2.06.08

Safety Review of Checkmate Chemicals

Checkmate LBAM-F is a biochemical pesticide designed for mating disruption of the light brown apple moth (LBAM). In early November 2007 aerial spraying of the pesticide was conducted over residential areas in Santa Cruz County as part of an ongoing “eradication” program. Aerial sprayings in Monterey County in September, October and November of 2007 included the use of a similar pheromone pesticide Checkmate OLR-F. Neither product is registered with the EPA’s Office of Pesticides for residential use. According to a spokesperson for the product manufacturer Suterra, Checkmate OLR-F is registered for use on California vineyards, but this is the first time Checkmate LBAM-F has been used in California or elsewhere (*Renner 12/5/07*).

The Checkmate LBAM-F formulation includes two types of synthetic moth pheromones, as well as a variety of “inert” ingredients. Though safety data sheets for the *inert* ingredients in the formulas have raised many serious health and safety concerns, materials presented by the CDFA (*CDFA 2007*; *DPR/OEHHA 2007*) have consistently focused on the safety of only the pheromone constituents, failing to address the preponderance of known toxicity data for the *inerts*. A 2007 CDFA *Questions and Answers* document on the LBAM states that “the ingredients in the formulation are water and biodegradable elements used to delay the release of the active ingredient” and that “the basic biodegradable building block is urea, a normal constituent of the human body that is derived from the breakdown of proteins that we eat.” However a review of the available research data as well as the MSDS sheets (Material Safety Data Sheets) for these chemicals indicates a high level of toxicity for many of the *inerts*.

The word “inert” as used on a pesticide label is commonly mistaken to mean inactive or benign. However the EPA states that “although the term “inert” may connote physical, chemical or biological inactivity, use of the word “inert” to describe a component in a pesticide product means only that the substance is not intended to exert a pesticidal effect … in that product. The “inert” ingredient may have biological activity of its own, it may be toxic to humans, and it may be chemically active” (*EPA 2002*). Though typical pesticide formulations are comprised largely of *inerts* (a review of 100 agricultural pesticide products found that the formulations contained on average 50% inert ingredients, with many containing 90% or more “inerts”; *NCAP 2006*) the majority of safety tests required to register a pesticide are performed with the active ingredient alone, not the complete formulation (*Cox & Surgan 2006*).

Numerous studies have shown that *inerts* can increase the toxicity of pesticides to body systems such as the nervous, cardiovascular, and hormonal systems, the mitochondria, and genetic material. *Inerts* can also interact with other chemicals in pesticide formulations, to increase human exposure levels to the pesticide. Additionally, *inerts* have been shown to raise the ecotoxicity of pesticide formulations; increasing the severity of toxic effects to plants, animals, and non-target microorganisms (*Cox & Surgan 2006*).

A comparison of potential health effects listed for the *inert* ingredients in the Checkmate formulas, with the actual adverse effects reported following the sprayings, indicates a remarkable consistency between the two. In fact a *DPR/OEHHA* (*2007*) consensus document provided by the CDFA states the following:

- "The toxicity data on the pheromone active ingredients as well as on microencapsulated pheromone product formulations suggest that exposure to a high dose of airborne Checkmate microcapsule particles could cause eye, skin, or respiratory irritation."
- "The toxicological information on the Checkmate product indicates that exposure to high levels of the applied material would be consistent with many of the reported symptoms. However, because the application rate was extremely low, it is likely that exposure occurred at levels below those that would be expected to result in health effects."

643 adverse reactions reported following the sprayings in Monterey and Santa Cruz counties (and documented by various governmental agencies and citizen groups) included the following:

- asthma attacks
- bronchial irritation
- lung congestion and soreness
- difficulty breathing and shortness of breath
- coughing or "wheezing"
- skin rashes (sometimes severe)
- vision blurred
- eye irritation
- sore throats
- nasal congestion
- sinus bleeding
- chest pains and tightness
- heart arrhythmia and tachycardia (irregular and rapid heartbeat)
- headaches (sometimes debilitating)
- an inability to concentrate and focus
- dizziness
- muscle aches
- body tremors
- intestinal pain and diarrhea
- nausea
- swollen glands and lymph nodes in neck and under arms
- feelings of lethargy and malaise
- menstrual cramping, an interruption to menstrual cycles, and in some cases a recommencement of menstrual cycles after menopause

(*HOPE 1/3/08*)

The particle size of the microcapsule shell is another issue that has raised serious health concerns. A consensus document provided by the CDFA in regard to the microencapsulated spray lists the particle size as 25 micrometers (microns) or larger (*DPR/OEHHA 2007*), however a UC Davis study on the spray discovered a wide range of particle sizes down to the 10 micron size (*Werner et al 2007*). The EPA classifies particles 10 microns in size or smaller as “particle pollution”, cautioning that this size particle can get deep into the lungs and cause or aggravate a variety of health problems including coughing, difficulty breathing, asthma, and other respiratory symptoms (*EPA website*). The sprayings in Monterey and Santa Cruz counties were followed by numerous reports of mild to severe respiratory and asthma-like symptoms (*HOPE 1/03/08*).

The Checkmate formula has also raised concerns regarding its potential as an environmental endocrine disruptor. An endocrine disruptor is defined as “an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations" (*European Commission*). The range of substances thought to cause endocrine disruption is wide and varied, including such synthetic chemicals as industrial, municipal, and agricultural wastes (*Environment Canada*). Environmental endocrine disruptors (EEDs) have been shown to affect both humans and wildlife. A wide variety of documented and suspected effects related to EEDs include female reproductive problems, increased incidence of breast cancer, endometriosis, decreased sperm counts, defects in male sexual development, increased incidence of prostate cancer, immune system damage, and behavioral and developmental problems in children (*Keith 1998*).

Butylated hydroxytoluene (BHT) (an *inert* in the formula) has been shown in studies to have estrogenic activity (*Miller et al. 2001; Wada et al. 2004*) and MSDS sheets state that chronic exposure to BHT may cause reproductive and fetal effects (*Acros MSDS*). Following the sprayings in Monterey and Santa Cruz counties, several women reported unusual menstrual symptoms including cramping, interruption of menstrual cycle, and postmenopausal recommencement of the menstrual cycle (*HOPE 1/03/08*).

Checkmate LBAM-F

Product Description

- an aqueous suspension of pheromone containing micro-bead/dispensers (*Suterra MSDS*)
- a biochemical for mating disruption of the Light Brown Apple Moth (*Epiphyas postvittana*) (*Suterra LBAM-F label*)

Toxicity

As stated on Suterra MSDS Product Sheet: the toxicity of the product is determined by the toxicity of the pheromone active ingredient. The toxicity of this pheromone will be similar to the toxicity of other lepidopteran pheromones, ie:

- ***oral*** (rat), LD_{50}: >5000 mg/Kg (*Suterra MSDS*)
- ***dermal*** (rabbit), LD_{50}: >2000 mg/Kg (*Suterra MSDS*)
- ***acute inhalation*** (rat), LC_{50}: >5 mg/L (*Suterra MSDS*)
- ***primary eye irritation*** (rabbit): mildly irritating (*Suterra MSDS*)
- ***primary skin irritation*** (rabbit): moderately irritating (*Suterra MSDS*)

Potential Health Effects (Warnings)

- ***ingestion*** - may cause upset stomach in large doses (*Suterra MSDS*)
- ***inhalation*** – due to product form exposure not expected (*Suterra MSDS*)
- ***eye*** – may cause transient irritation (*Suterra MSDS*)
- ***skin*** – may cause transient irritation (*Suterra MSDS*)
- ***ingestion*** – may cause upset stomach in large doses (*Suterra MSDS*)
- ***chronic*** – long-term studies on the active ingredients have not been done, however, no adverse effects expected (*Suterra MSDS*)
- ***recommended exposure limits*** – none established (*Suterra MSDS*)
- ***listed as carcinogen*** – no (*Suterra MSDS*)
- ***other health effects*** – no known adverse effects expected (*Suterra MSDS*)
- ***health hazard categories*** – EPA Toxicity Category III – Caution (*Suterra MSDS*)

Ecological Toxicity

- none listed on Suterra MSDS
- Suterra product information states the following:
  ENVIRONMENTAL HAZARD
  For terrestrial uses: For purposes of this Section 18 use only, this product may be applied in Riparian habitats, over water that is covered or partially covered by tree canopies, or over uncovered water that is close to such water bodies. Otherwise, do not apply directly to water, or to areas where surface water is present, or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment washwaters or rinsate.

<u>(E)-11-Tetradecenyl Acetate</u>

(E)-11-Tetradecen-1-YL Acetate (*As Listed on Checkmate LBAM-F MSDS*)

CAS Number - 33189-72-9

Class

- ***use type*** – pheromone (*PAN Database*)
- ***chem class*** – pheromone (*PAN Database*)

Toxicity

- no available weight-of-the-evidence summary assessment (*PAN Database*).

Potential Health Effects (Warnings)

- Based on low toxicity in animal testing, and expected low exposure to humans, no risk to human health is expected from the use of these pheromones. During more than 10 years of use of lepidopteran pheromones as pesticides, no adverse effects have been reported (*EPA website*).
- The safety record for lepidopteran pheromones has allowed the Agency to conclude that consumption of food containing residues of the pheromones presents no risk. In addition, these pheromones can be used experimentally without a permit on up to 250 acres, versus the 10-acre limit imposed on other pesticides (*EPA website*).
- ***carcinogenicity*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*).

Ecological Toxicity

- Adverse effects on non target organisms (mammals, birds, and aquatic organisms) are not expected because these pheromones are released in very small amounts to the environment and act on a select group of insects (*EPA website*).
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*).

(E,E)-9,11-Tetradecadienyl Acetate

(E,E)-9,11-Tetradecadien-1-YL Acetate (*As Listed on Checkmate LBAM-F MSDS*)

CAS Number - 54664-98-1

Class

- ***use type*** – information not available
- ***chem class*** – information not available

Toxicity

- information not available

Potential Health Effects (Warnings)

- information not available

Ecological Toxicity

- information not available

Crosslinked Polyurea Polymer

(generic term - actual chemical name unknown. According to Checkmate manufacturer Suterra, polymethylene polyphenyl isocyanate is used to create the encapsulation polymer, however they say that the PPI starter compound is used up during the reaction [*Renner 12/5/07*])

CAS Number – information not available

Crosslinked Polyurea Polymer is a component of the microcapsule shell. A DPR /OEHHA (Department of Pesticide Regulation/Office of Environmental Health Hazard Assessment) consensus document states that the polyurea shell biodegrades into urea. Research has linked urea to the occurrence of harmful algal blooms (HAB's), also known as red tides. Following the spraying, a harmful algal bloom (red tide) described by a water specialist with the Santa Cruz County Environmental Health Services as "one of the more dramatic ones in recent memory", hit the Monterey Bay (*Ragan 11/13/07*).

Class

- ***use type*** – information not available
- ***chem class*** – information not available

Toxicity

- information not available

Potential Health Effects (Warnings)

- information not available

Ecological Toxicity

- A DPR /OEHHA (Department of Pesticide Regulation/Office of Environmental Health Hazard Assessment) consensus document states that the polyurea shell biodegrades into urea. A number of studies have linked urea to the occurrence of harmful algal blooms (HAB's).
    - research published by scientists at San Francisco State University indicates that urea fuels the growth of potentially toxic algal blooms (*SFSU 2000*)
    - various studies have shown that urea increases levels of domoic acid (DA), a toxin occurring in several species of *Pseudo-nitzschia* algae (*Cochlan et al*. 2006, *Howard et al. 2007*)
    - *Pseudo-nitzschia australis* is present in the waters of the Monterey Bay (*Fire & Silver 2005*)
    - domoic acid has been linked to illness and mortality in a variety of species including birds, sea lions, seals, dolphins, and whales (*UCSC 2001*, *IBRRC 2007*, *Cempa 2000*, *SFSU 2000*)
    - domoic acid from *Pseudo-nitzschia* has also been implicated in sickness/death in humans (*NWFSC website*).

