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**To:** Victoria Peacey (Resolution Copper)

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**Cc:** Cameo Flood (Tetra Tech)

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**From:** Amy L. Hudson, Ph.D. (Tetra Tech)

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**Reviewed By:** Alex Norgren (Tetra Tech)

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**Date:** October 11, 2018

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**Subject:** Fate of Mill Reagents of Resolution Copper Mineral Processing

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## 1.0 FATE OF REAGENTS

This memorandum has been prepared as a response to the U.S. Forest Service's request for documentation of the fate of reagents used in the proposed Resolution Copper Mine concentrator to process the ore and their likelihood to persist in the tailings solute. Five reagents will be used to process the ore:

- AERO® 8989;
- Diesel
- MIBC;
- SIPX;
- NaHS; and
- Magnafloc 155.

It is anticipated that the exposure pathways for these chemicals will be related to surface water discharges directly from the tailings storage facility to the receiving water bodies. This would be monitored and managed through a state or federal discharge permit, including Whole Effluent Toxicity (WET) testing. There will be no such discharge from Resolution Copper tailings storage facility, eliminating the primary exposure pathway.

### 1.1 AERO® 8989

AERO® 8989 is proposed as the copper mineral collector in the flotation process. AERO® 8989 coats the mineral surface, rendering the copper mineral hydrophobic. The coated minerals attach to air bubbles blown into the flotation tank, allowing the copper-molybdenum concentrate to float to the top of the tank where it is skimmed off. The majority of the AERO® 8989 exits the process with the copper-molybdenum concentrate, which gets thickened and separated into copper concentrate and molybdenum concentrate and sent off site for additional processing. Water recovered from the concentrate thickeners is recycled back to the concentrator. .

### 1.2 DIESEL

Diesel is proposed as the molybdenum collector in the flotation process. Diesel coats the mineral surface, rendering the molybdenum hydrophobic. The coated minerals attach to air bubbles blown into the flotation tank, allowing the copper-molybdenum concentrate to float to the top of the tank where it is skimmed off. The majority of the diesel exits the process with the copper-molybdenum concentrate, which gets thickened and separated into copper concentrate and molybdenum concentrate and sent off site for additional processing. Water recovered from the concentrate thickeners is recycled back to the concentrator.

### 1.3 SIPX

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Sodium isopropyl xanthate (SIPX) is also a collector and is proposed for use after copper molybdenum flotation to float pyrite and all remaining sulfides to produce pyrite (PAG) tailings. SIPX adheres and coats the pyrite and other sulfide minerals and renders them hydrophobic. As such, the majority of this reagent would end up with the PAG tailings stream.

Decomposition of xanthates is a well-recognized phenomenon. The pyrite tailings storage facility is designed to recover water in the reclaim pond. The majority of residual SIPX that may remain after volatilization and biodegradation is recycled back to the concentrator for re-use in the process. A detailed discussion of the decomposition and fate of SIPX has been prepared by Enchemica (2018) for this project and is provided as an attachment to this memorandum.

### 1.4 MIBC

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Methyl isobutyl carbinol (MIBC) will be used as a neutral alcohol frother as part of the copper and molybdenum bulk flotation process along with AERO® 8989. The addition of MIBC lowers the surface tension of the water, thus strengthening the air bubbles in the flotation tank. The copper and molybdenum bearing minerals are coated with the AERO® 8989 and diesel and then attach to the bubbles which rise to the surface of the flotation tank, where they are collected with the concentrate and sent off site for additional processing. MIBC is also used in the pyrite (PAG) flotation circuit, where the pyrite and sulfide minerals are coated with SIPX and then attach to the bubbles which rise to the surface for collection as pyrite tailings.

The most common application of frothers, such as MIBC, is in the mineral processing industry, but recent research has considered the use of MIBC for use in water treatment unit operations (Temesgen, T., et al., 2017). MIBC readily biodegrades and volatilization and losses to the atmosphere are well recognized, as such the initial concentrations in the pyrite (PAG) tailings stream will very quickly disappear.

MIBC will volatilize during the flotation process within the concentrator building before transport to the tailings storage facility since the vapor pressure of MIBC is 4.97 hPa @20°C. This loss of MIBC from the pyrite tailings is incorporated in the emission inventory.

MIBC readily biodegrades in the environment at a rate of approximately 94% in 20 days or a decay constant of 14.1% per day (United Nations, 2005). The United Nations report (2005) also cited information from the U.S. Environmental Protection Agency (USEPA) that the potential risk to aquatic species is low due to the chemical's low persistence in the environment and the low potential for bioaccumulation.

The pyrite tailings storage facility is designed to recover water in the reclaim pond. Residual MIBC that may remain in the reclaim pond after volatilization and biodegradation would be recycled back to the concentrator for re-use in the process.

