Kirk-Othmer Encyclopedia of Chemical Technology.

XANTHATES

The salts of the *O*-esters of carbonodithioic acids and the corresponding *O,S*-diesters are xanthates. The free acids decompose on standing. Potassium ethyl xanthate was first prepared in 1822 by W. C. Zeise from potassium hydroxide, carbon disulfide, and ethanol. Most alcohols, including cellulose, undergo this reaction to form xanthates, but normally phenols do not (see Fibers, regenerated cellulosics). Potassium phenyl xanthate was prepared in 1960 from potassium phenoxide and carbon disulfide in dimethylformamide (1). The preparation of phenolic xanthates has been expanded by the use of dialkyl ethers of mono- or polyethylene glycols or sulfolane (2). Xanthates remained a laboratory curiosity until the turn of the twentieth century when the rubber industry developed a use for them in the curing and vulcanization of rubber (see Rubber chemicals; Rubber compounding). Cornelius Keller's invention of xanthates as flotation collectors for the nonferrous metal sulfides in 1927 (3) ranks as the chemical invention that had the greatest impact in flotation (4) (see Flotation). This is the principal use for the noncellulose xanthates; several of the alkali metal xanthates are commercially available.

1. Nomenclature

The names xanthogenic acid and xanthogen refer to the acid C_2H_5OCSSH and the radical $C_2H_5OCSS—$, respectively. Xanthogenic is still used instead of xanthic and xanthogenate for xanthate, eg, sodium methyl xanthogenate [6370-03-2] for sodium methyl xanthate. The term xanthogen is sometimes used for the radical $HOCSS—$, eg, methyl xanthogen acetic acid for $CH_3OCSSCH_2COOH$. Examples of the current nomenclature are listed in Table 1 with the corresponding common names. The latter names are used in this article.

2. Properties

The free xanthic acids are unstable, colorless, or yellow oils, and may decompose with explosive violence. They are soluble in the common organic solvents and are slightly soluble in water: methyl xanthic acid at 0°C, 0.05 mol/L; ethyl xanthic acid at 0°C, 0.02 mol/L; and *n*-butyl xanthic acid at 0°C, 0.0008 mol/L. Values for the dissociation constant for ethyl xanthic acid are $(2.0\text{–}3.0) \times 10^{-2}$ (5). Potentiometric determinations for C_1–C_8 xanthic acids show a decreasing acid strength with increasing molecular weight (6, 7). The values for the ethyl derivative are $(1.82\text{–}3.4) \times 10^{-3}$. Similar values determined by the same method are reported in Reference 8 for a series in dimethylformamide. Some pK_a values for alkyl xanthic acids are given in Table 2.

The alkali metal salts, in contrast to the free acids, are relatively stable solids, are pale yellow when pure, and sometimes have a disagreeable odor. Pyrolysis studies of the potassium salts of ethyl, isopropyl, *n*-butyl, *sec*-butyl, and *n*-amyl xanthic acids with separation of the gaseous products by gas chromatography are reported in Reference 11. All salts produce carbonyl sulfide, carbon disulfide, thiols, alcohols, sulfides, disulfides, and some aldehydes. A comparison of melting points of xanthates and the temperature interval

Table 1. Nomenclature of Some Xanthic Acids and Related Compounds

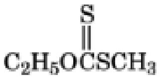
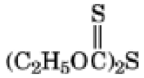
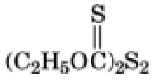
Formula	CAS Registry Number	CAS and IUPAC nomenclature	Common name
 $CH_3O\overset{S \atop \|}{C}SH$	[2042-42-4]	*O*-methyl carbonodithioic acid	methyl xanthic acid
 $C_2H_5O\overset{S \atop \|}{C}SNa$	[140-90-9]	sodium *O*-ethyl carbono-dithioate, sodium *O*-ethyl dithiocarbonate	sodium ethyl xanthate
 $C_2H_5O\overset{S \atop \|}{C}SCH_3$	[623-54-1]	*O*-ethyl *S*-methyl carbono-dithioate	methyl ethyl xanthate
 $(C_2H_5O\overset{S \atop \|}{C})_2S$	[2095-52-4]	diethyl thiodicarbonate, ([(HO)C(S)]$_2$S)	diethyl xanthogen monosulfide
 $(C_2H_5O\overset{S \atop \|}{C})_2S_2$	[502-55-6]	diethyl thioperoxy-dicarbonate	diethyl dixanthogen
 $C_2H_5O\overset{S \atop \|}{C}S\overset{O \atop \|}{C}OC_2H_5$	[3278-35-1]	diethyl thiodicarbonate, ((HO)C(O)SC(S)(OH)) 6-thioxo-3,7-dioxa-5-thio-4-nonane	diethyl xanthogen formate
 $C_2H_5O\overset{S \atop \|}{C}NHCH_3$	[817-73-2]	*O*-ethyl methylcarbamo-thioate, *O*-ethyl methyl-thiocarbamate	ethyl methylthiono-carbamate
 $CH_3O\overset{S \atop \|}{C}Cl$	[2812-72-8]	*O*-methyl carbonochlorido-thioate	methyl chlorothiono-formate
 $CH_3O\overset{S \atop \|}{C}NHC_6H_5$	[13509-41-6]	*O*-methyl phenylcarbamo-thioate, *O*-methyl phenyl-thiocarbamate	methyl phenylthiono-carbanilate
 $C_2H_5O\overset{S \atop \|}{C}SONH_4$	[73085-96-8]	*O*-ethyl carbonothio-(thioperoxate)	ammonium ethyl perxanthate

Table 2. pK_a For Xanthates

Xanthates	pK_a[a]	pK_a[b]
methyl	2.07	
ethyl	2.20	1.43
propyl	2.22	
1-methylethyl	2.44	
butyl	2.23	1.40
2-methylpropyl	2.25	
hexyl		1.51
octyl		1.65

[a] Ref. 9.
[b] Ref. 10.

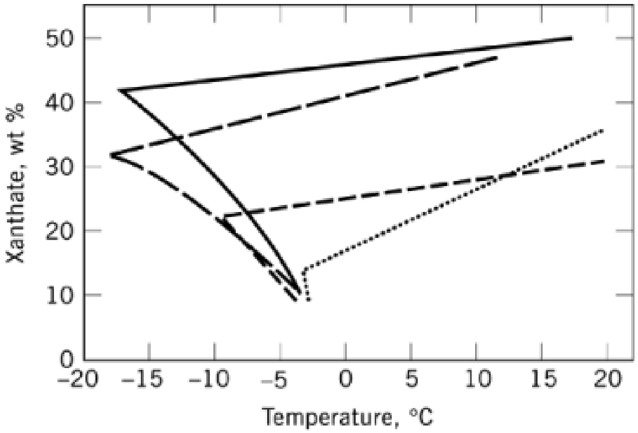


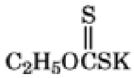
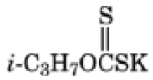
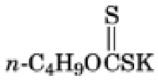
Fig. 1. Solubility of some commercial xanthates. (▬), Sodium isobutyl xanthate; (— —), sodium ethyl xanthate; (— — —), sodium isopropyl xanthate; (....), potassium amyl xanthate. Courtesy of Cytec Industries Inc.