Polymethylene Polyphenyl Isocyanate (PPI)

synonym – polymeric MDI (PMDI)

CAS Number – 9016-87-9

A document released by the EPA initially identified PPI as an ingredient in the Checkmate formula, however they subsequently retracted that information (*Ragan 10/18/07*). According to a statement by a Suterra representative, PPI is used to create the encapsulation polymer but reacts into different chemicals by the time the product is ready to use. Suterra maintains that the PPI starter compound is used up during the reaction (*Abraham 10/18/07; Renner 12/5/07*), however an NRDC (Natural Resources Defense Council) statement on the

spraying notes that trace amounts of PPI could be present in the final formula (*NRDC 2007*). The MSDS sheet on this chemical states that "the product reacts with water at the interface, forming CO_2 and a solid insoluble product with high melting point (polyurea). This reaction is accelerated by surfactants (e.g. detergents) or by watersoluble solvents." (*Pagel MSDS*)

Polymethylene Polyphenyl Isocyanate (PPI) is classified as harmful by inhalation, and as an irritant to the eyes, respiratory system, and skin under European classification. MSDS sheets warn against breathing the vapor or spray and caution individuals with asthma and other known respiratory problems to avoid exposure to the product. PPI is a known respiratory irritant associated with occupational asthma (*Carlisle MSDS*; *HAZ-MAP; IRIS data sheet; Seguin et al. 1987*). An EPA document from IRIS (Integrated Risk Information System) indicates that "exposure to isocyanates is a leading cause of occupational asthma worldwide". The document also cites a number of case reports describing occupational asthma and hypersensitivity pneumonitis, related to PMDI exposure (*IRIS data sheet*).

Following the sprayings in Monterey and Santa Cruz Counties there were numerous reports of respiratory symptoms including asthma, bronchial irritation, difficulty breathing, shortness of breath, coughing and wheezing, and lung congestion. Blurred vision, eye irritation, and skin rashes were also reported (*HOPE 1/03/08*).

Class

- ***use type*** – none listed (*PAN Database*)
- ***chem class*** – polymer (*PAN Database*)

European Classification

- ***hazard symbols*** – Xn (harmful), Xi (irritant) (*EC Annex II; Gestis Database*)
- ***risk phrases*** – R20 (harmful if inhaled), R36/37/38 (irritating to eyes, respiratory system, skin), R42/43 (inhalation/skin sensitization) (*EC Annex III*; *Gestis Database*)
- ***safety phrases*** – S(1/2) (keep locked up and out of reach of children), S23 (do not breathe gas/fumes/vapor/spray), S36/37 (use protective clothing and gloves), S45 (in case of accident or illness seek medical advice) (*EC Annex IV*; *Gestis Database*)

WHMIS Classification (Canada)

- D1A - very toxic material causing immediate and serious toxic effects (D1A classification applies to aerosol exposures. No LC50 values for vapor exposure were located. This chemical has a very low vapor pressure.) (*CCOHS data sheet; CSST data sheet*)
- D2A - very toxic material causing other toxic effects (*CCOHS data sheet; CSST data sheet*)
- D2B - toxic material causing other toxic effects (*CCOHS data sheet; CSST data sheet*)

WHMIS Health Effects Criteria Met by this Chemical (Canada)

- D1A - acute lethality - very toxic – immediate (*CCOHS data sheet*)
- D2A - chronic toxicity - very toxic – other (*CCOHS data sheet*)
- D2A - respiratory tract sensitization - very toxic – other (*CCOHS data sheet*)
- D2B - skin sensitization - toxic – other (*CCOHS data sheet*)

Toxicity

Acute toxicity - no available weight-of-the-evidence summary assessment (*PAN Database*).

- ***inhalation*** (rat), TC_{Lo}: 490 mg/m^3 per 4 hours (respirable aerosol) (*Carlisle MSDS*)
- ***inhalation*** (rat), LC_{50}: 370 mg as aerosol/m^3, 4,0 h of exposure (*Pagel Safety Data Sheet*)
- ***oral*** (rat), LD_{50}: >5000 mg/kg (*Carlisle MSDS*)
- ***oral*** (female rat), LD_{50}: >15000 mg/kg (*Pagel Safety Data Sheet*)

Potential Health Effects (Warnings)

- ***ingestion*** - single dose oral toxicity is considered to be extremely low. Can result in irritation and corrosive action in the mouth, stomach tissue and digestive tract (*Carlisle MSDS*)
- ***inhalation*** – irritation of upper respiratory tract and lungs, respiratory sensitization with asthma-like symptoms, pulmonary edema (with severe overexposure), allergic respiratory reactions; symptoms including coughing, dryness of throat, headache, nausea, breathing difficulty, tightness in the chest; impaired lung function has been associated with overexposure to isocyanates (*Carlisle MSDS*); persons with known respiratory or allergy problems must not be exposed to this product (*Carlisle MSDS*); in case of hypersensitivity of the respiratory tract (e.g. asthma, chronic bronchitis) it is inadvisable to work with the product (*Mehren Kjemi MSDS*); harmful by inhalation, may cause sensitization by inhalation, irritating to respiratory system (*Gestis Database*)
- ***eye*** – irritation, inflammation, damage to sensitive eye tissue; symptoms including watering or discomfort to eyes (*Carlisle MSDS*); irritating to eyes (*Gestis Database*)
- ***skin*** – irritation, reddening, dermatitis, sensitization (with prolonged or repeated exposure); allergic skin reactions (*Carlisle MSDS*); irritating to skin (*Gestis Database*); skin protection preparations do not protect sufficiently against the substance, isocyanates react with skin and cause contamination that is very hard to remove (*Gestis Database*)
- ***carcinogenicity*** – lung tumors observed in lab animals exposed to aerosol droplets of MDI/Polymeric MDI (6 mg/m3) for their lifetime. Tumors occurred concurrently with respiratory irritation and lung injury. (*Carlisle MSDS*); unclassifiable (because the data are incomplete or ambiguous) (*PAN Database*); Category 3 carcinogen: substances which possibly are carcinogenic for humans and thus give cause for concern (*Gestis Database*); classified as a Category 4 carcinogen by the German

MAK-Commission: substances which are carcinogenic with no or minor genetically toxical effects (*Gestis Database*)

- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*); classified as Pregnancy Group C, by the German MAK-Commission: there is no reason to fear risk of damage to the developing embryo or fetus when MAK or BAT values are adhered to (*Gestis Database*); MAK-value = 0,005 ppm *EPROS Safety Data Sheet; JCP MSDS*)
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*).

Ecological Toxicity

- classified as "hazardous waste" under the European Waste Catalogue Ordinance (AVV) (*Gestis Database*)
- ***decomposition*** – can polymerize vehemently in the warmth (*Gestis Database*); violent exothermic reaction, development of heat, development of hazardous gas or vapor with: water -> carbon dioxide (*Gestis Database*); isocyanates will react with water and generate carbon dioxide (*Carlisle MSDS*); hazardous decomposition products: isocyanate vapor and mist, carbon dioxide, nitrogen oxides, traces of hydrogen cyanide (*Carlisle MSDS*); reacts with water at the interface forming CO_2 and a solid insoluble product with a high melting point (polyurea). This reaction is accelerated by surfactants or by water soluble solvents (*Pagel Safety Data Sheet*).
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*); may be a hazard to drinking water sources when larger quantities get into groundwater (*Gestis Database*)
- ***aquatic ecotoxicity***
    - acute- fish LC_0 = > 1000 mg/l (*Pagel Safety Data Sheet*)
    - acute- bacteria EC_{50} = > 100 mg/l (*Pagel Safety Data Sheet*)
    - acute- daphnia EC_{50} = > 1000mg/l (*Pagel Safety Data Sheet*)

Butylated Hydroxytoluene (BHT)

synonym – 2,6-Di-tert-butyl-p-cresol
CAS Number – 128-37-0

Butylated Hydroxytoluene (BHT) is classified as irritating to the eyes, respiratory system, and skin under European classification. Allergic contact dermatitis and contact urticaria are associated with exposure to BHT (*HAZ-MAP*). It is currently listed as "unclassifiable" in regard to it's carcinogenicity in humans (due to limited human test data), however a variety of *in vitro* and animal studies have shown it to have carcinogenic, tumorigenic, mutagenic, and teratogenic effects in animals as well as in human cells (*Sigma-Aldrich MSDS*). Studies have also confirmed BHT to have estrogenic activity (*Miller et al. 2001; Wada et al. 2004*) and MSDS sheets state that chronic exposure to BHT may cause reproductive and fetal effects (*Acros MSDS*).

Following the sprayings in Monterey and Santa Cruz counties, several women reported unusual menstrual symptoms including cramping, interruption of menstrual cycle, and postmenopausal recommencement of the menstrual cycle (*HOPE 1/03/08*). A wide variety of respiratory symptoms, as well as blurred vision and eye irritation, and skin rashes were also reported (*HOPE 1/03/08*).

Class

- ***use type*** – preservative (*PAN Database*)
- ***chem class*** – phenol (*PAN Database*)

European Classification

- ***hazard symbols*** – Xn (harmful) (*EC Annex II; Chemblink data sheet*)
- ***risk phrases*** – R22 (harmful if swallowed), R36/37/38 (irritating to eyes, respiratory system, skin) (*EC Annex III*; *Chemblink data sheet*)
- ***safety phrases*** –S26 (in case of eye contact rinse w/ water, seek medical advice), S37/39 (use suitable gloves, eye/face protection) (*EC Annex IV*; *Chemblink data sheet*)

WHMIS Classification (Canada)

- has not yet been classified by the Service du repertoire toxicologique (*Science Lab MSDS*)

Toxicity

Acute toxicity – slight (*PAN Database*)

- ***acute oral*** (rat), $LD_{50:}$ 890 mg/kg (*Science Lab MSDS*)
- ***acute oral*** (mouse), $LD_{50:}$ 650 mg/kg (*Science Lab MSDS*)
- ***acute oral*** (guinea pig), $LD_{50:}$ 10700 mg/kg (*Science Lab MSDS*)

Potential Health Effects (Warnings)

- ***ingestion*** – acute symptoms include abdominal pain, confusion, dizziness, nausea, vomiting (*NIOSH - ICSC 0841*)
- ***inhalation*** – lung and respiratory tract irritant (*Science Lab MSDS*); acute symptoms include cough, sore throat (*NIOSH - ICSC 0841; PAN Database*)
- ***eye*** – irritant (*Science Lab MSDS*); redness, pain (*PAN Database*)
- ***skin*** – irritant (*Science Lab MSDS*); contact dermatitis, contact urticaria (diseases associated with exposure to this agent) (*Haz-Map.com*); redness (*PAN database*)
- ***exposure limits***
    - TWA: 10 (mg/m3) from OSHA (PEL) [United States] Inhalation
    - TWA: 10 (mg/m3) from ACGIH (TLV) [United States] Inhalation
    - TWA: 10 (mg/m3) from NIOSH [United States] Inhalation
- ***carcinogenicity*** – not classifiable for human; may cause cancer based on animal test data (*Science Lab MSDS*); unclassifiable (because the data are incomplete or ambiguous) (*PAN Database*); classified as a Category 4 carcinogen by the German MAK-Commission: substances which are carcinogenic with no or minor genetically toxical effects (*Gestis Database*)

- ***mutagenicity*** – may affect genetic material (mutagenic); mutagenic for mammalian somatic cells; mutagenic for bacteria and/or yeast (*Science Lab MSDS*); mutagenic effects have occurred in humans (*Acros MSDS*);
- ***teratogenicity*** – may cause adverse reproductive effects and birth defects (*Science Lab MSDS*)
- ***general*** – may be toxic to blood, liver, central nervous system (CNS). Repeated or prolonged exposure can produce target organs damage (*Science Lab MSDS*)
- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*); classified as Pregnancy Group C, by the German MAK-Commission: there is no reason to fear risk of damage to the developing embryo or fetus when MAK or BAT values are adhered to (*Gestis Database*); MAK-value = 0,005 ppm *EPROS Safety Data Sheet; JCP MSDS*); chronic exposure may cause reproductive and fetal effects (*Acros MSDS*)
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*); studies have shown BHT to have estrogenic activity (Miller et al. 2001).