### 1.5 NAHS

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Sodium hydrogen sulfide (NaHS) will be used in the molybdenum processing to separate the copper and molybdenum in the concentrate. The NaHS adheres to the copper minerals, causing them to sink to the bottom of the flotation cell, so the molybdenum can be floated to the top and skimmed from the surface. Copper concentrate and molybdenum concentrate are the only products of this processing, so no NaHS will be transported with the tailings stream.

### 1.6 MAGNAFLOC 155

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Magnafloc 155 is an anionic polyacrylamide flocculant proposed to be used to thicken the concentrate and tailings through flocculation of colloids and weakly associated compositions into larger particles to allow them to settle.

Flocculation is one of two methods typically employed to remove suspended solids for settling, and is commonly chosen over coagulation for water and wastewater treatment due to the strong bonds of the aggregates formed and the limited effect of pH changes on the effectiveness (Brostow et al., 2009). Water treatment to agglomerate solids is the principal application of chemical flocculants (Reynolds and Richards, 1996). Anionic polymers have a negative charge, making them non-toxic (USEPA, 2013). The settled particles will be collected and the water drawn off and recycled back into the concentrator.

Limited information is available regarding the environmental behavior of Magnafloc 155, but it is assumed that it will behave as other polyacrylamide compounds. Polyacrylamides are a family of polymers and copolymers that are commonly used to stabilize soils and have behavioral similarities. Flocculant has a propensity to bind with the mineral rich particles (Larroyd et al., 2002) in the concentrate thickeners and the tailings thickeners. Thus, flocculant would largely be associated with the copper and molybdenum concentrates as well as the tailings, both PAG and NPAG.

Based on research by Caulfield and others (2002), polyacrylamides are susceptible to photodegradation, while Woodrow and others (2008) found that iron can enhance the photodegradation of polyacrylamides. Neither study provided decay rates, thus a conservative estimate of the fate of the Magnafloc 155 would assume that the reagent transported with the pyrite (PAG) tailings and scavenger (NPAG) tailings slurry could be present in the pyrite and scavenger tailings portion of the TSF. However, it is also worth noting that flocculants are susceptible to mechanical degradation and destruction during passage through pumps, mixers, cyclones and other mechanical equipment during conveyance. The pyrite tailings storage facility is designed to recover water in the reclaim pond. Residual flocculant that may remain in the decant pond after degradation would be recycled back to the concentrator for re-use in the process.

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**ENCHEMICA, 2018. SODIUM ISOPROPYL XANTHATE DECOMPOSITION AND FATE AND  
TRANSPORT TECHNICAL MEMORANDUM**



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1-970-481-9338

## 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

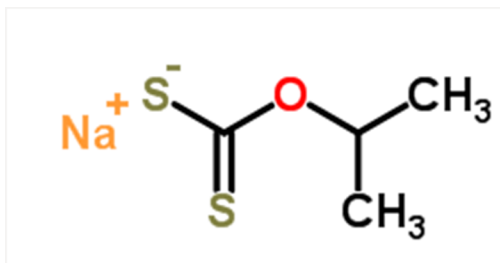
Sodium isopropyl xanthate is one of several different types of xanthate compounds used for mineral processing with the general formula of  $ROCS_2(Na,K)$ , where "R" refers to a hydrocarbon chain. The hydrocarbon chain may be ethyl, amyl, isobutyl, or isopropyl groups.

Some important properties specifically for SIPX are:

Chemical formula:  $C_4H_7OS_2Na$

Molecular weight: 158.2 g

Structure:

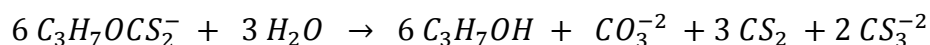


MSDS Example: <http://msds.orica.com/pdf/shess-en-cds-010-000030344501.pdf>

## 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

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October 11, 2018

Mr. Neil Bosworth  
US Forest Service  
Supervisor, Tonto National Forest  
2324 East McDowell Road  
Phoenix, AZ 85006-2496

**Subject:** Response to ANALYSIS DATA REQUEST #1 – Request for Analysis of Tailings Seepage – Item #3 Fate of Mill Reagents

Dear Mr. Bosworth,


In final response to your letter dated March 8, 2018, and to complete the response to item #3, the following document is enclosed:

**3. Fate of Mill Reagents:** It is our understanding that Resolution Copper has compiled pertinent information about the fate of various mill reagents and their likelihood to persist in tailings solute.

*Request: RCM to provide USFS with documentation on fate of mill reagents.*

**RCM Response:** In response, please see the attached technical memorandum titled “*Fate of Mill Reagents of Resolution Copper Mineral Processing.*”

Sincerely,



Vicky Peacey,

Senior Manager, Environment, Permitting and Approvals; Resolution Copper Company, as  
Manager of Resolution Copper Mining, LLC

Cc: Ms. Mary Morissette; Senior Environmental Specialist; Resolution Copper Company



Enclosure(s):

Tetra Tech, October 2018. Fate of Mill Reagents of Resolution Copper Mineral Processing