T_{dta} from the start to the end of the differential thermal analysis interval are given in Table 3 (11, 12). The potassium salts of several xanthates derived from tertiary alcohols were pyrolyzed and the yield of olefins was superior to the Chugaev decomposition of the corresponding *S*-methylesters (13). In most cases, the olefin product distributions were almost identical to those obtained from the esters.

When exposed to air, the sodium salts tend to take up moisture and form dihydrates. The alkali metal xanthates are soluble in water, alcohols, the lower ketones, pyridine, and acetonitrile. They are not particularly soluble in nonpolar solvents, eg, ether or ligroin. The solubilities of a number of these salts are listed in Table 4. Potassium isopropyl xanthate is soluble in acetone to ca 6 wt %, whereas the corresponding methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, isoamyl, and benzyl [2720-79-8] xanthates are soluble to more than 10 wt % (12). The solubilities of the commercially available xanthates in water are plotted versus temperature in Figure 1 (14).

The heavy metal salts, in contrast to the alkali metal salts, have lower melting points and are more soluble in organic solvents, eg, methylene chloride, chloroform, tetrahydrofuran, and benzene. They are slightly soluble in water, alcohol, aliphatic hydrocarbons, and ethyl ether (18). Their thermal decompositions have been extensively studied by dta and tga (thermal gravimetric analysis) methods. They decompose to the metal sulfides and gaseous products, which are primarily carbonyl sulfide and carbon disulfide in varying ratios. In some cases, the dialkyl xanthate forms. Solvent extraction studies of a large number of elements as their xanthate salts have been reported (19).

Table 3. Decomposition Temperatures of Alkali Metal Xanthates[a]

Compound	CAS Registry Number	T_{dta}, °C	Mp, °C
 $CH_3O\overset{\overset{S}{\|}}{C}SK$	[2667-20-1]	165–185	182–186
 $C_2H_5O\overset{\overset{S}{\|}}{C}SK$	[140-89-6]	210–225	225–226
 $n\text{-}C_3H_7O\overset{\overset{S}{\|}}{C}SK$	[2720-67-4]	220–240	233–239
 $i\text{-}C_3H_7O\overset{\overset{S}{\|}}{C}SK$	[140-92-1]	230–275	278–282
 $n\text{-}C_4H_9O\overset{\overset{S}{\|}}{C}SK$	[871-58-9]	235–255	255–256
 $i\text{-}C_4H_9O\overset{\overset{S}{\|}}{C}SK$	[13001-46-2]	250–265	260–270
 $s\text{-}C_4H_9O\overset{\overset{S}{\|}}{C}SK$	[141-96-8]	220–260	

[a] Refs. 11 and 12.

The solubilities of the heavy metal xanthates in water have been placed in the following orders of increasing solubility by two different authors (20, 21): Hg^{2+}, Ag^{+}, Cu^{+}, Co^{3+}, As^{3+}, Pb^{2+}, Tl^{+}, Cd^{2+}, Ni^{2+}, Zn^{2+}; and Hg^{2+}, $Hg^{2+}{}_2$, Au^{3+}, Ag^{+}, Cu^{+}, Bi^{3+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}. The solubility products of many of the salts are reported in references (9, 10, 22). The structure of xanthates is rather complicated. It has been shown that the formation and stability of insoluble iron xanthates depends critically on the xanthate concentration, pH, and redox potential of the solutions (23). A good literature survey and review of the chemistry of iron xanthates is given in (23). Critical micelle concentrations and Kraft points for the C_8–C_{12} xanthates are similar to those of other ionic surfactants with equivalent chain lengths (24, 25).

Table 4. Solubilities of Some Alkali Metal Xanthates

			Solubility, g/100 g soln				
Xanthate	CAS Registry Number	Solvent	0°C	10°C	20°C	35°C	Refer-ence
sodium ethyl	[140-90-9]	water	40.8	46.0	52.0		14
potassium *n*-propyl	[2720-67-4]	water	43.0			58.0	15
		n-propyl alcohol	1.9			8.9	15
sodium *n*-propyl	[14394-29-7]	water	17.6			43.3	15
		n-propyl alcohol	10.2			22.5	15
potassium isopropyl	[140-92-1]	water	16.6			37.2	15
		isopropyl alcohol				2.0	15
		IPA-H_2O azeotrope			6.9		16
sodium isopropyl	[140-93-2]	water	12.1			37.9	15
			24.5	27.3	30.5		14
			24.0	27.5	31.0	37.5	17
		isopropyl alcohol				19.0	15
potassium *n*-butyl	[871-58-9]	water	32.4			47.9	15
		n-butyl alcohol				36.5	15
sodium *n*-butyl	[141-33-3]	water	20.0			76.2	15
		n-butyl alcohol				39.2	15
potassium isobutyl	[13001-46-2]	water	10.7			47.7	15
		isobutyl alcohol	1.6			6.2	15
sodium isobutyl	[25306-75-6]	water	11.2			33.4	15
			46.2	48.2	50.5		14
			44.0	49.0	51.0	57.3	16
		isobutyl alcohol	1.2			20.5	15
sodium *sec*-butyl		water	29.4	34.0	38.8		14
potassium isoamyl	[928-70-1]	water	28.4			53.5	15
			16.9	26.0	35.0		14
			28.5	39.0	45.6	52.5	16
		isoamyl alcohol	10.9			15.5	15

Alkalies stabilize xanthate solutions somewhat and the solutions readily decompose at acidic pHs (26, 27). With a lower alkyl xanthate, the decomposition rate passes through a maximum at a low pH and then decreases smoothly as the acidity increases. However, this is not the case with salts of *tert*-butyl xanthic acid [110-50-9] (28). The decomposition accelerates at pH values above 10 or below 9; between these limits, no significant decomposition occurs during 24 h (29). The kinetic studies of the rate of decomposition of alkaline xanthate solutions show a minimum rate constant at pH 10 (30). The results of these studies agree with the report that over an 8-day period, 75% decomposition occurred at pH 6.5 and only 26% at pH 10.8 (31). In Figure 2, the effect of time, temperature, and concentration on aqueous solutions of sodium isopropyl xanthate is shown (14). The stability data for the other xanthates are similar; xanthates prepared from secondary alcohols are more stable than those prepared from the primary alcohols. Branching of the chain and increasing the molecular weight also tends to increase the stability. The benzyl xanthates are less stable, both as solids and in solution.

