in detergents and other household products, in foods and pharmaceuticals as emulsifiers, and in lubricants.[11, 12] They are ubiquitous in the environment due to their discharge through wastewater treatment systems, but are readily degraded by microbes.

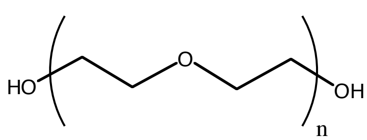
Sorbitan alkylpolyethoxylate is a nonionic surfactant prepared by reacting sorbitol, a sugar occurring naturally in fruits, with a carboxylic acid (often a fatty acid) and ethylene oxide. The type of carboxylic acid and the number of moles of ethylene oxide in the surfactant alters the properties of the surfactant. The identity of the carboxylic acid bound to sorbitol in Competitor is not specified.



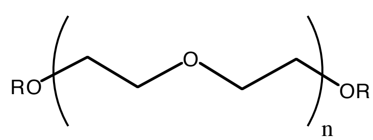
Sorbitan alkylpolyethoxylate

The "Tween" and "Polysorbate" family of surfactants are representative members of the sorbitan alkylpolyethoxylate class of surfactants and some of these compounds are used in foods, injectable and ingestible drugs, and personal care products.[13] The FDA has approved the use of several of the polysorbates as food additives.[9]

Dialkyl polyoxyethylene glycol (PEG): Polyethylene glycol is a polymer synthesized by reaction of glycol with varying amounts of ethylene oxide. The terminal hydroxyl groups can be alkylated to produce various dialkyl PEG compounds.



Polyethylene glycol (PEG)



Dialkyl polyethylene glycol
R = alkyl group

PEG is widely used in cosmetics,[14] toothpastes, and drugs such as laxatives. Wikipedia summarizes the clinical uses of PEG and PEG derivatives.[15]

> *"Polyethylene glycol has a low toxicity[3] and is used in a variety of products. It is the basis of a number of laxatives (e.g. macrogol-containing products such as Movicol and polyethylene glycol 3350, or MiraLax or GlycoLax). It is the basis of many skin creams, as cetomacrogol, and sexual lubricants, frequently combined with glycerin. Whole bowel irrigation (polyethylene glycol with added electrolytes) is used for bowel preparation before surgery or colonoscopy and drug overdoses. It is sold under the brand names*

__GoLYTELY__, __GlycoLax__, __Fortrans__, __TriLyte__, and __Colyte__. When attached to various protein medications, polyethylene glycol allows a slowed clearance of the carried protein from the blood. This makes for a longer acting medicinal effect and reduces toxicity, and it allows longer dosing intervals. Examples include PEG-interferon alpha which is used to treat hepatitis C and PEG-filgrastim (Neulasta) which is used to treat neutropenia. It has been shown that polyethylene glycol can improve healing of spinal injuries in dogs.[4] One of the earlier findings that polyethylene glycol can aid in nerve repair came from the University of Texas (Krause and Bittner).[5] Polyethylene glycol is commonly used to fuse B-cells with myeloma cells in monoclonal antibody production. PEG has recently been proved to give better results in constipation patients than tegaserod.[6]

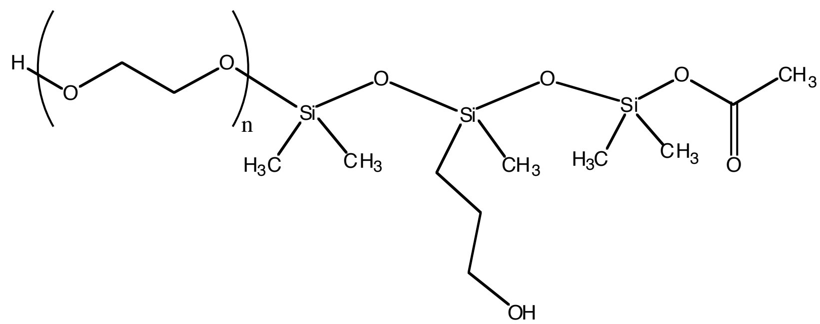
Research for New Clinical Uses
High-molecular weight PEG, e.g., PEG 8000, is a strikingly potent dietary preventive agent against colorectal cancer in animal models.[7]
The Chemoprevention Database shows it is the most effective agent to suppress chemical carcinogenesis in rats. Cancer prevention in humans has not yet been tested in clinical trials.
The injection of PEG 2000 into the bloodstream of guinea pigs after spinal cord injury leads to rapid recovery through molecular repair of nerve membranes.[8] The effect of this treatment to prevent paraplegia in humans after an accident is not known yet.
Research is being done in the use of PEG to mask antigens on red blood cells. Various research institutes have reported that using PEG can mask antigens without damaging the functions and shape of the cell.
PEG is being used in the repair of motor neurons damaged in crush or laceration incidence in vivo and in vitro. When coupled with melatonin, 75% of damaged sciatic nerves were rendered viable.[9]