Ecological Toxicity

- classified as a hazardous substance on California Director's List of Hazardous Substances (*Science Lab MSDS*)
- classified as hazardous by OSHA (*Science Lab MSDS*)
- harmful to aquatic organisms (*NIOSH - ICSC 0841*)
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*); may be a hazard to drinking water sources when larger quantities get into groundwater (*Gestis Database*)
- ***aquatic ecotoxicity***
    - fish – effects noted: accumulation, growth, histology, morphology, mortality (*PAN Database*)
    - mollusks – effects noted: behavior (*PAN Database*)
    - zooplankton – effects noted: growth, intoxication (*PAN Database*)

<u>Polyvinyl Alcohol (PVA)</u>
CAS Number – 9002-89-5

Polyvinyl Alcohol is currently listed as “unclassifiable” in regard to it’s carcinogenicity in humans (due to limited human test data), however animal test data has shown it to be tumorigenic (*Science Lab MSDS*). Inhalation or ingestion of PVA for a prolonged period of time may affect blood and metabolism, and behavior (*Science Lab MSDS*). Symptoms of PVA exposure include digestive tract irritation, respiratory irritation or cough, and red/irritated eyes.

Following the sprayings in Monterey and Santa Cruz counties there were numerous adverse effects reported, including nausea, diarrhea, coughing, wheezing, and eye irritation (*HOPE 1/03/08*).

Class

- ***use type*** – none listed (*PAN Database*)
- ***chem class*** – polymer (*PAN Database*)

European Classification

- ***hazard symbols*** – none listed
- ***risk phrases*** – none listed
- ***safety phrases*** –S24/25 (avoid contact with skin and eyes) (*EC Annex IV*; *Chemblink data sheet*)

WHMIS Classification (Canada)

- not controlled under WHMIS (*Science Lab MSDS*)

Toxicity

Acute toxicity – not acutely toxic (*PAN Database*)

- ***acute oral*** (mouse), LD_{50}: 14700 mg/kg (*Science Lab MSDS*)
- ***acute oral*** (rat), LD_{50}: 20000 mg/kg (*Science Lab MSDS*)

Potential Health Effects (Warnings)

- ***ingestion*** - may cause gastrointestinal (digestive) tract irritation; may affect behavior/central nervous system (symptoms may include general depressed activity, altered sleep time, muscle weakness); may also affect blood and metabolism (*Science Lab MSDS*)
- ***inhalation*** – cough (*NIOSH - ICSC 1489*); respiratory tract irritation (*Science Lab MSDS*)
- ***eye*** – redness (*NIOSH - ICSC 1489*); irritant (*Science Lab MSDS*)
- ***skin*** – irritant (*Science Lab MSDS*)
- ***carcinogenicity*** - not classifiable for human (*Science Lab MSDS*); may cause cancer (tumorigenic) based on animal studies (*Science Lab MSDS*); unclassifiable (because the data are incomplete or ambiguous) (*PAN Database*).
- ***general*** – inhalation or ingestion for prolonged periods of time may affect blood and metabolism, and behavior (*Science Lab MSDS*); animal studies showed a drop in hemoglobin and erythrocyte number with eventual complete coagulation inhibition (with chronic exposure) (*JT Baker MSDS*)
- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*).

Ecological Toxicity

- may be hazardous in the environment, special attention should be given to fish (NIOSH -*ICSC 1489*)
- ecotoxicity in water (LC_{50}):
    - bluegill -10000 mg/l 96 hours (*Science Lab MSDS*).
    - fathead minnow - >40000 mg/l 96 hours (*Science Lab MSDS*).
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*); may be a hazard to drinking water sources when larger quantities get into groundwater (*Gestis Database*)

- ***aquatic ecotoxicity***
    - fish – effects noted: mortality (*PAN Database*)

Tricapryl Methyl Ammonium Chloride
Tricaprylyl Methyl Ammonium Chloride (as reported by CDFA)
synonym – methyl trioctyl ammonium chloride
CAS Number - 5137-55-3

Tricapryl Methyl Ammonium Chloride is classified as irritating to the skin and risk of serious damage to eyes under European classification. Under Canadian classification it is listed as "material causing immediate and serious toxic effects". MSDS sheets warn that the substance is extremely hazardous in case of ingestion, inhalation, skin contact, and eye contact and that it causes severe skin and eye burns. Symptoms of inhalation exposure include irritation of the respiratory tract, burning pain in the nose and throat, coughing, wheezing, shortness of breath, and pulmonary edema. Symptoms of eye exposure include redness, watering, itching, eye burns, and possible corneal injury. Symptoms of skin exposure include inflammation characterized by itching, scaling, reddening, and occasionally blistering.

Respiratory symptoms reported following the sprayings in Monterey and Santa Cruz counties included asthma, bronchial irritation, difficulty breathing, shortness of breath, coughing and wheezing, sore throat, nasal congestion, sinus bleeding, lung soreness, lung congestion, and chest pain and tightness. Intestinal pain, diarrhea, nausea, blurred vision, eye irritation, and mild to severe skin rashes were also reported (*HOPE 1/03/08*).

Tricapryl Methyl Ammonium Chloride is classified as dangerous to the environment, and very toxic to aquatic organisms under European classification. European labeling warns against releasing the substance into the environment, cautioning that it may cause long-term adverse effects in the aquatic environment. Also known by the trade name Aliquat 336 (*Acros MSDS; de Oliveira & Bertazzoli 2007; Sigma-Aldrich MSDS*) tricapryl methyl ammonium chloride is a surfactant (*de Oliveira & Bertazzoli 2007; Gyenge & Oloman 2001*) which could change the surface tension of water and affect zooplankton (*Abraham 10/25/07*).

Following the sprayings in Monterey and Santa Cruz counties, hundreds of seabirds found dead or dying in the Monterey Bay were found to be covered with a waxy substance, which was determined by testing to be a surfactant protein. According to SIMoN (Sanctuary Integrated Monitoring Network for the Monterey Bay) surfactants act like a detergent to reduce the waterproofing ability of feathers. This same protein has also been associated with the recent red tide in the Monterey Bay (*SIMoN website*).

Class

- ***use type*** – adjuvant (used in pesticide products to increase the effectiveness of the active ingredients, make the product easier to apply, or to allow several active ingredients to mix in one solution. Solvents, emulsifiers, and spreaders fall in this category.) (*PAN Database*)
- ***chem class*** – quaternary ammonium compound (ammonium salts with four alkyl or aryl groups, typically used as microbiocides or algaecides) (*PAN Database*)

European Classification

- ***hazard symbols*** – Xn (harmful), N (dangerous for the environment) (*EC Annex II; Chemblink data sheet*)
- ***risk phrases*** – R22 (harmful if swallowed), R38 (irritating to skin), R41 (risk of serious damage to the eyes), R50/53 (very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment) (*EC Annex III; Chemblink data sheet*)
- ***safety phrases*** – S26 (in case of eye contact rinse w/ water, seek medical advice), S39 (use eye/face protection), S60 (this material and its container must be disposed of as hazardous waste), S61 (avoid release to the environment) (*EC Annex IV*; *Chemblink data sheet*)

WHMIS Classification (Canada)

- D1B: material causing immediate and serious toxic effects (TOXIC) (*Science Lab MSDS*)

Toxicity

- ***acute oral*** (rat), LD_{50} – 223 mg/kg (*Science Lab MSDS)*
- ***acute oral*** (mouse), LD_{50} – 280 mg/kg (*Science Lab MSDS)*
- no available weight-of-the-evidence summary assessment (*PAN Database*)

Potential Health Effects (Warnings)

- ***ingestion*** - extremely hazardous in case of ingestion (*Science Lab MSDS)*; harmful if swallowed; may cause severe and permanent damage to the digestive tract; causes gastrointestinal tract burns; may cause severe gastrointestinal tract irritation with nausea, vomiting and possible burns (*Acros MSDS*)
- ***inhalation*** – lung irritant, extremely hazardous in case of inhalation (*Science Lab MSDS)*; may cause respiratory tract irritation; may cause irritation of the respiratory tract with burning pain in the nose and throat, coughing, wheezing, shortness of breath and pulmonary edema; causes chemical burns to the respiratory tract (*Acros MSDS*)
- ***eye*** – extremely hazardous in case of eye contact (*Science Lab MSDS*); irritant, inflammation characterized by redness, watering, itching (*Science Lab MSDS*); risk of serious damage to eyes (*Science Lab MSDS*); causes severe eye burns (*JT Baker MSDS*); causes eye burns, may result in corneal injury (*Acros MSDS*)
- ***skin*** – irritant, extremely hazardous (corrosive, permeator); inflammation characterized by itching, scaling, reddening, occasionally blistering (*Science Lab MSDS*); causes severe skin burns (*JT Baker MSDS*);

causes skin burns; may cause severe irritation and possible burns (*Acros MSDS*)

- ***carcinogenicity***- no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*).

Ecological Toxicity

- classified as hazardous by OSHA (*Science Lab MSDS*)
- dangerous for the environment (*Sigma-Aldrich MSDS*)
- long term degradation products may arise, *products* of degradation more toxic (*Science Lab MSDS*)
- Hazardous decomposition products: carbon dioxide, carbon dioxide, oxides of nitrogen, hydrogen chloride gas (*JT Baker MSDS*)
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***aquatic ecotoxicity***
    - fish – effects noted: mortality (*PAN Database*)
    - insects – effects noted: mortality (*PAN Database*)
    - phytoplankton - effects noted: growth, physiology, population (*PAN Database*)
    - zooplankton – effects noted: intoxication, mortality (*PAN Database*)

<u>Sodium Phosphate</u>

(type of sodium phosphate not specified, PAN database lists 7 compounds with sodium phosphate in the name, could be any of the following or others)
Sodium Phosphate (Disodium Phosphate): **CAS Number** - 7558-79-4
Sodium Acid Phosphate (Monosodium Phosphate): **CAS Number** – 7558-80-7
Trisodium Phosphate (Sodium Phosphate): **CAS Number** – 7601-54-9

Sodium Phosphate (various types) -The exact type of sodium phosphate used in the Checkmate formulas is currently unspecified, and therefore it's not possible to give a precise description of potential adverse effects. However, it would be expected that the range of exposure symptoms would vary from mild to severe depending on the specific type of sodium phosphate used in the formula. Symptoms of exposure to the various kinds of sodium phosphate would range from mild to severe gastrointestinal effects (varying degrees of gastrointestinal irritation, abdominal pain/cramping, vomiting, diarrhea, nausea, abdominal discomfort, burning sensation), mild to severe respiratory symptoms (throat irritation, respiratory tract/mucous membrane irritation, coughing, sneezing, choking, difficulty breathing, pulmonary edema), mild to severe effects on the eye (irritation, redness, pain, conjunctival edema and corneal clouding [later cataract formation could occur], eye burns), and mild to severe skin symptoms (skin/mucous membrane irritation, dermatitis, local skin destruction, burning pain,

skin burns, blisters), depending on the specific type of sodium phosphate to which an individual was exposed.

Sodium Phosphate is a pH buffer, which could lead to algal blooms if runoff concentrations are high enough (*Abraham 10/25/07*). Increased phosphate levels are known to be a contributing factor in the occurrence of red tides (*Feyzioglu & Ogut 2006*; *Wikipedia*).

Following the sprayings in Monterey and Santa Cruz counties, a harmful algal bloom (red tide) described by a water specialist with the Santa Cruz County Environmental Health Services as "one of the more dramatic ones in recent memory", hit the Monterey Bay (*Ragan 11/13/07*).