It was found (32) that in the acid range (pH 4–6) the alkyl group does not influence the rate of decomposition, which is similar for all xanthates. In the alkaline range the rates are markedly influenced by the substitutional group, and the rates could be correlated with the Taft polar substituent constants established for the various groups.

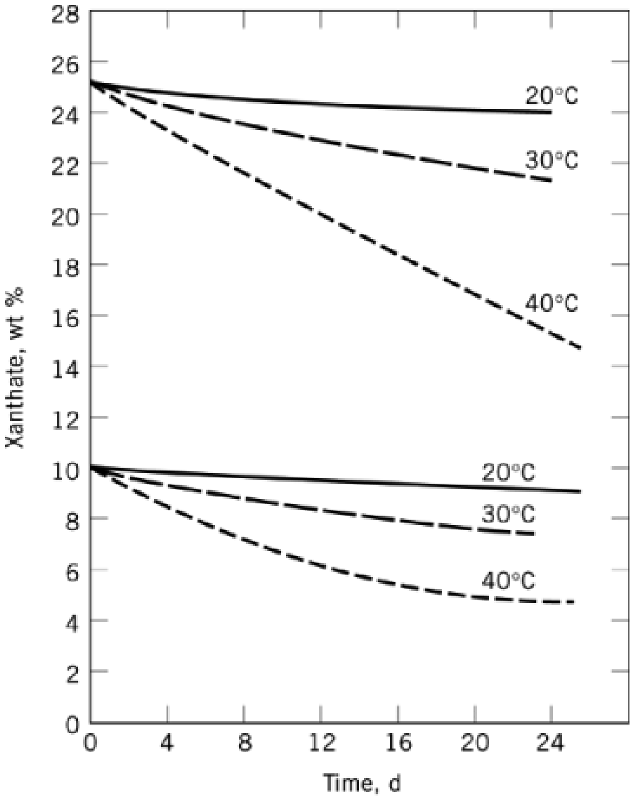


Fig. 2. Decomposition of commercial sodium isopropyl xanthate solutions. Courtesy of Cytec Industries Inc.

2.1. Reactions

The chemistry of the xanthates is essentially that of the dithio acids. The free xanthic acids readily decompose in polar solvents, the rate being 10^6 times greater in methanol than in hexane. The acids decompose at room temperature to carbon disulfide and the corresponding alcohol; the resulting alcohol autocatalytically facilitates the decomposition.

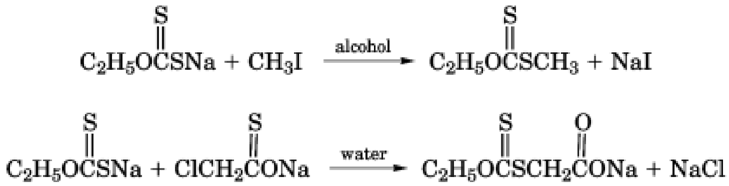
$$\mathrm{ROCSS^- + H^+ \rightleftharpoons RO\overset{\overset{S}{\|}}{C}SH \longrightarrow ROH + CS_2}$$

The initial hydrolysis of the xanthate in aqueous solutions at room temperature is characterized by the following reaction involving potassium ethyl xanthate:

$$\mathrm{6\,C_2H_5OCSK + 3\,H_2O \longrightarrow 6\,C_2H_5OH + 2\,KS\overset{\overset{S}{\|}}{C}SK + K_2CO_3 + 3\,CS_2}$$

Further hydrolysis of the carbon disulfide and the trithiocarbonate produces hydrogen sulfide, etc (33). In another study of the decomposition of sodium ethyl xanthate [140-90-9] in flotation solutions, eleven components of breakdown were studied. The dependence of concentration of those components vs time was examined by solving a set of differential equations (34).

The alkali metal xanthates react readily with the various alkylating reagents to form the *S*-esters:

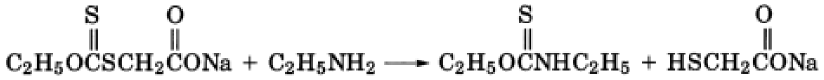


$$C_2H_5O\overset{S}{\overset{\|}{C}}SNa + CH_3I \xrightarrow{\text{alcohol}} C_2H_5O\overset{S}{\overset{\|}{C}}SCH_3 + NaI$$

$$C_2H_5O\overset{S}{\overset{\|}{C}}SNa + ClCH_2\overset{S}{\overset{\|}{C}}ONa \xrightarrow{\text{water}} C_2H_5O\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}ONa + NaCl$$

The reactions are exothermic and cooling may be required.

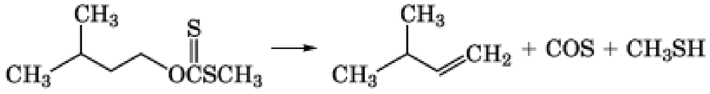
The dialkyl esters react readily with ammonia or alkylamines to give the corresponding thionocarbamates and thiols. In general, heating is not required. In the following reaction, the thionocarbamate is the only water-insoluble material and separates as an oil:



$$C_2H_5O\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}ONa + C_2H_5NH_2 \longrightarrow C_2H_5O\overset{S}{\overset{\|}{C}}NHC_2H_5 + HSCH_2\overset{O}{\overset{\|}{C}}ONa$$

Sterically hindered amines such as *tert*-butylamine react only with this intermediate to give the desired thionocarbamate.

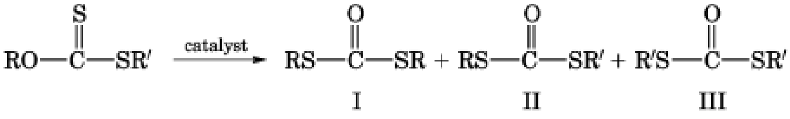
The Chugaev reaction, or thermal decomposition of the *S*-substituted esters of the xanthates, gives olefins without rearrangement (35, 36). For example:



methyl isoamyl xanthate
[*70061-61-9*]

Kinetics data and Arrhenius parameters for the Chugaev reaction are given in Reference 37.