8.2.2 Sylgard 309

Sylgard 309 is a nonionic organosilicone surfactant, containing > 60% of the ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane (CAS number 125997-17-3). The product also contains polyethylene glycol monoallyl acetate (CAS number 27252-87-5) and polyethylene glycol diacetate (CAS number 27252-83-1). The percent of the other ingredients in the product are not reported on the label. Sylgard 309 was specifically designed to enhance the efficacy of pesticides.[16]

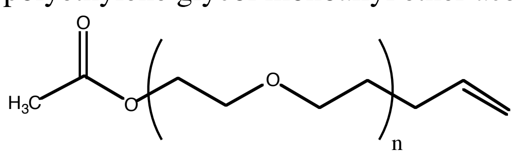
Ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane: Silicones are comprised of an Si-O-Si-O backbone with additional carbon-containing groups bound to the silicon atoms. There are many variations on the side chains that are attached to the silicone backbone, with each one imparting different properties to the resulting polymers. Silicones are widely used as sealants and additives to plastics and fibers, and in biomedical applications, heat-resistant coatings and non-stick coatings for food applications.

The ethoxylated acetate of 3-(3-(hydroxypropyl)-heptamethyltrisiloxane is a poly ethylene glycol polymer with a terminal silicone chain. In addition to its use as an adjuvant for pesticide applications, this compound is used as a defoamer in the manufacture of paper and paperboard intended for use in packaging, transporting, or holding food.[17, 18]

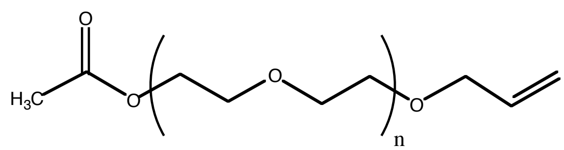


Ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane

Polyethylene glycol monoallyl acetate: There is some confusion over what compound this name refers to. There are two very similar compounds, polyethylene glycol monoallyl acetate and polyethylene glycol monoallyl ether acetate, differing by the presence of an additional oxygen atom (see structures below). The Sylgard 309 label refers to the monoallyl acetate, but confuses the issue further, by using the CAS number for the monomer—ethylene glycol monoallyl ether acetate. For the purposes of this review, we assume that the label is referring to polyethylene glycol monoallyl ether acetate.



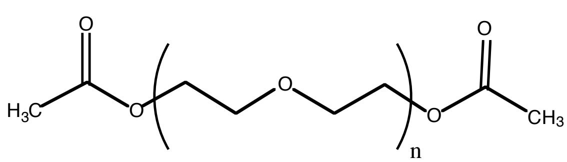
Polyethylene glycol (PEG) monoallyl acetate



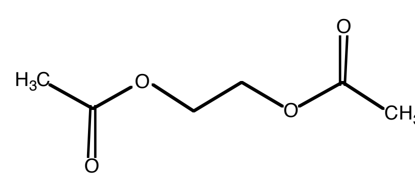
Polyethylene glycol (PEG) monoallyl ether acetate

This compound is used as an intermediate in the synthesis of other polymers. In addition to its use as an adjuvant for pesticide applications, this compound is used as a defoamer in the manufacture of paper and paperboard intended for use in packaging, transporting, or holding food.[17, 19]

Polyethylene glycol diacetate: In the industrial chemical literature and in patents, the terms polyethylene glycol diacetate and ethylene glycol diacetate are often used interchangeably. However, these are two different chemicals with different chemical properties (see structures below). The CAS number provided on the Wilbur-Ellis label (27252-83-1) is for ethylene glycol diacetate, but is probably referring to the PEG derivative of ethylene glycol diacetate.



