AERO* Xanthate HANDBOOK

AERO XANTHATE PRODUCTS

AMERICAN CYANAMID COMPANY

CYANAMID CANADA, INC.

CYANAMID INTERNATIONAL DIVISIONS

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INTRODUCTION

The information in this bulletin is provided mainly to assist customers in the application and handling of bulk and drum shipments of AERO Xanthate products.

AERO Xanthate products for American Cyanamid Company, Cyanamid International, and Cyanamid Canada Inc., are now manufactured by Cyanamid Canada Inc., in Niagara Falls, Ontario, Canada. The original plant began production in Niagara Falls in 1957.

Since 1917, Cyanamid has supplied chemicals and technical knowledge to mineral processors throughout the world. Research chemists and engineers at the mining chemicals research laboratory, Stamford, Connecticut, maintain a continuing quest for new and improved chemicals and processes for the mining industry. A Technical Service Group, staffed with qualified metallurgists, provides customers with recommendations and information pertaining to ores and mill samples submitted for evaluation. At this laboratory, information gathered from Cyanamid representatives is carefully assessed and added to a vast store of knowledge of mining and metallurgy. In addition, Cyanamid field engineers and technical representatives, skilled in mineral processing technology and trained to advise and assist, are located in mining districts throughout the world (see back page for addresses).

USES AND SPECIAL APPLICATIONS

AERO* Xanthates, under suitable conditions, are excellent collectors for all sulfide minerals. In the absence of modifying agents, they are essentially non-selective in their action. Generally their effectiveness as collectors increases with an increase in the carbon chain length and conversely they become less selective with an increase in carbon chain length. Thus, ethyl xanthate is the weakest and most selective xanthate, and amyl xanthates are the most powerful and least selective collectors. In conjunction with a sulfidizing agent, such as sodium sulfide, or sodium hydrosulfide, they are good collectors in the flotation of oxidized lead and copper ores. For this application, isopropyl and amyl xanthates are most frequently used.

Cyanamid produces xanthates in easily handled, pelletized form. The pelletized products have a higher bulk density than competitive powdered products. However, the pellets are small enough so that the rate of solubility is not unduly hindered.

The xanthates at present offered by Cyanamid are AERO 317, 325, 343, 350, and 355 Xanthates.

AERO 325 Xanthate - Sodium ethyl xanthate

This xanthate is essentially similar in action to flotation collectors; and being the shortest carbon chain xanthate, has found use particularly where maximum selectivity is desired. It can be used alone or in combination with one or more of the AEROFLOAT* Promoters.

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AERO 317 Xanthate - Sodium isobutyl xanthate

This is a strong, non-selective collector for all sulfide minerals. AERO 317 Xanthate is considered the best xanthate for the flotation of pyrite in natural circuits, that is, in circuits where the pH has not been adjusted with either lime or acid.

AERO 343 Xanthate - Sodium isopropyl xanthate

Because of its lower cost, AERO 343 Xanthate is chosen by mill operators for wide application in copper, lead and zinc sulfide flotation.

AERO 350 Xanthate - Potassium amyl xanthate

This is the most powerful of the AERO Xanthates. It is most useful in operations where a strong, non-selective sulfide collector is desired, and as the collector in "scavenger" flotation operations. AERO 350 Xanthate is chosen in the flotation of copper, copper-lead and copper-nickel minerals, where a strong collector is desired. Because of its nonselectivity, it is frequently the principal collector in the flotation of pentlandite and pyrrhotite minerals.

AERO 350 Xanthate is the preferred xanthate for the recovery of oxide lead and copper minerals after sulfidization, although AERO 343 Xanthate is also used for this purpose.

AERO 355 Xanthate - Sodium amyl xanthate

This addition to the xanthate group of products is, like its counterpart AERO 350 Xanthate, a very powerful nonselective sulfide mineral collector. It can be substituted for AERO 350 Xanthate under all conditions of flotation. Field testing of this product has indicated, in specific instances, superior performance over AERO 350 Xanthate at lower dosages resulting in cost savings.