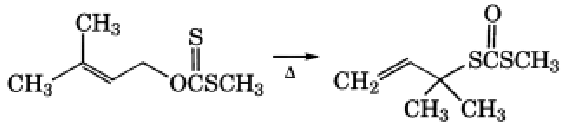
Esters derived from the primary alcohols are the most stable and those derived from the tertiary alcohols are the least stable. The decomposition temperature is lower in polar solvents, eg, dimethyl sulfoxide (DMSO), with decomposition occurring at 20°C for esters derived from the tertiary alcohols (38). Esters of benzyl xanthic acid yield stilbenes on heating, and those from neopentyl alcohols thermally rearrange to the corresponding dithiol esters (39, 40). The dialkyl xanthate esters catalytically rearrange to the dithiol esters with conventional Lewis acids or trifluoroacetic acid (41, 42). The esters are also catalytically rearranged to the dithiolesters by pyridine *N*-oxide catalysts (43):



$$RO-\overset{S}{\overset{\|}{C}}-SR' \xrightarrow{\text{catalyst}} \underset{\text{I}}{RS-\overset{O}{\overset{\|}{C}}-SR} + \underset{\text{II}}{RS-\overset{O}{\overset{\|}{C}}-SR'} + \underset{\text{III}}{R'S-\overset{O}{\overset{\|}{C}}-SR'}$$

The crossover reaction products I and III should be noted (43).

Double bonds in or dialkylamino groups on the alkyl group of the *S*-methyl ester may facilitate isomerization to the dithiol ester (44). For example:



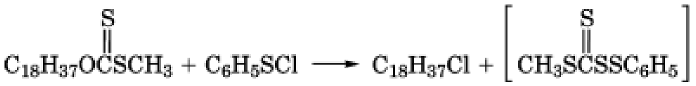
methyl (3-methyl-2-penten-1-yl) xanthate
[*3817-83-2*]

A number of catalysts of Pd(II), Pt(II), Rh(I), and Ir(I) induce rearrangements of *O*-allylic-*S*-methyl dithiocarbonates at 25°C (45).

In a relatively low temperature procedure, olefins readily form from certain classes of xanthate esters (46):

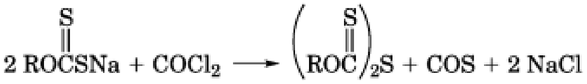
3-cyanoethyl cyclohexyl xanthate
[*85909-63-3*]

The reactions of the xanthate esters with some soft electrophiles proceed with good yields (47):



$$C_{18}H_{37}O\overset{S}{\overset{\|}{C}}SCH_3 + C_6H_5SCl \longrightarrow C_{18}H_{37}Cl + \left[CH_3S\overset{S}{\overset{\|}{C}}SSC_6H_5\right]$$

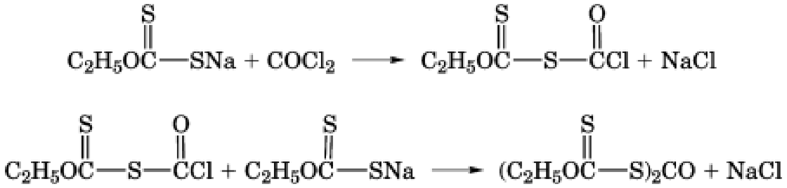
The reaction of phosgene with an aqueous solution of a xanthate and moist ether at 15–20°C gives the anhydrosulfide in good yield (48):



$$2\,RO\overset{S}{\overset{\|}{C}}SNa + COCl_2 \longrightarrow \left(RO\overset{S}{\overset{\|}{C}}\right)_2S + COS + 2\,NaCl$$

The anhydrosulfide forms in the ether layer and is readily separated.

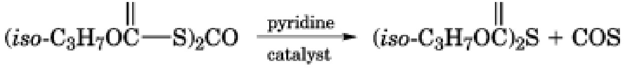
The reaction of xanthates with phosgene proceeds through the following steps (49, 50):



$$C_2H_5O\overset{S}{\overset{\|}{C}}{-}SNa + COCl_2 \longrightarrow C_2H_5O\overset{S}{\overset{\|}{C}}{-}S{-}\overset{O}{\overset{\|}{C}}Cl + NaCl$$

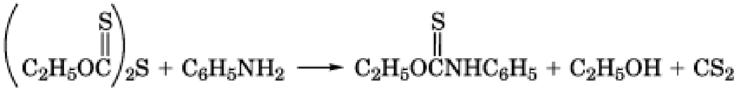
$$C_2H_5O\overset{S}{\overset{\|}{C}}{-}S{-}\overset{O}{\overset{\|}{C}}Cl + C_2H_5O\overset{S}{\overset{\|}{C}}{-}SNa \longrightarrow (C_2H_5O\overset{S}{\overset{\|}{C}}{-}S)_2CO + NaCl$$

In preparing the stable isopropyl derivative, it was found that the following rapid reaction took place (16):



$$(iso\text{-}C_3H_7O\overset{S}{\overset{\|}{C}}{-}S)_2CO \xrightarrow[\text{catalyst}]{\text{pyridine}} (iso\text{-}C_3H_7O\overset{S}{\overset{\|}{C}})_2S + COS$$

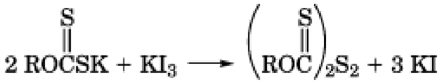
The anhydrosulfides are useful in the preparation of thionocarbamate, eg, by heating with an alcoholic solution of the arylamine:



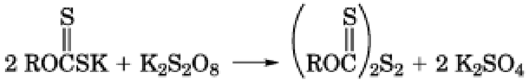
$$\left(C_2H_5O\overset{S}{\overset{\|}{C}}\right)_2S + C_6H_5NH_2 \longrightarrow C_2H_5O\overset{S}{\overset{\|}{C}}NHC_6H_5 + C_2H_5OH + CS_2$$

This method obviates the need to prepare the intermediate aryl isothiocyanate.