Polyethylene glycol (PEG) diacetate



Ethylene glycol diacetate

8.3 Surfactant Toxicity to Mammals

The acute toxicity of surfactants to mammals and birds is generally low, and these substances are widely used in personal care products, cosmetics, drugs (including drugs that are directly injected) and in some cases, in foods. Every substance is different however, and the physical properties and toxicity will vary depending on the specific functionality of each surfactant.

8.3.1 Competitor

Competitor is not acutely toxic to humans and terrestrial wildlife. The chronic toxicity of the mixture remains unknown, although additional information is available on some of the components of the mixture, discussed below. There is no information on the toxicity of the mixture of this surfactant with Aquamaster, Garlon 4 Ultra, or Transline.

Product mixture: The only information available on the toxicity of the mixture of ingredients sold as Competitor is on the label[6] or MSDS.[20] The oral LD_{50} for rats and the dermal LD_{50} for rabbits exposed to Competitor are both greater than 5,000 mg/kg. Competitor has a "Caution" signal word on the label, meaning that it has low acute toxicity. It is minimally irritating to the eyes and is not toxic or irritating to the skin.[20] There is no information available on chronic toxicity, including cancer, endocrine disruption, or reproductive and developmental toxicity.

Ethyl oleate: Ethyl oleate is a List 4 minimal risk "inert" and is considered to be non-toxic. It is approved for use in foods by the FDA.[9] The Environmental Working Group (EWG) Skin Deep Cosmetics database gives ethyl oleate a very low hazard ranking of 0 on a scale of 0–10.[21] Similar to pelargonic acid (see Chapter 7), this compound is readily metabolized through well-known metabolic pathways and is not anticipated to be toxic to humans or animals at levels that may result from use with herbicides on MMWD lands.

Sorbitan alkylpolyethyoxylate: Depending on the side chain, sorbitan alkylpolyethyoxylates are rated as either List 3 (unknown toxicity) or List 4 minimal risk "inerts." The monooleic, monolauric, monostearic and tristearic acid derivatives of polysorbate are approved for use in foods by the FDA,[9] and the same set of sorbate esters has been approved by EPA for exemptions from tolerances on foods.[22] The EWG Skin Deep Cosmetics database gives sorbitan alkyl ethoxylates a low to high hazard ranking of 0–9 on a scale of 0–10, depending on the side chain in the molecule. The studies that back up these rankings are not directly cited on the web site.

The National Toxicology Program has reviewed polyoxyethylene sorbitan monooleate (CAS number 9005-65-6) for developmental toxicity.[23] Rats were dosed at levels of 0, 500 or 5,000 mg/kg-day on gestation days 6–15, and the animals were evaluated for maternal and fetal toxicity effects. The data indicate a maternal LOAEL of 500 mg/kg-day based upon an increase in maternal relative liver weight at this dose. No definitive adverse effects on prenatal development were noted in this study, and the developmental NOAEL was deemed to be greater than 5,000 mg/kg/day.

The toxicity of the sorbitan alkylpolyethoxylate used in Competitor cannot be definitively evaluated without knowledge of the identity of the side chain alkyl group.

Dialkyl polyethylene glycol: The parent polymer polyethylene glycol (PEG) is a List 4 minimal risk "inert" and is considered to be non-toxic by EPA.[24] PEG has been patented for use bound to injectable proteins to increase their circulating time in the body.[25] The substitution of alkyl groups (identity unknown) for the hydroxyl groups in the parent polymer will probably alter the toxicity of the compound to some extent, but the precise effects are unknown.

8.3.2 Sylgard 309

Although information is sparse, Sylgard 309 does not appear to be acutely toxic to most forms of mammalian wildlife. The chronic toxicity of the product mixture remains unknown. There is no information on the toxicity of the mixture of this surfactant with Aquamaster, Garlon 4 Ultra, or Transline.

Product mixture: The only information available on the toxicity of the mixture of ingredients sold as Sylgard 309 is on the label[16] and the MSDS.[26] The acute toxicity of Sylgard 309 to mammals is low. The oral LD_{50} for rats and the dermal LD_{50} for rabbits exposed to Sylgard 309 are both greater than 2,000 mg/kg. Sylgard 309 has a "Warning" signal word on the label, and may cause irritation to the skin and severe irritation to the eyes. It is not a skin sensitizer. The MSDS describes a 28-day oral dosing study in rats, in which rats were fed doses of 0, 33, 300, or 1,000 mg/kg/day.[16]

> *During the study the animals were monitored for clinical signs of toxicity and mortality, body weight gain and food consumption. After 28 days, the rats were sacrificed and subjected to urinalysis and hematological and clinical chemistry analysis, and gross and microscopic tissue examination. No significant findings of biological relevance were seen in female rats. Minor treatment related effects, primarily body weight gain and food consumption, were seen in male rats of the 1000 mg/kg/day dose group.*

These results indicate a subchronic NOAEL of 300 mg/kg/day. There is no additional information available on chronic toxicity, including cancer, endocrine disruption, or reproductive and developmental toxicity.

Ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane: There is no information available on the toxicity of this specific siloxane to mammals.

Polyethylene glycol monoallyl ether acetate: There is no information available on the toxicity of this specific PEG derivative to mammals. PEG polymers in general have low acute toxicity, but it is not clear what effect the addition of the allyl and acetate groups would have on the toxicity of this specific polymer.

Polyethylene glycol diacetate: There is no information available on the toxicity of this specific PEG derivative to mammals. The parent ethylene glycol diacetate has low acute toxicity, with LD_{50} values for oral exposure in rats and guinea pigs of 6,860 mg/kg and 4,940 mg/kg, respectively. The dermal LD_{50} for guinea pigs is greater than 22,140 mg/kg.[27] PEG polymers in general have low acute toxicity.[24] These facts suggest, but do not prove, that the polymer of ethylene glycol monoallyl acetate would have low acute toxicity as well.

8.4 Surfactant Toxicity to Insects and Aquatic Organisms

The acute toxicity of surfactants to insects and aquatic organisms is highly variable, depending on the chemical structure of the surfactant and the organism. In general, aquatic organisms are more susceptible to adverse effects from surfactants than terrestrial organisms because surfactants can adsorb to biological membranes (skin, gills) and disrupt biological functions.[28]

Some surfactants can be more toxic than the herbicides themselves. As an example, consider the toxicity of Roundup Original compared to that of Roundup Biactive[29] and glyphosate alone (Table D-10 in Appendix D). Roundup Original contains the well-studied surfactant polyoxyethylene amine, or POEA, and Roundup Biactive contains an unidentified surfactant that is not POEA. The LC_{50} for frogs for Roundup Original was between 0.41-38 mg/L. In contrast, Roundup Biactive LC_{50} values for frogs range from 43 mg/L to 492 mg/L. The frog LC_{50} for glyphosate alone ranges from 39 mg/L to 400 mg/L.

8.4.1 Competitor

Competitor has only slight acute toxicity to aquatic organisms, and it is one of the least-toxic surfactants used as an herbicide adjuvant (see Table 8-1 below). The chronic toxicity of the mixture remains unknown, although additional information is available on some of the components of the mixture, discussed below. There is no information on the aquatic toxicity of the mixture of this surfactant with Aquamaster, Garlon 4 Ultra, or Transline.

Product mixture: Competitor is slightly toxic to aquatic organisms. The fish LC_{50} was 95 mg/L, and the LC_{50} for aquatic invertebrates was 100 mg/L.[3] The fish and aquatic invertebrate NOEC was 50 mg/L.[30]

Ethyl oleate: No specific data on the aquatic toxicity of ethyl oleate was found. An EPA assessment indicates that its aquatic toxicity is anticipated to be low.[36]

Sorbitan alkylpolyethyoxylate: Because the specific alkyl group is not identified, it is not possible to search for toxicity information. For comparison, the aquatic toxicity of Polysorbate 80, the oleic acid sorbitan ester was found to be low, at greater than 100 mg/L.[31]

Dialkyl polyoxyethylene glycol: There is no information available on the toxicity of this specific PEG derivative to aquatic organisms.

8.4.2 Sylgard 309

Very little information is available on the toxicity of Sylgard 309 or its components to aquatic organisms. There is some indication that silicone-based surfactants may adversely affect terrestrial insects at high doses.

Product mixture: The USFS review of surfactants indicated that silicone-based surfactants have the potential to affect terrestrial insects.[3]

> *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. 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 surfactants, which are less effective at reducing surface tension, can also cause the drowning effect. But as with the silicones, 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 lethal effect, combined with the fact that individuals, not colonies or nests of invertebrates, may be affected, there is little chance that the surfactants 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 surfactant.