Class

- ***use type*** (same for all three) – pH adjustment, fungicide, herbicide, microbiocide (*PAN Database*)
- ***chem class*** (same for all three) – inorganic (any chemical compound not containing hydrocarbon moieties *and* not one of the toxic metals) (*PAN Database*)

European Classification

- ***hazard symbols***
    - SP: none listed
    - SAP: none listed
    - TSP: Xi (irritant) (*EC Annex II; Gestis Database*); C (corrosive) (*EC Annex II; Chemblink data sheet*)
- ***risk phrases***
    - SP: none listed
    - SAP: none listed
    - TSP: R36/37/38 (irritating to eyes, respiratory system, skin) (*EC Annex III*; *Gestis Database*); R34 (causes burns) (*EC Annex III*; *Chemblink data sheet*)
- ***safety phrases***
    - SP: none listed
    - SAP: none listed
    - TSP: S26 (in case of eye contact rinse w/ water, seek medical advice) (*EC Annex IV*; *Gestis Database*); S36/37/39 (use suitable protective clothing, gloves and eye/face protection); S45 (in case of accident or illness, seek medical advice immediately) (*EC Annex IV*; *Chemblink data sheet*)

WHMIS Classification (Canada)

- SP: not controlled under WHMIS (*Science Lab MSDS*)
- SAP: not controlled under WHMIS (*Science Lab MSDS*)
- TSP: E: corrosive material (*Science Lab MSDS; CSST data sheet*)

Toxicity

- SP: slight (*PAN Database*)
    - ***acute oral*** (rat), LD_{50}: 17000 mg/kg (*Science Lab MSDS*)

- SAP: no available weight-of-the-evidence summary assessment (*PAN Database*)
    - ***acute oral*** (rat), LD_{50}: 8290 mg/kg (*Science Lab MSDS*)
- TSP: no available weight-of-the-evidence summary assessment (*PAN Database*)
    - ***acute oral*** (rat), LD_{50}: 4150 mg/kg (*Science Lab MSDS*)
    - ***acute dermal*** (rabbit), LD_{50}: 300 mg/kg (*Science Lab MSDS*)

Potential Health Effects (Warnings)

- ***ingestion***
    - SP: may cause irritation of the digestive tract and may cause purging. It is slowly absorbed. Expected to be a low ingestion hazard for usual industrial handling. Ingestion of large doses may affect behavior/central nervous system. If a significant amount of phosphate is absorbed, hypophosphatemia will occur. (*Science Lab MSDS*)
    - SAP: considered a low hazard for usual industrial handling and systemic reactions are unlikely when ingested (because they are slowly and incompletely absorbed in the intestinal tract). The most frequently seen effect is gastrointestinal irritation with abdominal pain and cramping, vomiting, diarrhea. If a significant amount of phosphate is absorbed, the following may occur: mineral imbalance in the body, adversely affecting the osmotic pressure of body fluids resulting in hyperphosphatemia, hypocalcemia, hypomagnesemia. The estimated fatal dose is 50 grams (*Science Lab MSDS*)
    - TSP: may be harmful if swallowed. May cause severe gastrointestinal (digestive) tract irritation with severe nausea, vomiting, abdominal discomfort, violent purging, diarrhea, and burning sensation. Ingestion of large amounts may induce hypocalcemia or hyponatremia characterized by tetanus-like spasms, due to the sequestration of calcium ions by the phosphate moiety. It may also cause caustic burns of the mouth oropharnyx, esophagus, or gastrointestinal tract
- ***inhalation***
    - SP: throat irritation(*PAN Database*)
    - SAP: none listed (*PAN Database*); dust may cause respiratory tract irritation and may affect respiration (*Science Lab MSDS*)
    - TSP: extremely hazardous in case of inhalation (lung corrosive) (*Science Lab MSDS*); repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage (*Science Lab MSDS*); may be harmful if inhaled; inhalation of dust may cause respiratory tract and mucous membrane irritation with coughing, sneezing, choking, difficulty breathing, and pulmonary edema (*Science Lab MSDS*); burning sensation, cough, shortness of breath, sore throat (*PAN Database*)
- ***eye***

    - SP: eye contact with concentrated alkali causes conjuctival edema and cornea destruction (*PAN Database*)
    - SAP: none listed (*PAN Database*); dust may cause eye irritation (*Science Lab MSDS*)
    - TSP: extremely hazardous in case of eye contact (corrosive) (*Science Lab MSDS*); repeated exposure of the eyes to a low level of dust can produce eye irritation (*Science Lab MSDS*); causes eye irritation; causes immediate and severe pain followed by conjunctival edema and corneal clouding; later cataract formation may occur; may cause eye burns (*Science Lab MSDS*); redness, pain, severe deep burns (*PAN Database*)
- ***skin***
    - SP: skin and mucous membrane irritation (*PAN Database*); causes mild skin irritation, may cause dermatitis (*Science Lab MSDS*)
    - SAP: none listed (*PAN Database*); may cause skin irritation (*Science Lab MSDS*)
    - TSP: extremely hazardous in case of skin contact (corrosive) (*Science Lab MSDS*); repeated skin exposure can produce local skin destruction, or dermatitis (*Science Lab MSDS*); causes skin irritation with possible burning pain and corrosive damage. may be absorbed through the skin (*Science Lab MSDS*); skin burns, pain, blisters (*PAN Database*)
- ***exposure limits***
    - SP: not available (*Science Lab MSDS*)
    - SAP: not available (*Science Lab MSDS*)
    - TSP:
        - TWA: 15 (mg/m3) from OSHA (PEL) (inhalation, total) (*Science Lab MSDS*)
        - TWA: 5 (mg/m3) from OSHA (PEL) (inhalation, respirable) (*Science Lab MSDS*)
        - TWA: 5 STEL: 5 (mg/m3) from AIHA Inhalation. Consult local authorities for acceptable exposure limits (*Science Lab MSDS*)
- ***carcinogenicity*** (same for all three) - no available weight-of-the-evidence summary assessment (*PAN Database*)
- ***mutagenicity*** –
    - TSP: may affect genetic material (*Science Lab MSDS*)
- ***developmental or reproductive toxin*** (same for all three) - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** (same for all three) - no available weight-of-the-evidence summary assessment (*PAN Database*)

Ecological Toxicity

- SP: classified as a hazardous substance on California Director's List of Hazardous Substances & CERCLA (*Science Lab MSDS*)
- SAP: none listed (*Science Lab MSDS*)

- TSP: classified as “hazardous waste” under the European Waste Catalogue Ordinance (AVV) (*Gestis Database*); classified as a hazardous substance on California Director's List of Hazardous Substances, CERCLA, & OSHA (*Science Lab MSDS*)
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*); may be a hazard to drinking water sources when larger quantities get into groundwater (*Gestis Database*)
- ***aquatic ecotoxicity***
    - bluegill sunfish
        - TSP: LC_{50}: 220 mg/l 96 hours (*Science Lab MSDS*)
    - rainbow trout
        - TSP: LC_{50}: 120 mg/l 96 hours (*Science Lab MSDS*)
    - daphnia
        - TSP: LC_{50}: 177 mg/l50 hours (*Science Lab MSDS*)
    - crustaceans – effects noted:
        - SP: none listed (*PAN Database*)
        - SAP: mortality (*PAN Database*)
        - TSP: none listed (*PAN Database*)
    - fish – effects noted:
        - SP: biochemistry, feeding behavior, growth, mortality (*PAN Database*)
        - SAP: biochemistry, feeding behavior, growth, mortality (*PAN Database*)
        - TSP: mortality (*PAN Database*)
    - mollusks – effects noted
        - SP: none listed (*PAN Database*)
        - SAP: development, mortality, physiology (*PAN Database*)
        - TSP: none listed (*PAN Database*)
    - phytoplankton - effects noted:
        - SP: biochemistry, population (*PAN Database*)
        - SAP: biochemistry, population (*PAN Database*)
        - TSP: biochemistry, population (*PAN Database*)
    - zooplankton – effects noted: (*PAN Database*)
        - SP: intoxication, mortality (*PAN Database*)
        - SAP: intoxication (*PAN Database*)
        - TSP: intoxication (*PAN Database*)
- increased phosphate levels are known to be a contributing factor in the occurrence of red tides (*Feyzioglu & Ogut 2006*; *Wikipedia*)

<u>Ammonium Phosphate</u>
(type of ammonium phosphate not specified, could be either of the following)
Monoammonium Phosphate: **CAS Number** – 7722-76-1
Diammonium Phosphate: **CAS Number** – 7783-28-0

Ammonium Phosphate - The exact type of ammonium phosphate used in the Checkmate formulas is currently unspecified, and could be either *monoammonium phosphate* or *diammonium phosphate*. *Monoammonium* is not listed under European classification however *diammonium* is classified as irritating to the eyes, respiratory system, & skin.

Symptoms of inhalation exposure include:
- *monoammonium* - mild respiratory tract irritation, nausea, vomiting (after inhalation of high concentrations of dust), coughing, shortness of breath
- *diammonium* - toxic to lungs and mucous membranes; irritation to the respiratory tract, coughing, shortness of breath

Symptoms of eye exposure include:
- *monoammonium* - mild irritation, redness, pain
- *diammonium* - inflammation characterized by redness, watering, itching, pain

Symptoms of skin exposure include:
- *monoammonium* - irritation, redness, itching, pain
- *diammonium* - hazardous in case of skin contact; irritation, redness, itching, and pain

Following the sprayings in Monterey and Santa Cruz counties there were numerous reports of respiratory symptoms including asthma, bronchial irritation, difficulty breathing, shortness of breath, coughing and wheezing, lung congestion/soreness, and chest pain/tightness. Nausea, blurred vision, eye irritation, and skin rashes were also reported (*HOPE 1/03/08*).

Ammonium Phosphate is a pH buffer, which could lead to algal blooms if runoff concentrations are high enough (*Abraham 10/25/07*). Increased phosphate levels are known to be a contributing factor in the occurrence of red tides (*Feyzioglu & Ogut 2006*; *Wikipedia*). Ammonium phosphate has also been implicated in fish die-offs, including one that killed 20,000 fish following the accidental dropping of an ammonium phosphate based fire retardant in an Oregon river (*Barnard 2007*).

Following the sprayings in Monterey and Santa Cruz counties, a harmful algal bloom (red tide) described by a water specialist with the Santa Cruz County Environmental Health Services as “one of the more dramatic ones in recent memory”, hit the Monterey Bay (*Ragan 11/13/07*).

Class
- ***use type*** –
  - Mono: not listed (*PAN Database*)
  - Di: fungicide, herbicide, insecticide, microbiocide, pH adjustment (*PAN Database*)
- ***chem class*** –

    - Mono: inorganic (any chemical compound not containing hydrocarbon moieties *and* not one of the toxic metals) (*PAN Database*)
    - Di: inorganic (any chemical compound not containing hydrocarbon moieties *and* not one of the toxic metals) (*PAN Database*)

European Classification

- ***hazard symbols***
    - Mono: none listed (*EC Annex II; Chemblink data sheet*)
    - Di: : Xi (irritant) (*EC Annex II; Chemblink data sheet*)
- ***risk phrases***
    - Mono: none listed (*EC Annex III*; *Chemblink data sheet*)
    - Di: R36/37/38 (irritating to eyes, respiratory system and skin) (*EC Annex III*; *Chemblink data sheet*)
- ***safety phrases***
    - Mono: S24/25 (avoid contact with skin and eyes) (*EC Annex IV*; *Chemblink data sheet*)
    - Di: S26 (in case of eye contact rinse w/ water, seek medical advice), S36 (use suitable protective clothing) (*EC Annex IV*; *Chemblink data sheet*)

WHMIS Classification (Canada)

- Mono: not controlled under WHMIS (*Science Lab MSDS*)
- Di: D2A: material causing other toxic effects (VERY TOXIC) (*Science Lab MSDS*)

Toxicity

Acute toxicity –

- Mono: no available weight-of-the-evidence summary assessment (*PAN Database*)
- Di: no available weight-of-the-evidence summary assessment (*PAN Database*)

Acute oral toxicity LD_{50}

- Mono: not available (*Science Lab MSDS*)
- Di: ***acute oral*** (rat), LD_{50} – 3000 mg/kg (*Science Lab MSDS*)

Potential Health Effects (Warnings)