Many oxidizing agents, including sodium nitrate, convert the alkali metal xanthates to the corresponding dixanthogen:

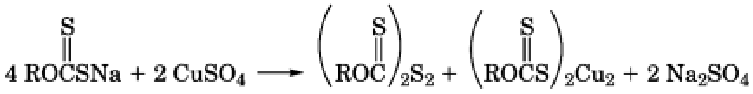


$$2\ RO\overset{S}{\overset{\|}{C}}SK + KI_3 \longrightarrow \left(RO\overset{S}{\overset{\|}{C}}\right)_2S_2 + 3\ KI$$



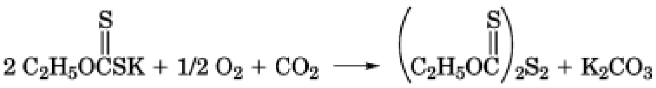
$$2\ RO\overset{S}{\overset{\|}{C}}SK + K_2S_2O_8 \longrightarrow \left(RO\overset{S}{\overset{\|}{C}}\right)_2S_2 + 2\ K_2SO_4$$

The reaction is generally carried out in water, and the resulting dixanthogen separates as a solid or oil. Copper salts also affect the oxidation:



$$4\ RO\overset{S}{\overset{\|}{C}}SNa + 2\ CuSO_4 \longrightarrow \left(RO\overset{S}{\overset{\|}{C}}\right)_2S_2 + \left(RO\overset{S}{\overset{\|}{C}}S\right)_2Cu_2 + 2\ Na_2SO_4$$

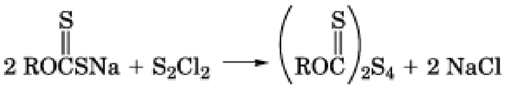
In the initial formation of the cupric xanthates, soluble xanthate complexes form prior to the precipitation of the cuprous xanthate with the concurrent formation of the dixanthogen (51). The dixanthogen can be separated by virtue of its solubility in ether. Older samples of alkali metal xanthates contain some dixanthogen, which is thought to form by the following reaction (33):



$$2\ C_2H_5O\overset{S}{\overset{\|}{C}}SK + 1/2\ O_2 + CO_2 \longrightarrow \left(C_2H_5O\overset{S}{\overset{\|}{C}}\right)_2S_2 + K_2CO_3$$

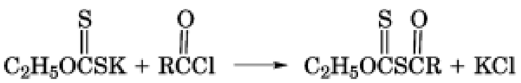
The dixanthogens derived from the aryl xanthates are reported in Reference 52.

The sulfur chlorides give higher xanthate sulfides. For example, the following product is obtained from sulfur monochloride and an ether suspension at room temperature:



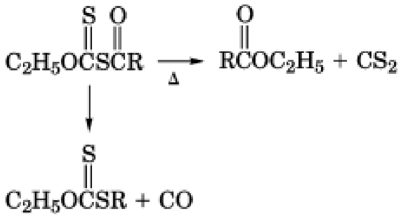
$$2\ RO\overset{S}{\overset{\|}{C}}SNa + S_2Cl_2 \longrightarrow \left(RO\overset{S}{\overset{\|}{C}}\right)_2S_4 + 2\ NaCl$$

Mixed anhydrosulfides can be readily obtained by adding an acetone solution of the xanthate to an acetone solution of the acyl halide at −35°C (53):

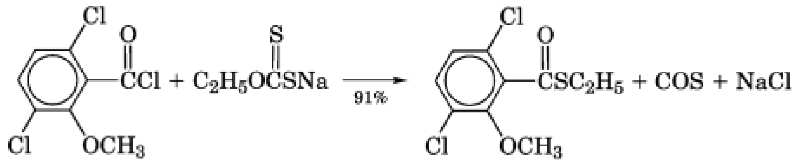


$$C_2H_5O\overset{S}{\overset{\|}{C}}SK + R\overset{O}{\overset{\|}{C}}Cl \longrightarrow C_2H_5O\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}R + KCl$$

The stability of these products varies (38). When R is methyl, the compound decomposes below room temperature, but when R is phenyl it is stable up to 40–45°C. Increasing the molecular weight of the alkyl group and introducing an electronegative group on the phenyl increases the stability. The aliphatic mixed anhydrosulfide can be decomposed by two different routes (53):



Thiol esters are obtained in 91% yield by the addition of aroyl chloride to a slurry of an alkaline salt xanthate in acetone without cooling (54):

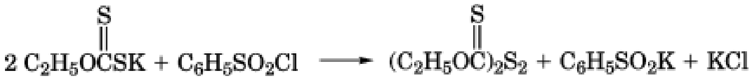


Benzoyl chloride and sodium isopropyl xanthate gave a mixed anhydride that was stable to pyridine catalyst, but a 2-year-old sample had turned to isopropyl benzoate (16).

The alkyl chloroformates react with cold ethereal dispersions of the xanthates to give the fairly stable xanthogen formates.

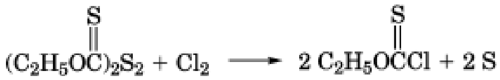
$$C_2H_5O\overset{S}{\overset{\|}{C}}SNa + C_2H_5O\overset{O}{\overset{\|}{C}}Cl \longrightarrow C_2H_5O\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}OC_2H_5 + NaCl$$

In the reaction between xanthates and sulfonyl chlorides, the xanthates convert to dixanthogens, and the sulfonyl chlorides reduce to sulfinic acids and other compounds (38):



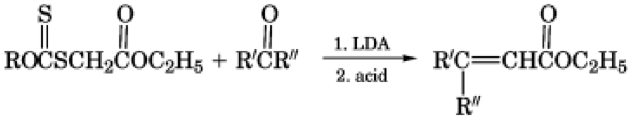
$$2\ C_2H_5O\overset{S}{\overset{\|}{C}}SK + C_6H_5SO_2Cl \longrightarrow (C_2H_5O\overset{S}{\overset{\|}{C}})_2S_2 + C_6H_5SO_2K + KCl$$

The acid chlorides of the xanthic acids can be prepared by the reaction of chlorine with a dixanthogen (55):



$$(C_2H_5O\overset{S}{\overset{\|}{C}})_2S_2 + Cl_2 \longrightarrow 2\ C_2H_5O\overset{S}{\overset{\|}{C}}Cl + 2\ S$$

The *S*-alkoxycarbonylmethylxanthate esters treated with lithium diisopropylamide (LDA) and an aldehyde or ketone give excellent yields of α,β-unsaturated esters (56):



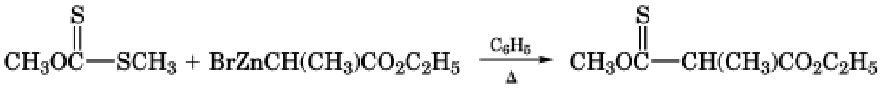
$$\mathrm{RO\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + R'\overset{O}{\overset{\|}{C}}R'' \xrightarrow[\text{2. acid}]{\text{1. LDA}} R'\underset{\underset{R''}{|}}{C}{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5}$$

The Knoevenagel reaction is unsatisfactory for the direct preparation of these reaction products.