PHYSICAL AND CHEMICAL PROPERTIES OF XANTHATE SOLUTIONS

A. Specific Gravity

The specific gravities for AERO Xanthate solutions are given in Figures 1-4 and in Table 1. The data were derived from testing solutions of three known concentrations at three temperature levels, 50° F (15° C), 68° F (20° C), and 77° F (25° C), using a hydrometer calibrated @ 60° F/ 60° F. Only the values for 68° F were plotted in the Figures, since specific gravity does not change significantly with temperature.

This information can be used: 1) to determine the rate of solution during the unloading of sparger cars 2) to control the concentration of xanthate solutions in storage and in process and 3) to determine the solution storage requirements for bulk shipments. An example of the latter is as follows:

Determination of the final volume of a 25% by wt. real AERO 343 Xanthate solution, to be prepared by dissolving a 20,000 lb. (as received) bulk shipment. From Figures 14 and 15, it is seen that 20,000 lb. of AERO 343 Xanthate, as received, will require 6,122 U.S.G. (5,100 i.g.) or 51,000 lb. of water to make a 25% by weight real xanthate solution; from Figure 3, page 9, it is seen that the specific gravity of this solution will be 1.101 at 68° F (20° C).

The final volume @ 68°F (20°C) can then be calculated.

Final volume, gallons =

Wt. xanthate (as received) lb. + wt. water required, lb.

 $Ib/gal \times specific gravity @ 68°F (20°C)$

Final volume, U.S.G. = $\frac{20,000 + 51,000}{8.33 \times 1.101}$ = 7,742 gal.

Final volume, i.g. = $\frac{20,000 + 51,000}{1000 + 51,000} = 6,449$ gal.

*Note: i.g. = IMPERIAL GALLON U.S.G. = UNITED STATES GALLON

TABLE I

SUMMARY OF PHYSICAL - CHEMICAL PROPERTIES OF

AERO XANTHATE SOLUTIONS

| | | Solution Conc., % Real Xanthate | S Hydrometer 59°F (15°C) | pecific Gravi calibrated @ 68°F (20°C) | ty 60°F ∕ 60° F 77 F (25°C) | †0 ዋ የF | Crystal oint °C | R 68°F (20°C) | Stability Average % Lo eal Xanthate/ 86°F (30°C) | oss ′Day 104°F (40°C) |
|---|-------------------|--|--------------------------------|--|-----------------------------------|-------------------|-----------------------|------------------|---|-----------------------------|
| | AERO 317 Xanthate | 10 25 35 | 1.036 1.087 1.118 | 1.034 1.084 1.117 | 1.032 1.081 1.112 | 27 16 9 | -3 -9 -13 | 0.6 0.6 | 1.8 1.6 | 3.6 4.0 |
| 6 | AERO 325 Xanthate | 10 25 35 | 1.048 1.122 1.174 | 1.046 1.119 1.171 | 1.045 1.117 1.168 | 27 12 •10 | -3 -11 -12 | 1.1 0.7 | 2.7 2.0 | 4.6 4.3 |
| | AERO 343 Xanthate | 10 25 30 | 1.041 1.103 | 1.040 1.101 | 1.039 1.098 1.116 | 25 •34 •>68 | -4 1 >20 | 0.3 0.2 | 0.6 0.7 | 1.8 1.7 |
| | AERO 350 Xanthate | 10 25 35 | 1.037 1.088 1.122 | 1.036 1.086 1.119 | 1.035 1.084 1.116 | 27 •48 •66 | -3 9 19 | 0.8 0.7 | 2.1 2.0 | 4.2 4.8 |

•The solid phase is xanthate, if no asterisk the solid phase is ice.

† The temperature at which crystals first appear and below which storage is not advisable.





FIGURE 2









×.



AERO 350 Xanthate SPECIFIC GRAVITY @ 68°F (20°C) VS. SOLUTION STRENGTH



B. Solubility

The solubility of AERO Xanthate solutions in water is given in Figures 5-8. Crystal points, taken from the Figures, are given in Table I. For a given concentration, storage at any temperature below the curves in Figures 5-8 will result in solids formation. It is evident from the Figures that even dilute solutions should not be stored outside in winter.

FIGURE 5 SOLUBILITY OF AERO 317 Xanthate











FIGURE 7 SOLUBILITY OF AERO 343 Xanthate









C. Stability

1. General

The decomposition of xanthate solutions occurs mainly by hydrolysis and is temperature dependent. It is also accelerated by low pH; this would only be a factor if acid were accidentally added to a xanthate solution.