- ***ingestion***
    - Mono: may cause gastrointestinal tract irritation with abdominal cramps, nausea, vomiting and diarrhea if large amounts are ingested (*Science Lab MSDS*)
    - Di: hazardous in case of ingestion (*Science Lab MSDS*); causes irritation to the gastrointestinal tract; symptoms may include nausea, vomiting and diarrhea (*Vinquiry MSDS*)
- ***inhalation***
    - Mono: mild respiratory tract irritation (irritation of the mucosa of nose and throat), nausea, vomiting (after inhalation of high concentrations of dust) (*Science Lab MSDS*); causes irritation to the respiratory tract, symptoms may include coughing, shortness of breath (*JT Baker MSDS*)

    - Di: toxic to lungs, mucous membranes (*Science Lab MSDS*); causes irritation to the respiratory tract; symptoms may include coughing, shortness of breath (*Vinquiry MSDS*)
- ***eye***
    - Mono: mild eye irritation (*Science Lab MSDS*); causes irritation, redness, and pain (*JT Baker MSDS*)
    - Di: very hazardous in case of eye contact (irritant); inflammation of the eye is characterized by redness, watering, and itching. (*Science Lab MSDS*); DSCL (EEC), R41 – risk of serious damage to eyes (*Science Lab MSDS*); redness, pain (*NIOSH - ICSC 0217; PAN Database*); causes irritation, redness, and pain (*Vinquiry MSDS*)
- ***skin***
    - Mono: skin irritation (*Science Lab MSDS*); causes irritation to skin, symptoms include redness, itching and pain (*JT Baker MSDS*)
    - Di: hazardous in case of skin contact (irritant); permeator (*Science Lab MSDS*); causes irritation to skin; symptoms include redness, itching, and pain (*Vinquiry MSDS*)
- ***carcinogenicity*** (same for both) - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***developmental or reproductive toxin*** (same for both) - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** (same for both) - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***general***
    - Di: repeated or prolonged exposure can produce target organ damage (*Science Lab MSDS*); cause damage to lungs, mucous membranes (*Science Lab MSDS*)
    - Di: a nuisance causing concentration of airborne particles can be quickly reached when dispersed, especially if powdered (*NIOSH - ICSC 0217*)

Ecological Toxicity

- Mono: classified as hazardous by OSHA (*Science Lab MSDS*)
- Di: classified as hazardous by OSHA; long term degradation products may arise, *products* of degradation more toxic (*Science Lab MSDS*)
- ***aquatic ecotoxocity***:
    - Mono:
        - none listed (*PAN Database*)
    - Di:
        - fish – effects noted: biochemistry, cells, enzymes, feeding behavior, mortality (*PAN Database*)
- ***ground water contaminant*** (same for both) - no available weight-of-the-evidence summary assessment (*PAN Database*); may be a hazard to drinking water sources when larger quantities get into groundwater (*Gestis Database*)

1,2-benzisothiazolin-3-one
1,2-benzisothiozoli-3-one (as reported by CDFA)
synonym – BIT (trade name)
CAS Number -2634-33-5

1,2-benzisothiazolin-3-one is a preservative associated with occupational asthma. Multiple accounts of occupational dermatitis have also been reported with exposure to the chemical.
Under European classification it is classified as irritating to the skin and risk of serious eye damage. Canadian classification lists it as causing skin sensitization in humans. BIT is a known irritant at the 1% level, and studies have confirmed the irritant effect even down to the 0.1% level. Individuals with chronic pulmonary or asthmatic conditions or chronic skin conditions are warned to avoid repetitive exposure to the chemical. According to data compiled by OSHA it has been shown to cause genetic damage in human cells. Symptoms of exposure include respiratory tract and mucous membrane irritation, severe eye irritation, skin irritation, and dermatitis.

Following the sprayings in Monterey and Santa Cruz counties a wide variety of mild to serious respiratory symptoms, as well as eye irritation and skin rashes were reported (*HOPE 1/03/08*).

1,2-benzisothiazolin-3-one is classified as dangerous to the environment and very toxic to aquatic organisms under European classification. European labeling warns against releasing the substance into the environment. It is classified as "hazardous waste" under the European Waste Catalogue Ordinance. It is classified as a "hazard to waters" under the European Administrative Regulation of Substances Hazardous to Water, and MSDS sheets for the chemical warn that water polluted with the substance should not be discharged into sewage or natural areas. EPA documents on the chemical state that it is highly toxic to green algae and other invertebrate species. The EPA also states that if it is used outdoors, BIT may possibly move with soil during rainfall events and potentially reach surface waters. The Santa Cruz county sprayings on November 8th & 9th were followed by a significant rainfall event on November 10th & 11th (*Weather Underground website*).

Class
- ***use type*** – microbiocide (kills microbes such as bacteria, viruses, and fungi and used in disinfectant or antibacterial products) (*PAN Database*)
- ***chem class*** – isothiazolone (*PAN Database*)

European Classification
- ***hazard symbols*** – Xn (harmful), Xi (irritant), N (dangerous for the environment) (*EC Annex II; Gestis Database*)
- ***risk phrases*** – R22 (harmful if swallowed), R38 (irritating to skin), R41 (risk of serious eye damage), R43 (skin sensitization), R50 (very toxic to aquatic organisms) (*EC Annex III*; *Gestis Database*)

- ***safety phrases*** – S(2) (keep out of reach of children), S24 (avoid skin contact), S26 (in case of eye contact rinse w/ water, seek medical advice), S37/39 (use gloves, eye, face protection), S61 (avoid release into the environment) (*EC Annex IV*; *Gestis Database*)

WHMIS Classification (Canada)

- D2B: toxic material causing other toxic effects - skin sensitization in humans (*CSST data sheet*)

Toxicity

Acute toxicity - no available weight-of-the-evidence summary assessment (*PAN Database*).

- ***acute oral*** (male rat), LD_{50}: 2.1 mg/kg w/ 95% confidence limits of 5.029 mg/kg (upper) and 877 mg/kg (lower) (*SCCNFP 2004*)
- ***acute dermal*** (rat), LD_{50}: > 5000 mg/kg (*SCCNFP 2004*)
- ***acute inhalation***: no data (*SCCNFP 2004*)
- ***repeated dose oral*** (rat): NOAEL = 15 mg/kg/day bw (12.63 mg a.i./kg/day) (*SCCNFP 2004*)
- ***repeated dose dermal***: no data (*SCCNFP 2004*)
- ***repeated dose inhalation***: no data (*SCCNFP 2004*)
- ***sub-chronic oral*** (rat): NOAEL = 10 mg/kg/day bw (8.42 mg a.i./kg/day) (*SCCNFP 2004*)
- ***sub-chronic dermal***: no data (*SCCNFP 2004*)
- ***sub-chronic inhalation***: no data (*SCCNFP 2004*)
- ***chronic toxicity***: no data (*SCCNFP 2004*)
- ***skin irritation*** (rabbit): well-defined moderate erythema and edema noted at all treated sites. Conclusion: moderately skin irritating (*SCCNFP 2004*)
- ***mucous membrane irritation*** (rabbit) : all treated eyes exhibited severe to maximal irritation including corneal opacity, iritis and conjunctivitis. Overall severity of irritation increased with time. Due to irreversible nature of the irritation, test was terminated after 48 hrs. Conclusion: severely irritating to the rabbit eye (*SCCNFP 2004*)
- ***cytotoxicity*** (mammalian cell lines): BIT (benzisothiazolinone) is less cytotoxic than CIT/MIT (chloromethylisothiazolinone/methylisothiazolinone), but more cytotoxic than other commonly used preservatives (parabens etc.) (*SCCNFP 2004*)
- ***dermal sensitization*** (guinea pigs): BIT is a moderate contact sensitizer (*SCCNFP 2004*)
- ***mutagenicity/genotoxicity*** **in vitro**(bacterial reverse mutation assay):
    - ***toxicity*** – in a preliminary study with a series of concentrations up to 5000 µg/plate, there was a decrease in the mean number of revertants from the concentrations up to 160 µg/plate(*SCCNFP 2004*)
    - this study could not be used for evaluation due to the high toxicity of the test item towards the bacterial cells (*SCCNFP 2004*)
- ***mutagenicity/genotoxicity*** **in vitro** (mammalian cell gene mutation test):

    - ***toxicity*** - in the presence of metabolic activation a toxic effect produced by the test item between 4 and 6 µg/ml was observed; in the absence of metabolic activation a toxic effect produced by the test item was observed between 2 and 4 µg/ml. The toxic doses reduced the survival to less than 50% of the untreated cells (*SCCNFP 2004*)
- ***mutagenicity/genotoxicity*** **in vitro** (mammalian chromosome aberration test):
    - ***toxicity*** – the test item was toxic at concentrations between 75 and 5000 µg/ml and between 14 and 58.94 µg/ml (*SCCNFP 2004*)
    - ***clastogenicity*** – the test item induced chromosome aberrations at the maximum tested dose in the presence of a metabolic activation, and at all concentrations in the absence of a metabolic activation system. The test item is clastogenic on CHO mammalian cells. (*SCCNFP 2004*)
- ***mutagenicity/genotoxicity*** **in vivo** (mammalian erythrocyte micronucleus test):
    - ***toxicity*** – a 250 mg/kg dose was found not toxic, while 450 and 900 mg/kg doses were toxic (*SCCNFP 2004*)
    - ***clastogenicity*** – the test item is not clastogenic in mice treated in vivo (*SCCNFP 2004*)
- ***mutagenicity/genotoxicity*** **in vivo** (unscheduled DNA synthesis (UDS) test with mammalian liver cells in vivo):
    - ***toxicity*** – doses of 1200 and 100 mg a.i./kg bw were found toxic to the animals (*SCCNFP 2004*)
    - ***DNA repair*** – the test item did not induce UDS in rat hepatocytes in *in vivo* treatment (*SCCNFP 2004*)

Potential Health Effects (Warnings)

- ***ingestion*** – harmful if swallowed (*Gestis Database; Sigma-Aldrich MSDS*)
- ***inhalation*** – none listed (*PAN Database*); occupational asthma reported (*Moscato et al.1997*); people with chronic pulmonary or asthmatic conditions should be prevented from repetitive exposure to the chemical (*INRS 2002*); may be harmful if inhaled; material may be irritating to mucous membranes and upper respiratory tract (*Sigma-Aldrich MSDS*)
- ***eye*** – none listed (*PAN Database*); risk of serious damage to eyes (*Gestis Database*); causes severe eye irritation (*Sigma-Aldrich MSDS*)
- ***skin*** – multiple accounts of occupational allergic contact dermatitis reported (*Damstra et al. 1992*; *Muhn & Sasseville 2003; Roberts et al. 1981; Taran & Delaney 1997; etc*.). BIT (synonym for 1,2-benzisothiazolin-3-one) is a known irritant at the 1% level, and test results confirm the irritation reaction all the way down to the 0.1% level (*Chew & Maibach 1997*; *Muhn & Sasseville 2003*); irritating to skin (*Gestis Database*); may cause sensitization by skin contact (*Gestis Database*); people with chronic skin conditions should be prevented from repetitive exposure to the chemical (*INRS 2002*); skin patch tests confirm a cause/effect link between exposure to the chemical and contact dermatitis (eczema) (*INRS*

2002); causes skin irritation (*Sigma-Aldrich MSDS*); may be harmful if absorbed through the skin (*Sigma-Aldrich MSDS*); may cause allergic skin reaction (*Sigma-Aldrich MSDS*)

- ***carcinogenicity*** - no available weight-of-the-evidence summary assessment (*PAN Database*)
- ***genotoxicity*** – shown to cause genetic damage in human cells, according to data compiled by OSHA (*Cox 2005*); see toxicity section above for specific studies
- ***mutagenicity*** – see toxicity section above for specific studies
- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*).