In the Leuckart thiophenol synthesis, the reaction of xanthates with diazonium compounds may be violent. The reaction can be controlled, however, by thermal decomposition of the intermediate azo compounds as it forms; this provides a convenient and easy method of preparing the aryl esters, which can be saponified to the thiophenols. The crude reaction mixture is a more complex mixture than just an aryl alkyl xanthate (57):

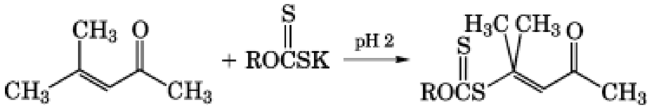
$$\mathrm{C_2H_5O\overset{S}{\overset{\|}{C}}SK + C_6H_5N_2Cl \longrightarrow C_2H_5O\overset{S}{\overset{\|}{C}}SC_6H_5 + N_2 + KCl} + \text{other products}$$

The Reformatskii reaction was carried with the dimethyl xanthate ester (58):



$$\mathrm{CH_3O\overset{S}{\overset{\|}{C}}{-}SCH_3 + BrZnCH(CH_3)CO_2C_2H_5 \xrightarrow[\Delta]{C_6H_5} CH_3O\overset{S}{\overset{\|}{C}}{-}CH(CH_3)CO_2C_2H_5}$$

Xanthates have been added to activated double bonds, eg, acrylic derivatives and α,β-unsaturated aldehydes and ketones (59–61):



The alkali metal xanthates react with the lower alkylamines in the presence of catalytic amounts of nickel or palladium salts to give dialkylthionocarbamates (62):

$$\mathrm{(CH_3)_2CHO\overset{S}{\overset{\|}{C}}SNa + C_2H_5NH_2 \xrightarrow{Ni^{2+}} (CH_3)_2CHO\overset{S}{\overset{\|}{C}}NHC_2H_5 + NaSH}$$

2.2. Peroxyxanthates

A new factor in the theory and practice of flotation was found in the Mount Isa, Australia, copper flotation solution. Secondary butyl perxanthate was formed by the reaction of the xanthate with hydrogen peroxide in dilute alkaline aqueous solution and was found to be identical to a substance from the flotation solution:

$$sec\text{-}\mathrm{C_4H_9O\overset{S}{\overset{\|}{C}}{-}SK + H_2O_2 \longrightarrow} sec\text{-}\mathrm{C_4H_9O\overset{S}{\overset{\|}{C}}{-}S{-}OK + H_2O}$$

The perxanthate was isolated as the ammonium salt [69848-99-3] (63).

3. Preparation and Manufacture

The alkali metal xanthates are generally prepared from the reaction of sodium or potassium hydroxide with an alcohol and carbon disulfide. The initial reaction is the formation of the alkoxide, which reacts with carbon disulfide to give the xanthate:

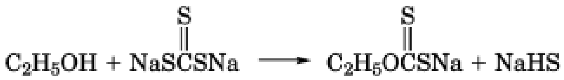
$$\mathrm{ROH + NaOH \rightleftharpoons RONa + H_2O}$$

$$\mathrm{RONa + CS_2 \longrightarrow RO\overset{\overset{S}{\|}}{C}SNa}$$

The overall heat of reaction for potassium isopropyl xanthate is 48.5 kJ/mol (11.6 kcal/mol) (64). The presence of water favors the principal side reaction:

$$\mathrm{6\ NaOH + 3\ CS_2 \longrightarrow 2\ Na_2CS_3 + Na_2CO_3 + 3\ H_2O}$$

Where no water is present, very pure xanthates form (65). Ethanol reacts slowly with sodium trithiocarbonate to produce sodium ethyl xanthate (66):



$$\mathrm{C_2H_5OH + NaS\overset{\overset{S}{\|}}{C}SNa \longrightarrow C_2H_5O\overset{\overset{S}{\|}}{C}SNa + NaHS}$$

The nature of the inorganic by-products in technical xanthates varies, depending upon their exposure to air. Thus, Na_2S, Na_2SO_4, and $Na_2S_2O_3$ may be present in older samples exposed to air (67).

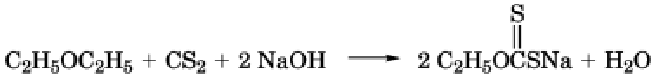
In the case of tertiary and some of the more complex alcohols, the use of alkali hydroxides is not feasible, and it is necessary to use reagents such as sodium hydride, sodium amide, or the alkali metal to form the alkoxide:

$$\mathrm{2\ ROH + 2\ K \longrightarrow 2\ ROK + H_2}$$

Powdered KOH in DMF (dimethylformamide) or DMSO reacts with carbon disulfide to give these xanthates.

Various xanthates can be readily prepared in the laboratory from alcohols (up to C_{16}), potassium hydroxide, and carbon disulfide (68).

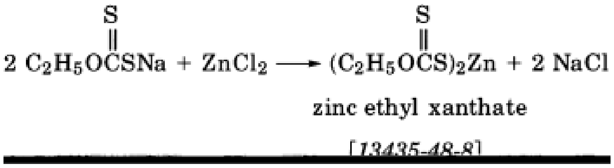
Another, quite different procedure is the preparation of xanthates from ethers (69):



$$\mathrm{C_2H_5OC_2H_5 + CS_2 + 2\ NaOH \longrightarrow 2\ C_2H_5O\overset{\overset{S}{\|}}{C}SNa + H_2O}$$

In a study of the influence of temperature (30–45°C) on the preparation of isopropyl xanthates, it was determined that increasing the temperature resulted in a decrease in the xanthate yield and an increase in by-products. Also, a decrease in the water content of the alcohol increases the xanthate yield (70).

Many of the heavy metal xanthates have been prepared from aqueous solutions of the alkali metal xanthates and the water-soluble compound of the heavy metal desired.



$$2\,C_2H_5O\overset{\overset{S}{\|}}{C}SNa + ZnCl_2 \longrightarrow (C_2H_5O\overset{\overset{S}{\|}}{C}S)_2Zn + 2\,NaCl$$

zinc ethyl xanthate

[13435-48-8]

A modified and detailed procedure is given for the preparation of the corresponding Cr^{3+}, In^{3+}, and Co^{3+} xanthates in good yields and high purity (18). A structural study review of inorganic xanthates (29 metals) of the common xanthates was presented. The emphasis was on single-crystal x-ray methods; some solid-state nmr studies were included. The average C–S bond distance of 1.682×10^{-4} microns is intermediate between the values expected for a single bond distance of 1.81×10^{-4} microns and a $C{=}S$ distance of 1.62×10^{-4} microns (71).