Table 1 gives the average percent loss of real xanthate per day. This is based on total xanthate content and it is not the same as numerical drop in assay. Thus a 25% solution of AERO 343 Xanthate stored at 20° C. with an average percent loss per day of 0.2% would have a 0.05% numerical drop per day initially.

The Figures 9-12 show the numerical drop of 10% and 25% solutions with time (or rate of decomposition).

2. Products of Decomposition

The mechanism by which xanthate decomposes is as follows:



(where X is sodium or potassium)

The decomposition products are alcohols, carbonate and trithiocarbonate salts and the flammable carbon disulfide. The latter is very hazardous if formed in sufficient quantity (see Safety Discussion, p. 31).

The amount of carbon disulfide released by decomposition has not been measured, but an estimate can be made using the preceding reaction equation which shows that three moles of carbon disulfide form when six moles of xanthate decompose. For example, in the case of AERO 343 Xanthate

> Ib. carbon disulfide released Ib. xanthate decomposed $3 \times \text{molecular wt. carbon disulfide}$ $6 \times \text{molecular wt. xanthate}$ $= \frac{3 \times 76}{6 \times 158} = 0.24$

If a mill had an inventory of 1,000 i.g. (1200 U.S.G.) gals. of a 10% solution of this xanthate, the amount of carbon disulfide released at a decomposition rate of 0.3% per day would be:

$$= \frac{0.3 \text{ lb. decomposed}}{(100 \text{ lb. xanthate}) (day)} \times 1,000 \text{ i.g. sol'n.}$$

$$= \frac{10.4 \text{ lb. sol'n.}}{\text{i.g.}} \times \frac{0.10 \text{ lb. xanthate}}{10.24 \text{ lb. carbon disulfide}}$$

$$\times \frac{0.24 \text{ lb. carbon disulfide}}{\text{lb. decomposed}}$$

= 0.7 carbon disulfide per day

Table 2 summarizes the maximum amount of carbon disulfide released per day by 10% and 25% solutions of xanthate products. On forming, some of the carbon disulfide will decompose to carbonate and thiocarbonate salts. Some of the remainder will evaporate and the rest will buildup in the xanthate solution until its solubility is exceeded when it will form a separate layer. This layer could also contain some xanthate and some alcohol, another decomposition product. The separate layer will form below the xanthate solution in AERO 325, and 343 Xanthates. It may accumulate in dead spaces such as the bottom of a storage tank or, with the proper piping arrangement, it can be purged continuously into the flotation circuit. However, the separate layer will form above the xanthate solution in AERO 317, 350, and 355 Xanthates, and present a serious fire hazard unless the storage tank is properly vented (see Safety Precautions, page 31).

TABLE 2

POUNDS CARBON DISULFIDE FORMATION PER DAY PER 1,000 i.g. (1,200 U.S.G.) of 10% and 25% SOLUTIONS

| | 10% Sc | Stored at: | 25% Solutions Stored at | | | |
|-------------------|--------|------------|-------------------------|------|-------|-------|
| Xanthate Type | 20°C | 30°C | 40°C | 20°C | 30°C | 40°C |
| AERO 317 Xanthate | 1.4 | 4.1 | *8.2 | 3.5 | •9.5 | •24.7 |
| AERO 325 Xanthate | 3.0 | •7.4 | +12.5 | •5.1 | +14.5 | •31.0 |
| AERO 343 Xanthate | 0.7 | 1.5 | 4.5 | 1.3 | 4.6 | 11.0 |
| AERO 350 Xanthate | 1.6 | 4.1 | •8.3 | 3.6 | 10.3 | •24.7 |

*Indicates formation of a separate layer of carbon disulfide in the solutions during two weeks storage.

The separate layer rises to the top in AERO 317, 350 Xanthate and 355 solutions and settles to the bottom in the others.