Ecological Toxicity

- classified as “dangerous for the environment” under European labeling (*Gestis Database*)
- classified as “hazardous waste” under the European Waste Catalogue Ordinance (AVV) (*Gestis Database*)
- may be a hazard to the surrounding atmosphere at larger quantities (*Gestis Database*)
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*); avoid escape into water, drainage, sewer, or ground (*Gestis Database*); hazard for drinking water sources when larger quantities get into groundwater (*Gestis Database*); water polluted with this chemical should not be discharged into sewage or natural areas (*INRS 2002*); classified as WGK 2 “hazard to waters” under the European Administrative Regulation of Substances Hazardous to Water (VwVwS) (*Gestis Database*)
- ***aquatic ecotoxicity***
    - very toxic to aquatic organisms (*Gestis Database*)
    - fish – effects noted: mortality (*PAN Database*)
    - mollusks – effects noted: intoxication (*PAN Database*)
    - zooplankton – effects noted: intoxication, mortality, reproduction (*PAN Database*)
- BIT is known to have strong antimicrobial activity even at low concentrations (*Muhn & Sasseville 2003*).
- according to the EPA reregistration document for this chemical:
    - the high toxicity of BIT to green algae and invertebrate species suggests that potential adverse acute effects could occur to some species if environmental contamination from BIT-treated oil recovery fluids occurs (*EPA 2005)*
    - birds & mammals – low to moderate toxicity (*EPA 2005*)
    - freshwater fish & invertebrates – moderate toxicity (*EPA 2005*)
    - marine/estuarine fish – slight toxicity (*EPA 2005*)
    - marine/estuarine invertebrates – high toxicity (*EPA 2005*)

- o if used outdoors, BIT may possibly move with soil during rainfall events and potentially reach surface waters (*EPA 2005*)

2-hydroxy-4-n-octyl benzophenone

2-hydroxy-4-n-octyloxybenzophenone (as reported by CDFA)
synonym – benzophenone 12
CAS Number – 1843-05-6

2-hydroxy-4-n-octyl benzophenone is a UV light absorber of unknown health impact, however related compounds in the benzophenone family have been shown to form estrogenic photoproducts, upon exposure to UV or sunlight (*Hayashi et al. 2006*). Under European classification it is classified as irritant, as may cause sensitization by skin contact, and as irritating to eyes, respiratory system and skin. Symptoms of exposure include reddening and irritation of the skin and eyes, mucous membrane irritation, and upper respiratory tract irritation.

Following the sprayings in Monterey and Santa Cruz counties, several women reported unusual menstrual symptoms including cramping, interruption of menstrual cycle, and postmenopausal recommencement of the menstrual cycle (*HOPE 1/03/08*), which would be consistent with exposure to endocrine disrupting/estrogenic compounds. A wide variety of mild to serious respiratory symptoms, as well as eye irritation and skin rashes were also reported.

2-hydroxy-4-n-octyl benzophenone is classified as harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment, under European classification. European labeling warns against releasing the substance into the environment. It is classified as hazardous by OSHA.

Class

- ***use type*** – not listed (*PAN Database*); polymer stabilizer (*Chemtura MSDS*); light absorber (*Cytec MSDS*)
- ***chem class*** – unclassified (*PAN Database*)

European Classification

- ***hazard symbols*** – Xi (irritant) (*EC Annex II; Great Lakes safety data sheet; Chemblink data sheet*)
- ***risk phrases*** – R-43 (may cause sensitization by skin contact), R-52/53 harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment (*EC Annex III*; *Great Lakes safety data sheet*); R36/37/38 (irritating to eyes, respiratory system and skin) (*EC Annex III*; *Chemblink data sheet*)
- ***safety phrases*** – S24 (avoid skin contact), S61 (avoid release into the environment) (*EC Annex IV*; *Great Lakes safety data sheet*); S26 (in case of eye contact rinse w/ water, seek medical advice), S36 (use suitable protective clothing) (*EC Annex IV*; *Chemblink data sheet*)

Canadian WHMIS Classification

- D2B (toxic materials) (*Ferro MSDS*)

Toxicity

Acute toxicity - no available weight-of-the-evidence summary assessment (*PAN Database*).

- ***acute oral*** (rat), LD_{50}: > 10.0 g/kg (*Cytec MSDS*)
- ***acute dermal*** (rabbit), LD_{50}: > 10.0 g/kg (*Cytec MSDS*)
- ***4-hour LC_{50} value*** (rat): estimated to be greater than 20 mg/L (*Cytec MSDS*)

Mammalian toxicity

- acute toxicity
  - rats > 10 g/kg (*Cytec/Ciba 2001*)
- repeated dose toxicity
  - rat 90-day dietary: NOEL = 0.6% (6000 ppm) (*Cytec/Ciba 2001*)
  - dog 120-day dietary: NOEL = 0.6% (6000 ppm) (*Cytec/Ciba 2001*)
  - rat 90-day dietary: NOEL = 0.15% (1500 ppm) (*Cytec/Ciba 2001*)
  - rats 90-day dietary: NOEL = 1000 ppm (*Cytec/Ciba 2001*)
- reproductive/developmental toxicity
  - rats NOEL = 0.6% (6000 ppm) for 4 successive generations (*Cytec/Ciba 2001*)
- skin sensitization (guinea pigs) - strong sensitizer in maximization test, with 60-78% positive for animals sensitized (*NPA MSDS*)

Potential Health Effects (Warnings)

- ***ingestion*** - may irritate digestive tract (*Ferro MSDS*)
- ***inhalation*** - over-exposure by inhalation may cause respiratory irritation (*Ferro MSDS*); mucous membrane and upper respiratory tract irritation (*Chemtura MSDS*)
- ***eye*** – none listed (*PAN Database*); may cause slight irritation (*Ferro MSDS*); reddening and irritation to eyes; may cause allergic skin reaction (*Chemtura MSDS*)
- ***skin*** - none listed (*PAN Database*); may cause sensitization by skin contact (*Great Lakes safety data sheet*); prolonged skin contact may cause skin irritation and/or dermatitis, may cause allergic skin reaction (*Ferro MSDS*); reddening and irritation to skin (*Chemtura MSDS*)
- ***exposure limits***
  - TWA: 15 (mg/m3) from OSHA (PEL) (*Chemtura MSDS*)
  - TWA: 10 (mg/m3) from ACGIH (TLV) (*Chemtura MSDS*)
- ***respirable dust level***
  - 5 mg/m3 (OSHA) (*Chemtura MSDS*)
  - 3 mg/m3 (ACGIH) (*Chemtura MSDS*)
- ***carcinogenicity*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***developmental or reproductive toxin*** - no available weight-of-the-evidence summary assessment (*PAN Database*).
- ***endocrine disruptor*** - no available weight-of-the-evidence summary assessment (*PAN Database*); compounds in the benzophenone family

have been shown to form estrogenic photoproducts, upon exposure to UV or sunlight (*Hayashi et al. 2006*)

- ***chronic toxicity*** - kidney injury may occur (*Ferro MSDS*)

Ecological Toxicity

- classified as hazardous by OSHA (*NPA MSDS*)
- harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment (*Great Lakes safety data sheet*);
- not readily biodegradable (*Great Lakes safety data sheet*)
- ***ground water contaminant*** - no available weight-of-the-evidence summary assessment (*PAN Database*)
- ***aquatic ecotoxicity***
    - zebra fish – LC_{50} (96 h) > 100mg/L (*Cytec/Ciba 2001*)
    - green algae – EC_{50} (0-72 h) > 100 mg/L (*Cytec/Ciba 2001*)
    - *Daphne magna*
        - EC_0 (24 h) > 10 mg/L (*Cytec/Ciba 2001*)
        - EC_{50} (24 h) > 52 mg/L (*Cytec/Ciba 2001*)
    - *Scenedesmus subspicatus* - EC_{50} (72 Hr) >100 mg/L (*Ferro MSDS*)
    - *Brachydanio rerio* - LC_{50} (96 Hr) >100 mg/L (*Ferro MSDS*)

References

Abraham K. 10/18/07. **Disclosure of moth pheromone product's inert ingredients incite a legal battle**. Monterey County Weekly website (accessed 1/11/08). http://www.montereycountyweekly.com/archives/2007/2007-Oct-18/Article.news_2/1/@@index

Abraham K. 10/25/07. **Spray what? ingredients in Checkmate LBAM-F.** Monterey County Weekly website (accessed 1/11/08). http://www.montereycountyweekly.com/archives/2007/2007-Oct-25/Article.news_1/2

Acros Organics. **Aliquat 336 MSDS**. (Tricaprylylmethylammonium chloride). Iowa State University Department of Chemistry website (accessed 1/28/08) http://avogadro.chem.iastate.edu/MSDS/aliquat_336.htm

Acros Organics. **Butylated Hydroxytoluene (BHT) MSDS**. (accessed 1/23/08) https://fscimage.fishersci.com/msds/96012.htm

Allsopp M, Walters A, Santillo D. 2005. **Factsheets on uses and hazards of chemical ingredients of Sanitized® preparations** [p 14 Factsheet on 1,2-Benzisothiazolin-3-one (BIT)]. Greenpeace Research Laboratories, Department of Biological Sciences. Greenpeace website (accessed 1/15/08). http://www.greenpeace.to/publications/sanitized_2005.pdf

Ayadi M, Martin P. 1999. **Pulpitis of the fingers from a shoe glue containing 1,2-benzisothiazolin-3-one (BIT)**. *Contact Dermatitis* 40:115–116.

Barnard J. 8/20/07. **Judge: Bush official faces contempt.** USA Today website (accessed 1/11/08). http://www.usatoday.com/news/nation/2007-08-20-1106556120_x.htm

Carlisle SynTec Incorporated. **Polymethylene Polyphenyl Isocyanate MSDS**. Carlisle SynTec website (accessed 1/14/08). http://www.carlisle-syntec.com/documents/reslib/CarlisleOlybond500BAPartA.pdf

CCOHS (Canadian Centre for Occupational Health & Safety)
http://ccinfoweb.ccohs.ca/whmis/search.html
Polymethylene Polyphenyl Isocyanate (accessed 1/23/08)
http://ccinfoweb2.ccohs.ca/whmis/Action.lasso?-database=cheminfo&-layout=Display&-response=detail.html&-op=eq&CHEMINFO+RECORD+NUMBER=80E&-search
Sodium Phosphate (Disodium Phosphate) (accessed 1/23/08)
http://ccinfoweb2.ccohs.ca/whmis/Action.lasso?-database=cheminfo&-layout=Display&-response=detail.html&-op=eq&CHEMINFO+RECORD+NUMBER=124E&-search
Sodium Acid Phosphate (Monosodium Phosphate) (accessed 1/23/08)
http://ccinfoweb2.ccohs.ca/whmis/Action.lasso?-database=cheminfo&-layout=Display&-response=detail.html&-op=eq&CHEMINFO+RECORD+NUMBER=101E&-search
Trisodium Phosphate (accessed 1/23/08)
http://ccinfoweb2.ccohs.ca/whmis/Action.lasso?-database=cheminfo&-layout=Display&-response=detail.html&-op=eq&CHEMINFO+RECORD+NUMBER=102E&-search
Monoammonium Phosphate
http://ccinfoweb2.ccohs.ca/whmis/Action.lasso?-database=cheminfo&-layout=Display&-response=detail.html&-op=eq&CHEMINFO+RECORD+NUMBER=128E&-search
Diammonium Phosphate
http://ccinfoweb2.ccohs.ca/whmis/Action.lasso?-database=cheminfo&-layout=Display&-response=detail.html&-op=eq&CHEMINFO+RECORD+NUMBER=127E&-search

CDFA. 2007. **Light brown apple moth (LBAM) questions and answers**. CDFA website (accessed 1/31/08)
http://www.cdfa.ca.gov/phpps/PDEP/lbam/pdfs/archives/ARCHIVE_LBAM_QandA_English_11_02_07.pdf

Cempa J. 2000. **Sea lions dying in record numbers in South County**. The Plankton Net (p 8). University of Maine website (accessed 1/14/08).
http://www.umaine.edu/umext/ssteward/PDF%20files/summer2000.pdf