3.1. Alkali Metal Xanthates

The commercially available xanthates are prepared from various primary or secondary alcohols. The alkyl group varies from C_2 to C_5 and the alkali metal may be sodium or potassium. Not all of the commercially available alcohols in the C_2–C_6 range are available as their xanthates, but most could be made if there were sufficient demand for them. Except for a few foreign articles and the old reports of the U.S. Office of Technical Services, most information on the manufacture of xanthates is in the patent literature. The important patent on flotation uses of xanthates appeared in 1927 (3), and all articles and patents on the manufacture of xanthates have appeared since then (72–82).

Steel (qv) generally is suitable as a material of construction for the apparatus used in the manufacture of xanthates. Cooling is required to minimize side reactions. The reaction temperature is generally maintained below 40°C. In one procedure, the reaction is carried out in an inert diluent, eg, petroleum ether (72–76). A plant in the former Federal Republic of Germany employed this method for the preparation of sodium amyl and sodium hexyl xanthate. The copper kettles were equipped with stirring and cooling apparatus. A petroleum ether slurry was made of equimolar quantities of powdered sodium hydroxide and the alcohol. Carbon disulfide was added and the temperature was maintained at ca 35–40°C. After 3 h, the product was separated by filtration, washed with petroleum ether, and dried. The Dow Chemical xanthate plant, which is no longer in operation, in a similar manner used pentane as a diluent and the heat of reaction was dissipated by the refluxing of the pentane (bp 36°C), which prevented overheating of the reaction mixture. The reactants and diluent were added to four steel reactors in series, which were equipped with stirrers and condensers. The product was fed from the last reactor to a spray dryer, then to a pelletizer, and finally to the drumming equipment. The spray dryer minimized the thermal decomposition of the product in the drying step. The volatile organic materials were recycled. The annual capacity of the plant was 13,600 metric tons of xanthates.

For the manufacturing of potassium ethyl xanthate, 400% excess of alcohol and equimolar quantities of 50 wt % aqueous potassium hydroxide and carbon disulfide were used (77). After 30 min at 40°C, the mixture was vacuum drum dried. The product was obtained in near quantitative yield and assayed at 95%. It is claimed that potassium amyl xanthate can be made with almost the same ratio of reactants and 80 wt % caustic potash (78).

Xanthates have been synthesized from C_6–C_8 oxo alcohols in a reactor with intensive stirring at 25°C. The water and unreacted alcohol are removed from the product at 40–50°C under vacuum to give a friable powder of 80% purity in 77% yield (79) (see Oxo process; Alcohols, higher aliphatic).

In another process, 50–150% excess carbon disulfide and a small excess of powdered alkali hydroxide are added, with stirring and cooling to the lower alkyl alcohol. After completion of the reaction, the excess CS_2 and resulting water of reaction are removed by applying a vacuum to the reactor (80).

The most important hazard in the manufacturing of xanthates is the use of carbon disulfide (qv) because of its low flash point, ignition temperature, and its toxicity. A report on the manufacture of sodium ethyl xanthate at Kennecott Nevada Mines Division discusses the various safety problems and the design of a facility (81). A plant layout and a description of the reagent preparations are also given.

One patent describes a continuous process involving an aqueous alkali metal hydroxide, carbon disulfide, and an alcohol (82). The reported reaction time is 0.5–10 min before the mixture is fed to the dryer. The usual residence time is on the order of hours. A study in the former USSR reported the use of the water–alcohol azeotrope for water removal from isobutyl or isoamyl alcohol and the appropriate alkali hydroxide to form the alkoxide prior to the addition of carbon disulfide (83).

Because of hydrate formation, the sodium salts tend to be difficult to dry. Excess water over that of hydration is believed to accelerate the decomposition of the xanthate salts. The effect of heat on the drying of sodium ethyl xanthate at 50°C has been studied (84):

Time of heating, h	Xanthate content, wt %
0	79.32
40	74.38
64	65.66
88	65.06
112	63.85
136	60.41

4. Economic Aspects

The two main producers of xanthates in the United States, ie, American Cyanamid and Dow, shut down their plants in the 1970s. American Cyanamid transferred its production to Canada, and since then has shut down that plant. Xanthates in solution are available in some areas of the United States and Canada and are transported locally by truck. The U.S. consumption of xanthates for froth flotation was ca 1,812 t/yr in 1985 (85). In the previously non-Soviet bloc the 1995 xanthate usage was estimated at 30,000 metric tons, and in China and Russia at 25,000 metric tons, for a worldwide total of 55,000 metric tons. The estimated current number of xanthate plants in the world is 14–16, with one in the United States and one in Canada.

General price information for 1996 on commercially available xanthates from a Canadian company is given in Table 5. Prices are approximate based on truckload shipments within the continental United States (excluding Alaska).

Table 5. Prices of Commercially Produced Canadian Xanthates, 1996[a]

Xanthate	Price, $/kg
sodium isopropyl	1.50
potassium ethyl	1.32
potassium isobutyl	1.58
potassium amyl	1.54

[a] Both the sodium and potassium salts are available in drums, FIBCs and boxed FIBCs.

5. Standards

The alkali metal xanthates are obtainable in the technical grade only, and they vary in particle size from powder to pellets. The color is any of various shades of yellow and the odor is unpleasant. There are no published specifications for the xanthates, but each manufacturer has its own standards. The assay on the commercial materials is usually ca 90–95%. The assay does not necessarily indicate the collector ability of a xanthate (see Flotation). Although all xanthates decompose to some extent on prolonged storage, such decomposition does not necessarily result in a corresponding reduction in mineral-collecting power. This lack of correlation between xanthate content and flotation-collecting ability has been noted in products produced by different methods. Apparently, some of the xanthate oxidation or decomposition products are effective as flotation agents.

The material is shipped in steel drums. The U.S. Department of Transportation (DOT) regulations for the xanthates is the hazardous material description ORM—A (other regulated material—regulated by air), NOS.

6. Analytical Methods

Although there are several published analytical procedures, many are either tedious or inaccurate. For example, when assayed by the standard KI_3 method, the copper sulfate method, or the aqueous acid method, certain of the inorganic impurities assay as xanthate, thereby giving high results (86, 87). When specifications are drawn up for xanthate content, the method of assay should be given. In a satisfactory procedure developed by The Dow Chemical Company, the xanthate content is determined by dissolving the sample in acetone, removing the inorganic solids by filtration, decomposing the xanthate with an excess of standard acid, and back-titrating with a standard base. The components of the inorganic solid left on the filter can be determined by any standard procedure. The water content can be determined by the Karl Fischer method (88). The nonxanthate organic material can be determined by extraction with ether. The uv absorption spectra of xanthates have been extensively used for the assay of dilute solutions of the latter (26, 89). The interference of trithiocarbonates can be avoided through the formation of a nickel xanthate. The latter is extracted into heptane and the absorbance spectrum (425 nm) is measured (90).

