



Performance Mining Reagents

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XANTHATES: Safety, Health & Environment Bulletin

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PROVISIONAL DOCUMENT

XANTHATE REAGENT: **CONTROL OF RISKS ASSOCIATED WITH STORAGE AND USE**

1. Introduction

Large quantities of various xanthate compounds are widely used in the world especially as flotation reagents in the mining industry for the separation of metal sulfides. It is mainly used for the separation of copper, nickel, lead, gold and zinc. Prior to use, the selected solid xanthate is mixed with water to form a dilute aqueous solution. Typically, concentrations in the order of 10% are produced. The pH of aqueous solutions typically range from 7 to 11. SNF Flomin (in most cases) has standardized on the pelletized form as it has proven to be the most stable to decomposition over time. The surface area is vastly reduced over powdered forms and drying to remove excess CS₂ and alcohols is more effective. Other producers manufacture xanthates as powders. Incidences have been recorded in the literature and elsewhere involving fires, explosions, and personnel exposure. The purpose of this bulletin is to highlight the risks associated with the use and storage of xanthate and to reiterate methods for the control of these risks.

2. Physical and Chemical Characteristics of Xanthates

Xanthates are delivered to operations as solid pellets in drums, bags, or in liquid form by bulk road tankers, depending on the transport distances and the make-up facilities on-site.

The color of xanthate pellets range from grey to pale yellowish green. They have a characteristic disagreeable odor due to the presence of small residual quantities of carbon disulfide (<1%). Xanthates hydrolyze very rapidly under acidic conditions and is stabilized by high pH (>12) conditions. It dissociates totally under pH 9 and very rapidly under pH 7.

Solid xanthates are hygroscopic and decompose in the presence of water to form carbon disulphide, hydrosulphide, carbonyl sulfide, pseudo-xanthate, alcohols, hydroxides, and mono-, di-, and trithiocarbonates. Two or more layers will form with very different densities. Care must be taken to sample the top and bottom to determine composition.

Some of these decomposition products pose risks to health, and may cause explosions and fires.

Both solid and liquid xanthates pose sizeable occupational risks. The risk of exposure increases during mixing stages for solid xanthates, and storage of the liquid product. Care must be taken to handle xanthates in any form. In addition to inhalation and ingestion hazards, skin contact and absorption of chemicals may lead to irritation, eye damage, nausea, vomiting and even blood contamination. MSDS' recommendations for personal protective equipment must be adhered to.

Liquid xanthates have a limited shelf life and should be kept below 15^oC and must be consumed within a prescribed period (30 days). At higher temperatures liquid xanthates will decompose and lose 1-2% activity per week. This rate is greater at elevated temperatures.

3. Risks Associated With Xanthates

WARNING! Xanthates are spontaneously combustible. Even with strict drying methods a small concentration of carbon disulfide is present in the product from the time of manufacture and increases with decomposition over time. Avoid contact with heat, moist air, and water. Xanthate dust or mist may be irritating to nose, throat, and respiratory system. Xanthate dust and liquid solutions may cause eye and skin burns. Harmful if swallowed. Excessive heating or contact with moisture may liberate toxic and flammable carbon disulfide (CS₂ and other products identified earlier in this document.

In addition, xanthates decompose on aging to form a number of byproducts, depending on the pH, temperature, etc. Fire and explosion risks associated with xanthate are, therefore, a function of the breakdown of the product or un-reacted raw materials remaining in the product.

The vapor-space above the liquid will always be a flammable atmosphere. Due to this fact, the area in proximity of the vents from storage/makeup/day tanks should be treated with the appropriate flammability hazard classification. Any work that has the potential for creating sparks or flames must be first monitored for hazardous chemicals and placed under site specific hot work permitting procedures.

Refer to the SNF Flomin product specific MSDS for more detailed information.