Chemblink http://www.chemblink.com/index.htm
Butylated Hydroxytoluene data sheet. Chemblink website (accessed 1/22/08) http://www.chemblink.com/products/128-37-0.htm
Polyvinyl Alcohol data sheet. Chemblink website (accessed 1/22/08) http://www.chemblink.com/products/9002-89-5.htm
Tricapryl Methyl Ammonium Chloride data sheet. Chemblink website (accessed 1/22/08) http://www.chemblink.com/products/5137-55-3.htm
Trisodium Phosphate data sheet. Chemblink website (accessed 1/22/08) http://www.chemblink.com/products/7601-54-9.htm
2-Hydroxy-4-n-octoxybenzophenone data sheet. Chemblink website (accessed 1/22/08) http://www.chemblink.com/products/1843-05-6.htm

Chemtura. **2-Hydroxy-4-n-octoxybenzophenone MSDS**. Hope for Truth website (accessed 1/15/08) http://www.hopefortruth.com/LBAM_Forms/2-HYDROXY.pdf

Chew AL, Maibach HI. 1997. **1,2-Benzisothiazolin-3-one (Proxel1): irritant or allergen?** *Contact Dermatitis* 36: 131–136. PubMed (accessed 1/15/08). http://www.ncbi.nlm.nih.gov/sites/entrez?orig_db=PubMed&db=pubmed&cmd=Search&TransSchema=title&term=chew%5Bfirst%20author%5D%20AND%20proxel

Cochlan WP, Herndon J, Ladizinsky NC, Kudela RM. 2006**. Inorganic and organic nitrogen uptake capabilities of the toxigenic diatom *Pseudo-nitzschia australis***. *Eos Trans*. AGU, 87(36), Ocean Sci. Meet. Suppl., Abstract. (accessed 1/14/08). http://www.agu.org/cgi-bin/SFgate/SFgate?&listenv=table&multiple=1&range=1&directget=1&application=os06&database=%2Fdata%2Fepubs%2Fwais%2Findexes%2Fos06%2Fos06&maxhits=200&="OS15M-02"

Cox C. 2005. **2,4-D: Herbicide Factsheet**. *Journal of Pesticide Reform* Vol. 25, No. 4. NCAP (Northwest Coalition for Alternatives to Pesticides) website (accessed 1/22/08) http://www.pesticide.org/24D.pdf

Cox C, Surgan M. 2006. **Unidentified inert ingredients in pesticides: implications for human and environmental health**. *Environ Health Perspect* 114:1803–1806. EHP website (accessed 1/31/08). http://www.ehponline.org/members/2006/9374/9374.pdf

CSST (Service du répertoire toxicologique) http://www.reptox.csst.qc.ca/Documents/SIMDUT/CasAng/Htm/CasAng06.htm

1,2-Benzisothiazolone
http://www.reptox.csst.qc.ca/DetailSimdut.asp?no_produit=87718&langue=A
Polymethylene Polyphenyl Isocyanate
http://www.reptox.csst.qc.ca/DetailSimdut.asp?no_produit=12005&langue=A
Monosodium Phosphate
http://www.reptox.csst.qc.ca/DetailSimdut.asp?no_produit=261263&langue=A
Trisodium Phosphate
http://www.reptox.csst.qc.ca/DetailSimdut.asp?no_produit=11502&langue=A

Cytec. **2-hydroxy-4-n-octyl benzophenone MSDS.** Cytec website. (accessed 1/15/08).
http://www.cytec.com/specialty-chemicals/pdf/cyasorbuv531.pdf

Cytec/Ciba. 2001. **Date summary & test plan for 2-Hydroxy-4-n-Octoxybenzophenone.** EPA website (accessed 1/15/08).
http://epa.gov/hpv/pubs/summaries/2hydrox/c13209tp.pdf

Damstra RJ, van Viotten WA, van Vinkel CJ. 1992. **Allergic contact dermatitis from the preservative 1,2-benzisothiazolin-3-one (1,2-BIT; Proxel): a case report, its prevalence in those occupationally at risk and in the general dermatological population, and its relationship to allergy to its analogue Kathon CG**. *Contact Dermatitis* Aug;27(2):105-9. PubMed (accessed 1/14/08)
http://www.ncbi.nlm.nih.gov/pubmed/1395609?ordinalpos=3&itool=EntrezSystem2.PEntrez.Pubmed.Pubmed_ResultsPanel.Pubmed_RVDocSum

de Oliveira B, Bertazzoli R. 2007. **THE ROLE OF THE SURFACTANT ALIQUAT 336 ON THE OXYGEN REDUCTION AND ON THE H2O2 GENERATION RATE**. 58th Annual Meeting of the International Society of Electrochemistry, September 9 -14 Banff, Canada. ISE website
(accessed 1/28/08) http://event07.ise-online.org/ise/files/ise071506.pdf

DPR (Department of Pesticide Regulation) / OEHHA (Office of Environmental Health Hazard Assessment). 10/31/2007. **Consensus statement on human health aspects of the aerial application of microencapsulated pheromones to combat the light brown apple moth**. CDFA website (accessed 1/11/08).
http://www.cdfa.ca.gov/phpps/PDEP/lbam/pdfs/FactSheets/Consensus_Statement_on_Human_Health_Aspects.pdf

Environment Canada. **Endocrine disrupting substances in the environment**. Environment Canada website (accessed 2/6/08)
http://www.ec.gc.ca/eds/fact/broch_e.htm

EPA (Environmental Protection Agency). **Lepidopteran pheromones fact sheet**. EPA website (accessed 1/11/08).
http://www.epa.gov/oppbppd1/biopesticides/ingredients/factsheets/factsheet_lep_pheromones.htm

EPA (Environmental Protection Agency). **Particulate matter**. EPA website (accessed 1/14/08).
http://www.epa.gov/air/particlepollution/

EPA (Environmental Protection Agency). 2005. **Reregistration eligibility decision (RED) for benzisothiazoline-3-one.** EPA website (accessed 1/14/08).
http://www.epa.gov/oppsrrd1/REDs/benzisothiazolin_red.pdf

EPA (Environmental Protection Agency). **Toxicological review of methylene diphenyl diisocyanate (MDI)**. EPA website (accessed 1/25/08).
http://www.epa.gov/iris/toxreviews/0529-tr.pdf

EPA. 2002. **The office of pesticide program's guidance document on methodology for determining the data needed and the types of assessments necessary to make FFDCA section 408 safety determinations for lower toxicity pesticide chemicals**. (p. 9) EPA website (accessed 1/31/08).
http://www.epa.gov/oppfead1/cb/csb_page/updates/lowertox.pdf

EPROS. **Polyurethane Foam MSDS**. Fernco website. (accessed 1/17/08)
http://www.fernco.com/docs/MSDS_SummerResin.pdf

European Commission. **Directive 67/548/EEC.** European Commission website (accessed 1/15/08).
http://ec.europa.eu/environment/dansub/consolidated_en.htm

- Annex II – hazard symbols
  http://ec.europa.eu/environment/dansub/pdfs/annex2_en.pdf
- Annex III – risk phrases
  http://ec.europa.eu/environment/dansub/pdfs/annex3_en.pdf
- Annex IV - safety phrases
  http://ec.europa.eu/environment/dansub/pdfs/annex4_en.pdf

European Commission. **Endocrine Disruptors.** European Commission Endocrine Disruptors website (accessed 2/6/08).
http://ec.europa.eu/environment/endocrine/definitions/endodis_en.htm

Ferro. **2-hydroxy-4-n-octyloxybenzophenone MSDS**. Harwick Standard website (accessed 1/23/08)
http://www.harwickstandard.com/web/MSDS/0290101.pdf

Feyzioglu AM, Ogut H. 2006. **Red tide observations along the Eastern Black Sea Coast of Turkey**. *Turk J Bot* 30 375-379. (accessed 1/14/08)
http://journals.tubitak.gov.tr/botany/issues/bot-06-30-5/bot-30-5-5-0512-5.pdf

Fire SE, Silver MW. 2005. **Domoic acid in the Santa Cruz wharf fishery**. *California Fish and Game* 91 (3):179-192. https://www.glf.dfo-mpo.gc.ca/dapr-radp/docs/fire_&__silver_calif_fish_&_game_2005.pdf

Gestis Substance Database. BGIA website (accessed 1/16/08). http://biade.itrust.de/biaen/lpext.dll/Infobase/uberschrift03658?f=templates&fn=main-h.htm&2.0

Great Lakes Chemical Corporation**. 2-Hydroxy-4-n-octoxybenzophenone safety data sheet.** Great Lakes website (accessed 1/16/08). http://www.e1.greatlakes.com/common/msdspdf/04410846.pdf

Gyenge EL, Oloman CW. 2001. **Influence of surfactants on the electroreduction of oxygen to hydrogen peroxide in acid and alkaline electrolytes**. Journal of Applied Electrochemistry, Vol.31, No.2, 233-243. Cheric website (accessed 1/28/08). http://www.cheric.org/research/tech/periodicals/vol_view.php?seq=284454

Hayashi T, Okamoto Y, Ueda K, Kojima N. 2006. **Formation of estrogenic products from benzophenone after exposure to sunlight**. *Toxicol Lett* 167 1-7. http://www.ncbi.nlm.nih.gov/sites/entrez?orig_db=PubMed&db=pubmed&cmd=Search&TransSchema=title&term=hayashi%5Bauthor%5D%20AND%20benzophenone (abstract)

HAZ-MAP http://hazmap.nlm.nih.gov/

HOPE (Helping Our Peninsula's Environment). 1/03/08. **Complaints of adverse reactions to aerial spraying in Monterey and Santa Cruz counties**. HOPE website (accessed 1/11/08). http://www.1hope.org/SPRAYCOMPL2.PDF

HOPE (Helping Our Peninsula's Environment). 1/03/08. **Executive summary of complaints and recommendations**. HOPE website (accessed 1/11/08). http://www.1hope.org/SPRAYCOMPLES.PDF

Howard MDA, Ladizinsky N, Cochlan WP, Kudela RM. 2007. **Nitrogenous preference of toxigenic *Pseudo-nitzschia australis* (Bacillariophyceae) from field and laboratory experiments**. Harmful Algae 6 (2007) 206–217. CalPReEMPT website (accessed 1/14/08) http://calpreempt.ucsc.edu/pdfs/Howard%20et%20al.2007.pdf

International Bird Rescue Research Center. 28 April 2007. **Algae bloom kills sea birds, other sea life in Southern California in record numbers**. ScienceDaily (accessed 1/14/08). http://www.sciencedaily.com/releases/2007/04/070427084149.htm

INRS (l'institut national de recherché scientifique - French National Institute of Scientific Research). 2002. **1,2-Benzisothiazol-3(2H)-one**. (accessed 1/23/08) http://www.inrs.fr/INRS-PUB/inrs01.nsf/27DA5C7238C13A77C1256CE8005A3ACC/$File/ft243.pdf

IRIS (Integrated Risk Management System). **Methylene Diphenyl Diisocyanate (monomeric MDI) and polymeric MDI (PMDI) (CASRN 101-68-8, 9016-87-9)**. EPA website (Accessed 1/25/08) http://www.epa.gov/iris/subst/0529.htm

JCP. **Polyurethane Foam MSDS.** JCP Fixings website (accessed 1/17/08) http://www.jcpfixings.co.uk/index_files/COSHH/foam.pdf

JT Baker. **Ammonium Phosphate MSDS**. JT Baker website (accessed 1/14/08) http://www.jtbaker.com/msds/englishhtml/a6108.htm

JT Baker. **Polyvinyl Alcohol MSDS**. JT Baker website (accessed 1/14/08) http://www.jtbaker.com/msds/englishhtml/P5282.htm

JT Baker. **Tricaprylmethylammonium Chloride MSDS**. JT Baker website (accessed 1/14/08) http://www.jtbaker.com/msds/englishhtml/t4770.htm

Keith L. 1998. **Environmental endocrine disruptors**. *Pure & Appl. Chern.,* Vol. 70, No. 12, pp. 2319-2326. (accessed 1/31/08) http://www.iupac.org/publications/pac/1998/pdf/7012x2319.pdf

Mehren Kjemi. **Dexcoat 800 Component B** (Polymethylene Polyphenyl Isocyanate) **MSDS**. Mehren Kjemi website (accessed 1/25/08). http://www.mehrenkjemi.no/img/MSDS_Dexcoat800_B_2006_02.pdf

Miller D, Wheals BB, Beresford N, Sumpter JP. 2001. **Estrogenic activity of phenolic additives determined by an in vitro yeast bioassay**. *Environ Health Perspect* 109:133–138. EHP website (accessed 1/30/08) http://www.ehponline.org/members/2001/109p133-138miller/miller.pdf

Monterey County Herald. 10/22/07. **Spray ingredients released**. Red Orbit website (accessed 1/11/08). http://www.redorbit.com/news/science/1111962/spray_ingredients_released_sacramento_governor_also_orders_spraying_to_resume/index.html

Moscato G, Omodeo P, Dellabianca A, Colli MC, Pugliese F, Locatelli C, Scibilia J. 1997. **Occupational asthma and rhinitis caused by 1,2-benzisothiazolin-3-one in a chemical worker**. *Occup. Med* Vol. 47, No. 4, pp. 249-251. Oxford Journals website (accessed 1/14/08) http://occmed.oxfordjournals.org/cgi/reprint/47/4/249

Muhn C, Sasseville D. 2003. **Occupational allergic contact dermatitis from 1,2-benzisothiazolin-3-one without cross-sensitization to other isothiazolinones**. *Contact Dermatitis* 48(4): 230-231.