Same and



AERO 317 Xanthate SOLUTIONS









DECOMPOSITION OF AERO 343 Xanthate SOLUTIONS







D. Determination of Active Xanthate in Xanthate Solutions by the Acetone Method

1. Apparatus

Fisher Vacuum Filtrator (tall-form) equipped with a long stem funnel and Witt plate

A source of heat maintained between 45°C and 55°C (hot plate or water bath)

- 1 25-ml. Pipette
 2 50-ml. Burettes
 1 250-ml. Erlenmeyer Flask with Stopper
 1 250-ml. Volumetric Flask
 2 150-ml. Beakers
 1 Transfer Funnel
 Glass Stirring Rods
- 2. Reagents

Hydrochloric Acid — 0.1N Standard Sodium Hydroxide — 0.1N Standard Acetone (Dry) Methyl Red Indicator — 0.2% Aqueous Aqueous slurry of long fiber asbestos

3. Procedure

Weigh an 8-gram sample to the nearest milligram. Keeping the volume to approximately 100-ml., wash the sample into a 250-ml. Erlenmeyer flask with acetone. Stopper the flask and shake and allow the sample to stand for at least five minutes.

In the meantime, prepare an asbestos pad on the Witt plate of the filtrator funnel. Carefully wash the asbestos first with distilled water and then with acetone under vacuum. Discard all washings.

The same asbestos pad can be reused several times by washing with hot water and then with acetone after each test. Filter the sample into a clean, dry 250-ml. volumetric flask under vacuum in the filtrator assembly. Rinse the sides of the Erlenmeyer flask and funnel and the Witt plate with acetone, allowing the filtrate to mix with the sample solution. Dilute to mark with acetone and mix thoroughly.

Add 35-ml. 0.1N HCl to each of two 150-ml. beakers.

Pipette a 25-ml. aliquot of the sample solution to one of the beakers. Place both beakers in a bath maintained between 45°C-55°C for 15 minutes, with occasional agitation. Remove the beakers and allow the contents to cool to room temperature. Add 2 to 3 drops of methyl red indicator and titrate to an orange-yellow endpoint with 0.1N sodium hydroxide.

4. Calculations

Net Titer = ml. of 0.1N NaOH required for blank ml. of 0.1N NaOH required for sample

Net Titer \times N of NaOH \times M.W. \times 100

% Xanthate = Sample Weight 250 × 25 × 1000

Molecular Weights of Xanthates

172.3 for AERO 317 Xanthate 144.2 for AERO 325 Xanthate 158.2 for AERO 343 Xanthate 202.4 for AERO 350 Xanthate

HANDLING SHIPMENTS

A. Equipment Required for Handling Sparger Car/Truck Shipments of Solid Xanthates

The solid xanthate is shipped in tank cars or tank trucks. The cars usually contain two compartments with 40M lb. per compartment or four compartments with 20M. lb. per compartment. Tank truck shipments can contain up to 40M lb.

For dissolution of the xanthate in the shipment, the following equipment is required.

-1 storage tank (for size required see page 4)

1 pump (SRL centrifugal pump 2" x 3" is satisfactory)

water supply

low pressure steam supply to maintain dissolution temperature in winter

flexible hose with quick coupling connections.

Carbon steel is adequate for the storage tank, all piping and the pump. The flexible hose can be made of rubber. Copper and brass are not recommended for xanthate service.

B. Procedure for Dissolution

- 1. With the tank car/truck connected up as in Figure 13, add the required amount of water to the storage tank. The required amount of water to make 10% and 25% solution strengths can be obtained from Figure 14. All xanthates absorb heat during dissolution so, to achieve rapid dissolution, the water used should be preheated. However, high temperatures (>21°C) should be avoided to limit decomposition. The sodium xanthates heat up in the presence of small quantities of water due to the formation of hydrates and some decomposition could occur; this can be avoided by adding the water for dissolution rapidly.
- 2. Pump water into the tank car/truck and overflow back to the storage tank. The tank car/truck is now under pressure (see note below).
- 3. Recirculate until xanthate is all dissolved, which can be checked by specific gravity measurements in tank car/truck and storage tank.
- NOTE: It is imperative that the safety valve on the tank compartment be in working order when the xanthate is being dissolved and that pressure setting of this valve not be over 15 p.s.i.g. Normally, while the tank car/truck is in transit, the safety valve is inactivated and must be reactivated before the dissolving operation is commenced.

Procedure for Final Unloading

Connect the tank car/truck drain nozzle to the pump suction (Figure 13) and pump the solution into the storage tank.