The successful separation of xanthate-related compounds by high performance liquid chromatography (hplc) methods has been reported (91–93). The thin-layer chromatography procedure has been used to determine the nature of the alcohols in a xanthate mixture. A short run of 3 cm at a development time of 25 min gives a complete separation of C_1–C_5 alkanol xanthates (94).

The analysis of solutions of technical xanthates by Ag^+ potentiometric titration, with the addition of ammonium hydroxide, has been successfully used at Dow (95).

The separation of xanthates by ion-interaction reversed-phase column chromatography is described for the determination of eight different xanthates in reagents commonly used in flotation plants. The separated species were detected spectroscopically at a wavelength of 305 nm (96).

7. Health and Safety Factors, Toxicology

Most of the published data on the toxicity of the xanthates are given in the foreign literature. The xanthates are low in acute and oral toxicity, as indicated in Table 6. Potassium amyl xanthate causes extensive pain and slight corneal injury to the eye and may burn the skin on prolonged contact. In a chronic toxicity study of this xanthate, an aqueous aerosol was applied to dogs, rabbits, rats, and mice. There were no adverse effects in the latter three at 23 mg/m^3, but liver damage occurred in dogs exposed to this level. A no-effect level was not determined. The recommended airborne industrial hygiene guide (IHG) is 1 mg/m^3 (100). The maximum permissible concentrations recommended for ethyl xanthogenate is 0.5 mg/m^3 and 1.0 mg/m^3 for isopropyl, isobutyl, and isoamyl xanthogenates (102). Note: Consumption of alcohol and exposure to xanthates have a synergistic effect (103).

Table 6. Oral Toxicity of Xanthates

Xanthate	Species	LD_0, mg/kg	LD_{50}, mg/kg	References
sodium ethyl	rat	500		97
potassium ethyl	rat	500	1700	(97, 98)
	mouse		583	98
sodium isopropyl	rat	250		97
potassium isopropyl	rat		1700	98
	mouse		583	98
potassium *n*-butyl	mouse		411, 465	(99, 100)
sodium isobutyl	rat	500		97
potassium isobutyl	rat		1290	98
	mouse		480	98
sodium *sec*-butyl	rat		>2000	97
potassium amyl (mixed)	rat	1000	1000–2000	(97, 101)
potassium isoamyl	rat		765	98
	mouse		470	98

The alkali metal xanthates are fairly safe to handle. The standard precautions of rubber gloves, dust mask, and goggles are sufficient when handling the solid or the solution. If xanthates come in contact with the body, dermatitis may result, although susceptibility varies from person to person. Contaminated clothing should be laundered before being worn again. Internally, whether in the form of dust or fumes, the xanthates act similarly to carbon disulfide. The possible formation of carbon disulfide in xanthate solutions requires that proper care be taken in the preparation and handling of these solutions to avoid possible fires and explosions (14).

Under regulations for the enforcement of the Federal Insecticide, Fungicide, and Rodenticide Act, products containing over 50 wt % sodium isopropyl xanthate must bear the label “Caution. Irritating dust. Avoid breathing dust, avoid contact with skin and eyes” (104). Rubber goods in repeated contact with food may contain diethyl xanthogen disulfide not to exceed 5 wt % of the rubber products. The upper limit for butyl dixanthogen [105-77-1], for diisopropyl xanthogen polysulfide (a 1:2:1 mixture of the trisulfide [52584-27-7], tetrasulfide [69303-50-0], and the pentasulfide), and for zinc butyl xanthate [150-88-9] is 1.5 wt % (105, 106).

Xanthate drums should be kept as cool and dry as possible. Protection from moisture is the most important factor. A combination of moisture and hot weather causes sodium ethyl xanthate to ignite spontaneously (14).

7.1. Environmental Concerns

Concern for the well-being of the environment has resulted in studies on the effects of mining chemicals, including the xanthates, on various aquatic organisms worldwide (107–110). In a thorough and detailed study of three typical mill operations, it was concluded that residual organic flotation reagents do not seem to present widespread problems in effluent disposal. A large portion of the reagents used never reached the final discharge. Biodegradation appears to be the commonest method of reagent removal. At levels below 20–25 mg/L, the xanthates are biodegradable (111).

8. Uses

Besides the importance of cellulose xanthates in the manufacture of rayon and cellophane, the primary use for the alkali metal xanthates is as collectors in the flotation of metallic sulfide ores. The xanthates are the principal metal sulfide collectors. A great deal of experimental work on the production methods and potential uses of the starch xanthates has been reported (112). Allyl amyl xanthates are still useful reagents in the flotation of copper–molybdenum sulfide ores. Other uses of the xanthates are very minor. This is not so much the result of the lack of activity or performance of these compounds as it is the fact that superior products are available. Xanthates and derivatives have been recommended for the vulcanization of rubber (see Rubber chemicals; Rubber compounding), as herbicides (qv), insecticides, fungicides, high pressure lubricant additives, and for analytical procedures (see Insect control technology; Fungicides, agricultural; Lubrication and lubricants).

In addition to a continued increase in the number of use patents in these fields, a new use of xanthates as inhibitors of fertilizer nitrogen transformation in soil has been reported, as well as the use of certain metal xanthates as color developers for image-recording materials (113, 114) (see Fertilizers; Color photography). For several years, sodium isopropyl xanthate was used as an intermediate in the manufacture of saccharin (see Sweeteners).

Xanthates are used in a froth flotation process of soils contaminated with mercury. The soil to be treated is run through hydrocyclones, and the slurries are flocculated, dewatered, and removed to a secure landfill. The effluent water is recycled. The process is suitable for treating industrial land sites contaminated with mercury droplets (115).

9. Derivatives

The principal derivatives are of four types. The dixanthogens, shown herein, were

$$(\mathrm{RO}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}})_2\mathrm{S}_2$$

produced at one time as additives for polymers and isopropyl dixanthogen is now available from a Mexican producer of xanthates. The mixed anhydrosulfides, ie, the xanthogen formates, are used in acid pulp flotation of sulfide ores. The most important one, diethyl xanthogen formate, has been used in Chile for over 50 yr. Dialkyl thionocarbamates are used in the flotation of copper and zinc sulfides, in particular where the rejection of iron pyrites is important. The two principal products are isopropyl ethylthionocarbamate and butyl ethylthionocarbamate. The *S*-alkyl xanthate esters ($\mathrm{ROCS{-}S{-}CH_2{-}CH{=}CH_2}$, $\mathrm{R{=}C_{4-6}}$) have been found to be particularly effective on molybdenite and copper–molybdenite ores.

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