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## TECHNICAL MEMORANDUM

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**TO: Vicky Peacey, Resolution Copper**

**FROM: Ted Eary, Enchemica**

**DATE: July 18, 2018**

**SUBJECT: Sodium Isopropyl Xanthate: Decomposition and Fate and Transport**

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### 1 INTRODUCTION

Resolution Copper plans to use sodium isopropyl xanthate (SIPX;  $C_4H_7OS_2Na$ ) as a collector agent for sulfide mineral processing. The purpose of this technical memorandum is to provide a summary of the use, properties, decomposition kinetics, and decomposition products for SIPX. This information is used to evaluate the environmental fate and transport characteristics of SIPX relevant to the tailings storage facility (TSF) for the Resolution Copper Project.

#### 1.1 Use

SIPX would be used predominantly in the pyrite scavenger flotation circuit for the collection of pyrite. The normal rate of use of SIPX in the pyrite scavenger flotation circuit is estimated to be 20 g/tonne of ore. This rate is equivalent to a solution concentration of 6.3 mg/L as isopropyl xanthate ( $C_4H_7OS_2^-$ ), assuming a slurry density of 30% for the flotation circuit and 100% purity for the SIPX reagent. Because SIPX will be used as a collector for pyrite, the resulting isopropyl xanthate is expected to be predominantly contained in pyrite tailings.

### 2 PROPERTIES

#### 2.1 Physical Chemistry

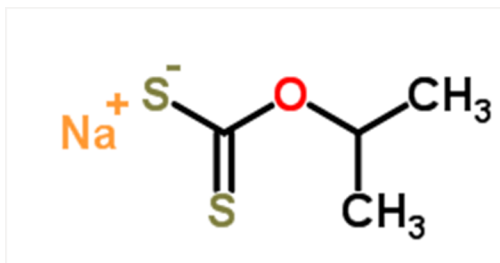
Sodium isopropyl xanthate is one of several different types of xanthate compounds used for mineral processing with the general formula of  $ROCS_2(Na,K)$ , where "R" refers to a hydrocarbon chain. The hydrocarbon chain may be ethyl, amyl, isobutyl, or isopropyl groups.

Some important properties specifically for SIPX are:

Chemical formula:  $C_4H_7OS_2Na$

Molecular weight: 158.2 g

Structure:

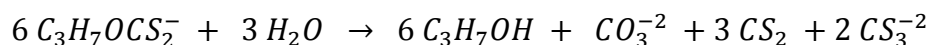


MSDS Example: <http://msds.orica.com/pdf/shess-en-cds-010-000030344501.pdf>

## 2.2 Decomposition

SIPX added to water will dissociate to form dissolved sodium ( $\text{Na}^+$ ) and xanthate anion ( $\text{C}_4\text{H}_7\text{OS}_2^-$ ). The xanthate anions are unstable in aqueous solutions and decompose by three different reaction pathways (AGPS, 1995; 2000; Marsden and House, 2006):

1. Hydrolysis to xanthic acid which decomposes to carbon disulfide ( $\text{CS}_2$ ) and alcohol
2. Oxidation to dioxathion ( $\text{C}_3\text{H}_5\text{OS}_2$ )<sub>2</sub>
3. Hydrolytic decomposition to form alcohol, carbonate ion, and carbon disulfide; for isopropyl xanthate, this reaction is:



The first two reactions occur in acidic solutions. The third reaction occurs in neutral to alkaline solutions and is auto-catalytic in that the alcohol produced by decomposition accelerates the reaction AGPC (1995).

The third reaction pathway is the most important reaction expected to occur during mineral processing and after deposition of tailings slurries where the pH is expected to range from neutral to slightly alkaline values (AGPC, 1995). Two of the products of decomposition of alcohol and carbonate are unlikely to result in significant changes to tailings solution chemistry given a starting concentration of about 6.3 mg/L of  $\text{C}_4\text{H}_7\text{OS}_2^-$  for the following reasons. In saturated tailings and reclaim ponds, the alcohol will be rapidly consumed by microbes and will promote development of anoxic conditions that minimize the potential for oxidation of sulfide minerals. The carbonate will hydrolyze to  $\text{HCO}_3^-$ , but that reaction will have a very small effect on pH given the low concentrations expected to be produced from a starting isopropyl xanthate concentration.

Carbon disulfide is the primary decomposition product from the third reaction pathway. The fate and transport characteristics of xanthate and carbon disulfide are summarized in the following section.

## 3 FATE AND TRANSPORT

### 3.1 Xanthate Stability

The rate of xanthate decomposition is dependent primarily on temperature and pH according to kinetic studies. Initial xanthate concentration and metal cation concentrations also have some effect on decomposition rate. De Donato et al. (1989) measured decomposition rates for potassium amyl xanthate that yielded half-lives from 10 to 40 days for pH values of 5 and 8.5, respectively. Maillott et al. (1984) measured decomposition rates for potassium ethyl xanthate that yielded half-lives from about 1 hr to 13 days for pH values of 4 and 7, respectively. Half-lives for various xanthates are reported to range from 1 to 4 days under near neutral pH conditions expected for most freshwater systems (Boening 1998; Xu et al. 1988).