Water



RECIRCULATION AND DISSOLVING



UNLOADING









Water Required

U.S. Gallons in Thousands





<u>|</u> 70

SAFETY DISCUSSION

A. General

Solid xanthates are stable for months when kept cool and dry. The ignition temperature of dry solid xanthates is in the 250°C range. However, upon exposure to moisture and/or heat, decomposition results and spontaneous combustion can occur. Heat generated by hydration and/or decomposition may raise the temperature to the auto-ignition point of the decomposition product, carbon disulfide (100°C). Occasionally, material in punctured drums has ignited due to circulation of moist air through the pelletized mass. In the event of ignition, the fire may be extinguished with water.

Freshly-prepared xanthate solutions do not normally exhibit a flash point by standard methods until heated to a point, well above room temperature, where decomposition is rapid. However, since xanthates decompose in solution, even at room temperature, hazards develop with aging. The main hazards are due to the decomposition product carbon disulfide (see page 16).

Pertinent properties and characteristics of carbon disulfide are:

| Physical State | Liquid |
|---|---|
| Auto-Ignition Temperature | 100°C |
| Flammable Limits | 1% to 50% by volume in air |
| Flash Point | —30° C |
| Color | Clear, Colorless |
| Odor | Odorless when pure |
| Solubility in water, % CS ₂ in water @ 20°C | 0.210 |
| Specific Gravity @ 20° C/4° C | 1.263 |
| Vapor Pressure @ 28°C | 400 mm Hg (about 4 times higher than acetone) |
| Threshold Limit | 20 ppm or 60 mg/M3 |

B. Safety Precautions in Handling

To avoid any problems with xanthate and its decomposition products, the following precautions are recommended.

- 1. Keep solid xanthates dry and reasonably cool.
- 2. Limit xanthate dusting as much as possible.
- 3. Maintain xanthate solutions at as low a temperature as practical.
- 4. Before pumping xanthate solution from one vessel to another, make sure that all vessels and equipment are properly grounded or bonded to avoid buildup of static electricity.
- 5. Add the water as quickly as possible when dissolving solid xanthate.
- 6. When draining the tank car/truck, drain from the lowest point. This will allow continuous drainage of any separate carbon disulfide layer below the xanthate solution. For the same reason, the solution storage, mixing and mill head tanks should have sloping bottoms and should be drained from their lowest points. If the latter is not possible a syphon should be installed to remove any separate layer. Unless the layer is continuously removed into the flotation circuit it must be collected under a blanket of water.
- 7. The vapor space in a storage tank should have a forced exhaust or purge to atmosphere to prevent any buildup of carbon disulfide to the explosive limits (1% to 50% in air). If possible, the vapor space should be checked regularly with an explosimeter.
- 8. Before returning the empty truck, flush out any remaining

xanthate solution with water. Allow enough space in the xanthate storage tank to take care of the water flush.

- 9. The xanthate storage tank and immediate area must be free from any source of ignition, as contact of carbon disulfide vapors with any surface above 100° C. will cause ignition. Only explosion proof classified light fixtures, conduit, and motors should be used. Smoking must be prohibited and non-sparking tools should be used when opening drums or working on a tank or tank/truck in xanthate service.
- 10. No maintenance work should be performed on a xanthate storage tank or pipe lines leading to or from the tank without first thoroughly washing the tank and pipe lines to remove any sludge. This applies especially to all hot work including soldering, brazing, welding, heating and burning. An explosive test must be taken prior to any hot work.
- 11. Wear eye protection (goggles and face shield) when working directly with xanthate solution. Rubber gloves should also be worn when working with these solutions.
- 12. Solutions of xanthate in sufficient quantity and concentration may be harmful to fish and other aquatic life. Therefore, no solutions of xanthate should be discharged into any well, lake, river, pond, spring, reservoir, or other watercourse.

C. Medical Management

Solutions of xanthate may cause a mild to severe irritation of skin and eye. Prolonged or repeated skin contact and splashes of the product near or into the eyes should be avoided.

In case of contact of solutions with the eyes, the eyes should be flushed immediately with plenty of water for at least 15 minutes, and a physician should be called. Spills on the skin should be washed off promptly with water.

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