The main hazards are from carbon di-sulphide (CS₂), alcohols, and sodium/potassium hydroxide. Hydrogen sulfide (HS⁻ not H₂S) is also a decomposition product that may pose similar risks as H₂S.

Carbon Di-sulphide

Fire

CS₂ is both a reagent in the manufacture, as well as a decomposition product of xanthates. It has an extremely low flash point (-27^oC) and will start to burn with a spark or even a hot surface in the presence of oxygen. CS₂ has an auto-ignition temperature of 90-95^oC. This means that even a steam trap can

cause ignition. It is heavier than air and therefore tends to travel long distances along the ground and collect in low lying areas. CS₂ is relatively insoluble in water and heavier than water and, therefore, it will collect in a layer under water. Spills or CS₂ fires in containment areas are therefore easier to manage by the use of water. In other areas the use of water to extinguish CS₂ fires may lead to spreading of the fire along the water run-off routes. Refer to MSDS' for CS₂ to determine proper fire fighting methods.

In areas where solid xanthates are stored care must be taken not to wet boxes or bags containing xanthates to avoid contact with the pellets/powder. Further decomposition and production of CS₂ may be triggered.

Plastic bags and shrink wrapping used for packaging and transport of xanthates are prone to static build-up. Care should be taken when opening especially with metal knives. Static discharges are sufficient to cause fires enabled by carbon disulfide that is present with xanthates inside the bags.

Skin Exposure/Inhalation/Ingestion

There is a potential for high worker exposure to xanthates and carbon disulphide during the mixing process, depending on the degree of automation. During tipping of the drums there is a likelihood of dust generation and spillage of the powder or pellets which could lead to worker exposure. Physical contact is caused if proper PPE is not used during handling of xanthate in its packaging or spills.

Inhalation - Acute Exposure: Inhalation of vapor, mist, aerosol or fume of carbon disulfide may cause headache, nausea, and drop in blood pressure, dizziness, unconsciousness and possibly death. High concentrations of CS₂ vapor may cause irritation of the nose. The acute LC₅₀ (mice) for this product CS₂ is 220 ppm for a 1-hour exposure. Inhalation of vapor, mist, aerosol or fume of carbon disulfide may cause headache, nausea, drop in blood pressure, dizziness, unconsciousness and possibly death. High concentrations of the vapor may cause irritation of the nose.

Chronic exposure: Rats were exposed to concentrations of approximately 50, 300 or 800 ppm for 6 hours/day, 5 days/week for a period of 90 days. The NOEL was 50 ppm. Reproductive, neurological and cardiac effects have been reported in humans following repeated or prolonged inhalation exposure.

Inhalation of vapors from solid xanthates in a 30-day study produced adverse effects on the liver in dogs, rats and mice. The other affected organs were the kidneys in rats and the central nervous system in mice.

Skin Contact - Acute Exposure: Carbon disulfide can cause skin irritation. Splashes on the skin may cause blistering. This product is readily absorbed through the skin resulting in nerve damage near the site of absorption. Symptoms are similar to those for inhalation. Acute contact: Dermal toxicity (LD50) is not available for this product. This product is readily absorbed through the skin resulting in nerve damage near the site of absorption. Symptoms are similar to those for inhalation. Chronic contact: Prolonged or repeated contact can cause loss of skin oils resulting in dry and scaly skin. Moderate skin irritation can occur.

Eye Contact - Acute Exposure: Eye contact may cause severe irritation. Contact may cause permanent eye damage if not flushed out immediately.

Ingestion - Acute Exposure: If swallowed, this product may cause severe irritation or burns of the mouth, throat, oesophagus and stomach. Swallowing small amounts may cause vomiting, diarrhoea and headache. Swallowing large amounts may result in loss of consciousness and convulsions. Death has been reported following ingestion of small amounts of carbon disulfide. The oral LD50 for this product is greater than 2000 mg/kg (rat). **Chronic Exposure:** Studies have reported adverse (harmful) effects on the central and peripheral nervous systems and blood vessels. Exposure to carbon disulfide also carries a possible risk of impaired fertility and harm to the unborn child.