Marsden and House (2006) provide a compilation of half-lives for xanthates as functions of pH and temperature (Table 1). These data provide a means to estimate the half-life for the xanthate that would be produced from the use of SIPX by Resolution Copper given the following assumptions about pH and temperature:

- The pyrite reclaim ponds for all but one of the different tailings facility alternatives currently under evaluation are expected to have pH values in the range of 7.5 to 8.5, reflecting the conditions of mineral processing and prevention of oxidation by maintenance of water covers. The exception is the pyrite pond for the Silver King alternative, which is expected to contain acidic water due to runoff from exposed pyrite tailings.
- The temperatures for tailings slurry exiting the mill are estimated to be about 40 to 50°C given the elevated temperature of the ore at depth and heat generated by grinding. The tailings slurry and water in the reclaim pond will cool over time to about 25 to 30°C, which is the general range for average annual temperature for Superior, Arizona (WRCC, 2016).

Using the information in Table 1, the half-life for isopropyl xanthate contained in pyrite tailings is estimated to range from 16.5 days (40°C and pH 8) to 109.5 days (25°C and pH 8). After 4 half-lives, which would be equal to 66 days at 40°C and pH 8 to 1.2 years at 25°C and pH 8, the initial isopropyl xanthate concentration of 6.3 mg/L would be reduced to about 0.4 mg/L due to decomposition reactions. Under acidic conditions, which may be expected for the pyrite pond for the Silver King TSF alternative, decomposition would be more rapid (Table 1).

**Table 1. Xanthate half-lives under nitrogen from Marsden and House (2006)  
(converted from original values in hours to days)**

pH	Xanthate Half-life (days)					
	Isopropyl	Ethyl	n-Propyl	Isobutyl	n-Butyl	Amyl
<b>25°C</b>						
10	113.4	29.5	36.1	49.5	42.5	45.0
9	122.0	30.0	38.0	49.0	43.1	49.8
8	109.5	29.5	36.4	48.8	43.5	46.8
7	30.3	16.8	20.0	19.8	20.5	19.5
6	3.0	2.6	2.6	2.6	2.1	2.4
<b>40°C</b>						
10	21.5	5.2	6.6	8.7	7.6	8.1
9	21.3	5.3	6.8	8.9	7.8	8.8
8	16.5	5.1	6.3	7.7	6.7	7.4
7	2.9	2.6	3.0	3.7	3.0	3.1
6	0.6	0.6	0.6	0.7	0.6	0.6

### 3.2 Xanthate Adsorption

Xanthates are used as collectors for sulfide mineral processing because of their strong affinity for the surfaces of sulfide minerals. Xanthates bind to sulfide minerals and to a lesser extent on other minerals through adsorption of xanthate anions (e.g.,  $C_4H_7OS_2^-$ ) via the polar sulfur group, which can bind directly with the metals in sulfides (Fuerstenau et al. 1990a; 1990b; Chandra et al. 2012; Mustafa et al. 2004). Due to the negative charge of xanthate, adsorption densities on sulfide surfaces tend to increase with decrease in pH (Fuerstenau et al. 1990a; 1990b). Valdivieso et al. (2005) also describe a process of involving oxidation of xanthate to dixanthogen coupled to reduction of ferric hydroxides that results in adsorption of the dixanthogen to pyrite surfaces. These adsorption reactions are

expected to greatly limit the aqueous mobility of xanthate anions in porous media that contain sulfide minerals such as tailings.

### 3.3 Carbon Disulfide

Decomposition of xanthates (Section 0) can be expected to produce carbon disulfide under the conditions expected for pyrite tailings deposition and reclaim ponds. Carbon disulfide is partially soluble in water (2.0 to 2.3 g/L at 20 to 22°C; Montgomery, 2007), but volatilizes relatively rapidly due to a Henry's law constant of 1748 Pa·m<sup>3</sup>/mol and vapor pressure of 48.2 kPa at 25°C (Newhook et al. 2002). The half-life for carbon disulfide from a saturated solution is reported to range from 11 minutes and 2.6 hours according to studies by Peyton et al. (1978) and Newhook et al. (2002). At operating TSFs where flotation tailings containing xanthate collectors are used, the presence of volatilized carbon disulfide is commonly detectable at spigot points due to its sulfur-type odor (AGPC, 1995).

Carbon disulfide in the aqueous phase is not strongly adsorbed or partitioned to mineral surfaces (Environment Canada 2000; Newhook et al., 2002). Studies in Environment Canada (2000) have reported that it can be slowly consumed by microbial processes with a half-life of about 230 days. Carbon disulfide will also undergo abiotic hydrolysis and oxidation to form hydrogen sulfide, carbonyl sulfide, and carbon dioxide. This process is relatively slow with a half-life estimated at 1.1 years at pH 9 (Peyton et al. 1978).