Table 8-1 summarizes the aquatic toxicity of various surfactants used in herbicide applications. There are no data for Sylard 309. Other silicone-based surfactants with similar ingredients such as Dye-Amic and Kinetic are slightly toxic to aquatic organisms, with LD_{50} values ranging from 14–61 mg/L; however, the precise aquatic toxicity of Sylgard 309 is not known.

Ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane: There is no information available on the toxicity of this specific siloxane to aquatic organisms.

Polyethylene glycol monoallyl ether acetate: There is no information available on the toxicity of this specific PEG derivative to aquatic organisms.

Polyethylene glycol diacetate: There is no information available on the toxicity of this specific PEG derivative to to aquatic organisms.

8.5 Issues Related to Herbicide Use with Surfactants

The USFS has done a thorough review, updated in 2007, of issues related to the use of herbicides in combination with surfactants.[3] Here, we include the primary conclusions from that report and refer the reader to the report for additional details.

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 to increase the mobility of other materials throughout the soil profile is a function of the concentration of the surfactant in the soil solution. Surfactants have been used as tools for site amelioration of soil pollution, through their ability to solubilize hydrophobic compounds.

Surfactants 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. Based on the studies that follow, for desorption to occur, concentrations of surfactants must be high, in the range of 1,000 ppm or more. This level is unlikely to be reached in normal applications.

Table 8-1: Comparison of the Aquatic Toxicity of Various Surfactants

Product	Ingredients	Surfactant Type	Taxa Group	LC_{50} Range (mg/L)	NOEC Range (mg/L)	References
Competitor	Ethyl oleate, soribtan alkyl polyethoxylate ester, dialkyl polyoxyethylene glycol	Nonionic	Fish	95	50	4, 30
			Aquatic invertebrates	>100	50	4, 30
Sylgard 309	Heptamethyl trisiloxane, ethoxylated acetate, polyethylene glycol monallyl acetate, polyethylene glycol diacetate	Nonionic, silicone	Fish	NA	NA	
			Aquatic invertebrates	NA	NA	
Dye-Amic	Organosilicone, methylated vegetable oil	Silicone, oil-based	Fish	23.2	NA	4
			Aquatic invertebrates	60	NA	4
Kinetic	Organosilicone, polyoxypropylene-polyoxyethylene copolymer	Silicone	Fish	13.9	NA	4
			Aquatic invertebrates	60.7	NA	4
R-11	80% octylphenoxypolyethoxy-ethanol, 20% butanol and compounded silicone	Nonionic, silicone, OPE	Fish	0.7–4.2	0.1-1.9	4, 32
			Aquatic invertebrates	0.42–19	8.4	4, 32
X-77	Alkylarylpoly (oxyethylene) glycols, free fatty acids, isopropyl alcohol	Nonionic, NPE/OPE	Fish	4.2–4.3	NA	4
			Aquatic invertebrates	2		4
Liberate	Phosphatidylcholine (lecithin), methyl esters of fatty acids, alcohol ethoxylate	Nonionic, lecithin-based	Fish	17.6	12.5	4
			Aquatic invertebrates	9.3	7.5	4
LI-700	Phosphatidycholine (lecithin), methylacetic acid, alkyl polyoxyethylene ether	Nonionic, lecithin-based	Fish	17–700	NA	4
			Aquatic invertebrates	170	NA	4
Mon 0818	Polyoxyethyleneamine, 75%	Nonionic, amine	Fish	1.4–4.9	NA	33
			Amphibians	1.1–2.7	NA	34, 35
Cygnet Plus	75% d-limonene and related isomers, 15% methylated vegetable oil, 10% alkyl hydroxypoly oxyethylene	Nonionic	Fish	45	15–30	4
			Aquatic invertebrates	6.6	3	4
Agridex	Proprietary, heavy range parrafin-based petroleum oil with polyol fatty acid esters and polyethoxylated derivatives	Nonionic, oil-based	Fish	271–386	NA	4
			Aquatic Invertebrates	>1,000	NA	4

LC_{50} = lethal concentration for 50% of the test organisms. NOEC = No Observed Effect Concentration. NA = not available. OPE = octylphenol ethoxylate. NPE = nonylphenol ethoxylate.

It appears that biodegradation of pesticides can be affected by surfactants in the soil, however this too is concentration dependent similar to desorption effects. It appears that effects to pesticide biodegradation are through preferential degradation of the surfactant rather than through a toxic action on microorganisms.