Carcinogenicity: IARC, NTP, ACGIH and OSHA do not classify this material or its components as a carcinogen or suspect carcinogen.

Neurotoxicity: Prolonged or repeated exposure to high levels of carbon disulfide can cause effects to the central and peripheral nervous systems (decrease in conduction velocity).

Other Toxicological effects: Several studies have indicated an increased risk of coronary heart disease from exposure to carbon disulfide. In addition, effects on blood pressure and cholesterol levels have been reported in some epidemiology studies.

Target Organs: Eyes, skin, respiratory system, central and peripheral nervous systems, cardiovascular system and reproductive system.

Medical conditions aggravated by exposure: Persons with pre-existing conditions related to central and peripheral nervous systems, eyes, cardiovascular system, kidneys, liver and alcoholism.

Alcohols

Alcohols are both reagents used in the manufacture, as well as decomposition products of xanthates. The specific alcohol depends on the xanthate species. The alcohols in question include among others ethyl, isopropyl, isobutyl, n-butyl, and amyl alcohol.

Fire: They have low flash points (about 12°C to 50°C) and they burn easily. They also have low vapour pressures and will form explosive mixtures with air in confined spaces (e.g. the vapour space above the xanthate solution in enclosed tanks). Ignition of these vapors has been reported. .

Skin: Prolonged exposure may cause de-fatting of the skin which may lead to dermatitis.

Inhalation: May cause irritation to the respiratory system.

Acute: High concentrations may cause the central nervous system to be depressed causing headaches, nausea, and dizziness. Prolonged exposure may cause unconsciousness and even death.

Sodium/Potassium Hydroxide (Refer to specific MSDS')

These chemicals are used in the manufacturing process for xanthates and are present in the final product as an excess to maintain pH above 12. Xanthates decompose at pH <9. They react violently in contact acids and oxidizing reagents.

Skin: Irritation (possibly severe), burns, and redness.

Inhalation: Irritation (possibly severe), burns, pulmonary oedema.

Ingestion: Irritation (possibly severe), burns, vomiting, nausea.

Eye Contact: irritation, burns, redness, corneal damage, blindness.

4. Control of Xanthate Risks

On the basis of the risks highlighted above a number of control measures are recommended by SNF Flomin for the safe handling of both solid and liquid xanthates.

Storage and Monitoring

- Pelletized xanthates are relatively stable if kept dry and cool. Store in closed containers in a cool, well ventilated area away from sources of heat or ignition.
- Precautions should be taken to avoid static electricity discharge especially when opening bags and/or removing shrink wrap. For drums, the plastic liner is tied and sealed at the top. The sealed portion should be cut with shears rather than slicing open the bag. For super sacks made of polypropylene are prone to high static charges. Slicing blades should be incorporated above the make-up tank rather than manual slicing the underside of the bag.
- Partially used bags of xanthates should be used or disposed off within a few days as they are susceptible to moisture and contamination by oxidizing chemicals. Bags should be resealed and store in clearly defined areas.
- Care must be taken to dispose of xanthate floor sweepings. Xanthate should never be placed in trash receptacles or open containers due to the potential of fires from contamination or moisture.
- Most pelletized xanthate may be stored for up to 1 year if inner polyethylene liner seals are not broken and boxes stored dry and cool. Storage areas should be monitored for explosive environments due to decomposition products. Hot work permits are required in and around xanthate storage areas. The inner liner should be hermetically sealed and not manually tied. Solid xanthates are hygroscopic and when exposed to moisture in air decompose, releasing carbon disulphide and other flammable compounds mentioned previously.
- Liquid xanthate may be stored for up to 30 days at pH > 12. Tanks must be kept cool to reduce the decomposition rate of xanthate and to limit the alcohol vapor concentration. The temperature should preferably be below 15 °C and above 5°C to prevent crystallization.
- Storage and mixing tanks should be designed with conically shaped bottoms that slope towards the transfer pump suction to facilitate removal of carbon disulphide and sludge that may accumulate at the bottom.
- Storage and mixing tanks should be routinely flushed high pH water to prevent build up of carbon disulfide especially if flat bottomed or have dead spots.
- Storage and make-up areas should be monitored for CS₂ especially near vents, open covers, and overflow drains. Several companies manufacture devices including the GASMAX II from GDS Corp. and LC100 from International Sensor Technology. Each site should determine what automatic measures are to be triggered on positive detection. Portable devices should be used to monitor other areas as well. These multi-gas units are available from several manufacturers including Dräger, MSA, BW Technologies, and RAE. Product selected should show % oxygen, LEL, H₂S and CO.
- Warning signs must be posted showing the prohibition of all ignition sources e.g. no smoking, no naked flames, only explosion proof electric motor, only propane forklifts, no mobile phones, etc.
- Restrict access to storage areas only to personnel trained in the awareness and handling of xanthate. Training should include a review of this document and MSDS for the xanthates involved. Videos are available from Akzo Nobel and various internet sites for Carbon Disulfide awareness. SNF Flomin frequently conducts these training sessions at customer sites upon requests as part of our **Responsible Care**[®] initiatives.