NCAP (Northwest Coalition for Alternatives to Pesticides). 2006. **Inert ingredients in common agricultural pesticide products**. NCAP website (accessed 2/1/08). http://www.pesticide.org/agriculturalinerts.html

NIOSH (National Institute for Occupational Safety and Health). **Ammonium Phosphate Dibasic – ICSC 0217**. CDC website (accessed 1/14/08). http://www.cdc.gov/niosh/ipcsneng/neng0217.html

NIOSH (National Institute for Occupational Safety and Health). **Butylated Hydroxytoluene - ICSC 0841**. CDC website (accessed 1/14/08). http://www.cdc.gov/niosh/ipcsneng/neng0841.html

NIOSH (National Institute for Occupational Safety and Health). **Polyvinyl Alcohol - ICSC 1489.** CDC website (accessed 1/14/08). http://www.cdc.gov/niosh/ipcsneng/neng1489.html

NPA (Network Performance Additives). **2-Hydroxy-4-n-octoxybenzophenone MSDS**. Ed Lynne Network website (accessed 1/22/08) PANNA website (accessed 2/5/08). http://www.edlynnnetwork.com/data/products/MSDS/MSDS%20ELC-531.pdf

NRDC (Natural Resources Defense Council). 11/14/07. **NRDC position statement on spraying for the light brown apple moth in California**. http://www.panna.org/documents/nrdcLbamPosition20071114.pdf

NWFSC (Northwest Fisheries Science Center). (accessed 1/14//08) http://www.nwfsc.noaa.gov/hab/habs_toxins/marine_biotoxins/da/index.html

Pagel. **Diphenylmethane Diisocyanate MSDS**. (syn polymethylene polyphenyl isocyanate). Pagel website (accessed 1/17/08). http://www.pagel.com/all/pdf/msds/gb/pu1_hardener_msds_gb.pdf

PAN (Pesticide Action Network) Pesticides Database. http://www.pesticideinfo.org/
(E)-11-Tetradecenyl acetate
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC35902
Polymethylene polyphenyl isocyanate
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34157
Butylated hydroxy toluene
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC33712
Polyvinyl alcohol

http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34876
Tricapryl methyl ammonium chloride (synonym Methyl trioctyl ammonium chloride) http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC32795
Sodium phosphate
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34417
Sodium acid phosphate
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34345
Trisodium phosphate
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34419
Diammonium phosphate
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34320
1,2-benzisothiazolin-3-one
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC33776
2-hydroxy-4-n-octyl benzophenone (synonym 2-hydroxy-4-n-octyl benzophenone)
http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34775

Ragan T. 11/13/07. **Red tide hits Santa Cruz**. Santa Cruz Sentinel website (accessed 1/11/08).http://www.santacruzsentinel.com/printstory.php?sid=45002&storySection=Local

Ragan T. 10/18/07. **Suterra's bid to conceal pesticide contents denied by judge**. Santa Cruz Sentinel website (accessed 2/5/08). http://www.santacruzsentinel.com/printstory.php?sid=35179&storySection=Local

Renner R. 12/05/07. **Weapons of moth destruction**. ES&T Online News (accessed 1/11/08). http://pubs.acs.org/subscribe/journals/esthag-w/2007/dec/science/rr_inerts.html

Roberts D L, Messenger A G, Summerly R. 1981. **Occupational dermatitis due to 1,2-benzisothiazolin-3-one in the pottery industry**. *Contact Dermatitis* 7: 145–147. PubMed (accessed 1/15/08). http://www.ncbi.nlm.nih.gov/pubmed/6456109?ordinalpos=28&itool=EntrezSystem2.PEntrez.Pubmed.Pubmed_ResultsPanel.Pubmed_RVDocSum

San Francisco State University. 28 February 2000. **Sewage may spur growth of harmful algal blooms**. ScienceDaily. (accessed 1/14/08). http://www.sciencedaily.com/releases/2000/02/000227142140.htm

SCCNFP (The Scientific Committee on Cosmetic Products and Non-food Products Intended for Consumers). 2004. **The SCCNFP opinion concerning benzisothiazolinone**. European Commission website (accessed 1/15/08). http://ec.europa.eu/health/ph_risk/committees/sccp/documents/out289_en.pdf

ScienceLab http://www.sciencelab.com/msdsList.php

http://www.sciencelab.com/xMSDS-Ammonium_phosphate_monobasic-9927077 (accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Ammonium_phosphate_dibasic-9927337(accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Butylated_hydroxytoluene-9923084 (accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Polyvinyl_alcohol-9927396 (accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Sodium_phosphate_dibasic-9925023 (accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Sodium_phosphate_monobasic_Anhydrous-9925022 (accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Sodium_phosphate_tribasic-9925028 (accessed 1/15/08)
http://www.sciencelab.com/xMSDS-Tricaprylmethylammonium_chloride-9925306 (accessed 1/15/08)

Séguin P, Allard A, Cartier A, Malo JL. 1987. **Prevalence of occupational asthma in spray painters exposed to several types of isocyanates, including polymethylene polyphenylisocyanate**. *J Occup Med* Apr; 29(4):340-4. PubMed website (accessed 1/25/08).
http://www.ncbi.nlm.nih.gov/pubmed/3585565?dopt=Abstract

Sendijarevic V, Sendijarevic A, Sendijarevic I, Bailey RE, Pemberton D, Reimann KA. 2004.
Hydrolytic stability of toluene diisocyanate and polymeric methylenediphenyl diisocyanate based polyureas under environmental conditions. *Environ Sci Technol*. Feb 15;38(4):1066-72. PubMed website (accessed 1/25/08).
http://www.ncbi.nlm.nih.gov/pubmed/14998020?ordinalpos=6&itool=EntrezSystem2.PEntrez.Pubmed.Pubmed_ResultsPanel.Pubmed_RVDocSum

Sigma-Aldrich. **1,2-Benzisothiazolin-3-one MSDS** version 1.5. ChemQuik MSDS Management System (linked from UCSC http://ehs.ucsc.edu/msds_and_chemical_info/uc_msds_info.php). (accessed 1/29/08). http://www.actiocms.com/chemquik/mainpage.cfm (type in CAS # 2634-33-5, click on chemical name)

Sigma-Aldrich. **Butylated Hydroxytoluene MSDS** version 1.4. (accessed 1/25/08)
http://www.glue.umd.edu/~choi/MSDS/Sigma-Aldrich/2,6-DI-TERT-BUTYL-4-METHYLPHENOL.pdf

Sigma-Aldrich. **Butylated Hydroxytoluene MSDS** version 1.7. (accessed 1/25/08) http://agrippina.bcs.deakin.edu.au/bcs_admin/msds/msds_docs/2,6-Di-tert-butyl-4-methylphenol.pdf

Sigma-Aldrich. **TRICAPRYLYLMETHYLAMMONIUM CHLORIDE MSDS**. Sigma-Aldrich website (accessed 1/28/08) http://www.sigmaaldrich.com/catalog/search/ProductDetail/FLUKA/91042

SIMoN (Sanctuary Integrated Monitoring Network). 2007. **Seabird mortality event Fall 2007**. SIMoN website (accessed 1/11/08). http://www.mbnms-simon.org/other/moreLinks/whats_new_seabird_mortality_07.php

Suterra LLC. **Checkmate LBAM-F label**. USDA-APHIS website (accessed 1/11/08). http://www.aphis.usda.gov/plant_health/plant_pest_info/lba_moth/downloads/CheckMate%20LBAM.pdf

Suterra LLC. **Checkmate LBAM-F MSDS sheet**. CDFA website (accessed 1/11/08). http://www.cdfa.ca.gov/phpps/PDEP/lbam/pdfs/FactSheets/LBAM_F_MSDS.pdf

Suterra LLC. **Checkmate OLR-F label**. CDMS (Crop Data Management System) website (accessed 1/11/08). http://www.cdms.net/LDat/ld26E004.pdf

Suterra LLC. **Checkmate OLR-F MSDS sheet**. CDMS (Crop Data Management System) website (accessed 1/11/08). http://www.cdms.net/LDat/mp26E003.pdf

Taran JM, Delaney TA. 1997. **Allergic contact dermatitis to 1,2-benzisothizolin-3-one in the carpet industry**. *Australas J Dermatol* 38: 42–43. PubMed website (accessed 1/15/08). http://www.ncbi.nlm.nih.gov/sites/entrez?orig_db=PubMed&db=pubmed&cmd=Search&TransSchema=title&term=taran%5Bfirst%20author%5D%20AND%20allergic%20contact%20dermatitis

University Of California, Santa Cruz. 11 January 2001. **Researchers trace toxins from algal blooms through the marine food web in Monterey Bay**. ScienceDaily (accessed 1/14/08) http://www.sciencedaily.com/releases/2001/01/010111074158.htm

Urbansky ET. 10/11/07. Personal communication to Monterey County mayor Jeff Haferman. PANNA (Pesticide Action Network of North America) website (accessed 1/11/08). http://www.panna.org/documents/urbanskyCheckmate20071011.pdf

Vinquiry. **Diammonium Phosphate MSDS**. Vinquiry website (accessed 1/29/08) http://www.vinquiry.com/pdf/MSDS/DAP%20(diammonium%20phosphate).pdf

Weather Underground. Historical weather data for Santa Cruz county November 10/11. (accessed 1/30/07)
http://www.wunderground.com/US/CA/Santa_Cruz.html
Scotts Valley 11/10/07
http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KCASCOTT4&month=11&day=10&year=2007
Scotts Valley 11/11/07
http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KCASCOTT4&month=11&day=11&year=2007
Soquel 11/10/07
http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KCASOQUE5&month=11&day=10&year=2007
Soquel 11/11/07
http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KCASOQUE5&month=11&day=11&year=2007

Wada H, Tarumi H, Imazoto S, Narimatsu M, Ebisu S. 2004. **In vitro estrogenicity of resin composites**. *J Dent Res* 83(3):222-226. (accessed 1/30/08) http://jdr.iadrjournals.org/cgi/reprint/83/3/222.pdf

Werner I, Deanovic LA, Markiewicz D. 2007. **Toxicity of Checkmate® LBAM-F and *Epiphyas postvittana* pheromone to *Ceriodaphnia dubia* and fathead minnow (*Pimephales promelas*) larvae.** CDFA website (accessed 1/11/08). http://www.cdfa.ca.gov/phpps/PDEP/lbam/pdfs/Reports/ATL_Pheromone_Toxicity_Testing_112807.pdf

Wikipedia. **Algal Bloom**. (accessed 1/29/08)
http://en.wikipedia.org/wiki/Algal_bloom