Most of the carbon disulfide generated from xanthate decomposition in tailings is expected to be volatilized during spigotting and deposition of tailings on exposed surfaces and ponds. Low concentrations of carbon disulfide may occur in water saturated tailings not directly exposed to the atmosphere where volatilization may be reduced. Xanthate adsorbed to sulfide mineral surfaces in high-sulfur pyrite tailings will decompose over time, resulting in a slow generation of carbon disulfide over time that will eventually be volatilized or be retained at low concentration in the aqueous phase. Carbon disulfide may have a small effect for promoting development of anoxic conditions through consumption of dissolved oxygen.

## 4 CONCLUSIONS

The use of SIPX for ore processing at Resolution Copper will result in initial xanthate concentrations of about 6.3 mg/L in the water portion of pyrite tailings slurry. For each of the TSF alternatives, nearly all the xanthate is expected to be associated with high-sulfur pyrite tailings and stored under water-saturated conditions. A small amount of xanthate will also be deposited with scavenger tailings in embankments and beaches under variably saturated conditions. Under both these depositional conditions, the xanthate will decompose with some portion also being recycled back to the process circuit in reclaim water.

Xanthate decomposition will produce carbon disulfide; however, most of the carbon disulfide will volatilize from slurries as they are deposited. The remaining amount is expected to be volatilized over time. Because of these processes and containment within the tailings impoundment and seepage collection systems, it is not expected that xanthates or its decomposition products will be a source of mobile contaminants that will affect groundwater systems. This conclusion is consistent with conclusions made in AGPC (1995) about the environmental fate of xanthate used for mineral processing for operations where tailings are confined to well-constructed tailings dams.

## 5 REFERENCES

- AGPC (1995) Sodium Ethyl Xanthate, Priority Existing Chemical No. 5., May 1995, AGPS Press, Australian Government Publishing Service, GPO Box 84, Canberra ACT 2601.
- AGPC (2000) Sodium Ethyl Xanthate, Priority Existing Chemical, Secondary Notification Assessment Report No.5S., February 2000. National Industrial Chemicals Notification and Assessment Scheme, 334-336 Illawarra Road Marrickville, NSW 2204 Australia.
- Boening, D.W. (1998) Aquatic toxicity and environmental fate of xanthates. *Mining Engineering*, September 1998, 65-68.
- Chandra, A. P., L. Puskar, D.J. Simpson, and A.R. Gerson (2012) Copper and xanthate adsorption onto pyrite surfaces: implications for mineral separation through flotation. *Int. J. Mineral Processing*, 114-117, 16-26.
- De Donate, P., J.M. Cases, M. Kongolo, A. Cartier, and J.L. Rivail (1989) Stability of the amyloxanthate ion as a function of pH: modelling and comparison with the ethylxanthate ion. *Int. J. Mineral Processing*, 25, 1-16.
- Environment Canada (2000) Priority Substances List Assessment Report: Carbon Disulfide. Environment Canada, Health Canada, May 2000.
- Furstenau, M., C.A. Natalie, and R.M. Row (1990a) Xanthate adsorption on selected sulfides in the virtual absence and presence of oxygen, Part 1. *Int. J. Mineral Processing*, 29, 89-98.
- Furstenau, M., C.A. Natalie, and R.M. Row (1990b) Xanthate adsorption on selected sulfides in the virtual absence and presence of oxygen, Part 2. *Int. J. Mineral Processing*, 29, 111-119.
- Maillott, M. J.L. Cecile, and R. Bloise (1984) Stability of ethylxanthate ion in neutral and weakly acidic media. Part 1: Influence of pH. *Int. J. Mineral Processing*, 14, 193-210.
- Marsden, J.O. and C.I. House (2006) *The Chemistry of Gold Extraction*, Second Edition. Society for Mining, Metallurgy, and Exploration, 8307 Shaffer Parkway, Littleton, Colorado, USA., p. 414-417).
- Montgomery, J.H. (2007) *Groundwater Chemicals Desk Reference*, 4<sup>th</sup> Edition. CRC Press Taylor & Francis Group, Boca Raton, Florida, pp. 210-212.
- Newhook, R., M.E. Meek, and D. Caldbick (2002) Carbon Disulphide. Concise International Chemical Assessment Document 46, World Health Organization, Geneva, Switzerland.
- Peyton, T.O, R.V. Steele, and W.R. Mabey (1978) Carbon disulfide, carbonyl sulfide: Literature Review and Environmental Assessment. Final Report EPA-600/9-78-009 (June 1978), U.S. Environmental Protection Agency, Office of Health and Ecological Effects, Washington, D.C.
- Valdivieso, A.L., A.A.S. López, and S. Song (2005) On the cathodic reaction coupled with the oxidation of xanthates at the pyrite/aqueous solution interface. *Int. J. Mineral Processing*, 77, 154-164.
- WRCC (2016) Western Regional Climate Center, Superior, AZ (028348). <http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?azsupe>, accessed September 27, 2016.
- Xu, Y., J.P. Lay, and F. Korte (1988) Fate and effects of xanthates in laboratory freshwater systems. *Bull. Environ. Contam. Toxicol.* 41, 682-689.