Personnel Protection

Respiratory: Wear a properly fitted NIOSH/MSA approved respirator whenever significant exposure to vapor or mist is likely. Simple dust masks are not adequate to protect against chemical fumes.

Hands: Neoprene, polyvinyl, butyl rubber or nitrile rubber gloves are suitable.

Eyes: Wear chemical splash proof goggles or face shield.

Skin: Wear coveralls and/or chemical apron and rubber footwear where physical contact can occur. Wash hands before breaks and immediately after handling the product. Do not eat or store food and drinks where this product is stored and used.

Maintenance

Occasionally it is necessary to do maintenance work in and around storage areas for solid & liquid xanthate. Tanks must be prepared for vessel entry or any activity where sparks may be generated. Each site should already have specific procedures (safety permits.....) to cover these activities. The following should be included:

- Tanks, piping and equipment should be cleaned of solvents and any possible accumulation of carbon disulfide. Cleaning with high pH (water with caustic or lime) is recommended. Steaming for several hours may be effective in removing residual traces of hazardous organic chemicals.
- The space should be tested to determine if any chemical hazards are present. Portable multi-gas detectors are effective. Several units are available from manufacturers such as MSA (Orion, Altair) and Draeger.
- Rotating equipment and electrical devices in and around areas where xanthates are stored or dissolved (especially vents/overflows) should be rated for explosion-proof. Seals for electrically conduits/piping should be checked routinely for integrity. Grounding should be provided for any material transfer operations e.g. drums.
- Ensure that chemical hazards are below levels necessary for safe entry and work. Test in the following order: Oxygen, combustible gases (LEL), toxic gases and vapors.

Waste disposal

- Segregate floor sweepings of xanthates. Dispose of immediately. Dissolve in high pH water, and reuse if possible. Do not cross contaminate with oxidizing agents or acids. Xanthates will smolder or cause an open fire.
- Empty bags should be disposed of as hazardous waste. Consult local regulations.
- Empty plywood/reconstituted particle boards comprising the xanthate boxes are usually recycled or burned as general refuse. If recycled, the metal reinforcements on the corners should be removed prior to sending to a recycling facility. Consult local authorities for proper disposal guidelines.

References:

1. Anglo-American: Safety, Health & Environment Bulletin, May 2002
2. Australian Government Publishing Service: Sodium Ethyl Xanthate, May 1995
3. Akzo Nobel Functional Chemicals LLC MSDS No. 16 - 084803
4. "Decomposition of Xanthates in Flotation Solutions" - Horst Dautzenberg, Andrzej Kowal, Joanna Kowal and Wolfgang Dietzel.

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