Although the potential exists for surfactants to affect the environmental fate of herbicides in soil, any potential effects would be unlikely under normal conditions because of the relatively low concentration of surfactants in the soil/water matrix. Localized effects could be seen if a spill occurred on soil, so that concentrations of surfactant approached or exceeded about 1,000 ppm.

Do mixtures of herbicides and surfactants represent a greatly increased risk over the individual compounds alone (i.e., synergism)?

Surfactants, by their very nature, are intended to increase the effect of a pesticide by increasing the amount of pesticide that is in contact with the target (by reducing surface tension). This is not synergism, but more accurately is a reflection of increased dose of the herbicide active ingredient into the plant.

Although there is not much data in the technical literature, the references included in this paper indicate a lack of synergistic effects between surfactants and pesticides.

Do surfactants represent a unique risk to aquatic organisms?

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 nonylphenol ethoxylates (NPE) and octylphenol ethoxylates (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.

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.

Do surfactants represent a unique risk to mammals?

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. There is more information on alkylphenol ethoxylates, such as nonylphenol ethoxylates (NPE). The interest in the alkylphenol ethoxylates surfactants is largely driven by findings of estrogenic effects. 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.

Do surfactants affect the absorption rate of herbicides through the skin?

Various surfactants 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 a surfactant to increase the absorption of another compound, the surfactant must affect the upper layer of the skin. Without some physical effect to the skin, there will be no change in absorption as compared to the other compound alone.

The studies discussed below indicate that in general non-ionic surfactants have less of an effect on the skin, and hence absorption, then 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. 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.

8.6 Blazon Blue Dye Toxicity

There is even less information on the identity and toxicity of dyes than there is on surfactants. The blue dye, Blazon, is added to herbicide application mixtures to mark areas that have been treated. It is a water-soluble, nonionic polymeric colorant. As with most colorant products, the active ingredients are proprietary; the MSDS only indicates that it is non-hazardous and non-toxic. The report from the San Francisco Estuary Spartina Project Report found a single LD_{50} for rats of >5,000 mg/kg for Blazon. Blazon is considered practically non-toxic by the oral route, is a mild skin irritant and not mutagenic. No other information is available.

The product information sheet reports that the product is non-staining to the skin or clothing. The colorant is typically added at a rate of 3 quarts per 100 gallons of solution, or 16 to 24 ounces per acre sprayed. The effects of Blazon Blue dye on nontarget terrestrial and aquatic species is unknown.

8.7 Environmental Fate and Transport

Several studies are available regarding the environmental fate of the components in the surfactants Competitor and Sylgard 309 or the dye Blazon. For those with no data, generalizations can be made based on molecular structure and data on related compounds, but no detailed studies are available for most of the specific ingredients in these products. Without essential information such as half-life, water solubility, K_{oc}, K_H, and K_{ow}, it is difficult to predict the potential for long-term runoff, as well as potential dermal and inhalation exposures for workers, the general public and wildlife.

Ethyl oleate: Ethyl oleate has low water solubility (10 mg/L), moderate vapor pressure (0.01 mm Hg), and a high K_{oc} of > 10,000 mL/g,[36] indicating a strong tendency to bind to the organic matter in soils. Similar to pelargonic acid (see Chapter 7), ethyl oleate is degraded rapidly in the environment through microbial action.[37] The degradation product, oleic acid has a half-life of less than one day, and a log K_{ow} of approximately 3.0.[38]

Sorbitan alkylpolyethoxylates: Because the alkyl group that is part of this polymer is not identified, no environmental fate data specific to this compound could be found.

Dialkyl Polyethylene glycol (PEG): The hydroxylated form of PEG is soluble in water, and has been found to be relatively stable to degradation in soil.[39] A two-phase decomposition process occurs: A fast initial phase (up to 21 days), followed by a much slower phase (after 28 days). The measured half-life was found to be 1,127 days for free PEG and 735 days for PEG bound to organic matter. These data suggest that PEG is relatively persistent in the environment. The dialkyl derivatives are likely to have similar persistence, based on the unreactivity of the ether linkage.[40] Several studies show that >98% of PEG ingested by animals is excreted in the feces.[41]

Ethoxylated acetate of 3-(3-Hydroxypropyl)-heptamethyltrisiloxane: There is no information available on the environmental fate of this specific siloxane.

Polyethylene glycol monoallyl ether acetate: See dialkyl polyethylene glycol, above.

Polyethylene glycol diacetate: See dialkyl polyethylene glycol, above.

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