Dianzuo Wang

Flotation Reagents: Applied Surface Chemistry on Minerals Flotation and Energy Resources Beneficiation

Volume 2: Applications

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Dianzuo Wang
Chinese Academy of Engineering
Beijing
China

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Preface

The development of minerals processing over one hundred years has shown flotation, a predominant process of materials separation. Nowadays, flotation is widely used in minerals separation, treatments of slag and wastes, materials separation and valuables recovery in metallurgical, coal, and chemical engineering. Flotation reagents have played vital roles in the progress of flotation process. The development and application of the reagents have made it possible for more and more traditional refractory ores and materials to be treated by flotation process with high efficiency.

Several books on flotation principles and reagents have been published, however, for further improvement of current minerals processing performance and for the treatment and recovery of refractory and nontraditional mineral and energy resources, scientists need to develop new reagents and innovative processes.

The author of this book took up investigation of flotation reagents in 1960s. The fundamentals and approaches of surface chemistry have been applied in the round to discuss the structure, performance of the reagents, and the interaction between the reagents and minerals, as well as to set up theoretical criteria for collector performance. Molecular orbit method incorporating with molecular design was used to have obtained quantum chemistry parameters, steric configuration, HOMO, and LUMO surface of various reagents. This book has summarized the results that the author has achieved on functional principle of flotation reagents in the last fifty years.

The Chinese edition of this book was published in 1982 and reprinted in 1994 by Metallurgical Industry Press. This English edition, on the basis of Chinese edition, has incorporated the new findings on the topic in particular the molecular design of reagents achieved by the author and his research group. This book is intended for worldwide university teachers, researchers, R&D engineers, and graduate students in minerals processing, extractive metallurgy and resources utilization who wish to explore innovative reagents and technologies that lead to more energy-efficient and environmentally sustainable solutions.

In time of publication of the English edition, I would like to acknowledge cooperation and contributions to the contents of this book from my colleagues and graduate students. A special acknowledgment is warranted to Dr. Guihong Han, who completed the onerous translation of this book with his dedication and persistence. I give my sincere thanks to Prof. Tao Jiang, who undertook the proposal for the publication and helped to review the first draft. Thanks also to Mr. Xiaofeng Liu (editor of Metallurgical Industry Press), who encouraged and helped to complete this project.

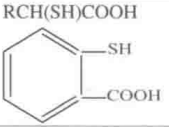
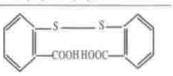
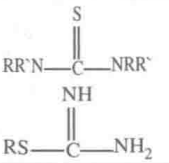
Beijing, China
December 2015

Dianzuo Wang

Contents

Chapter 1
Collectors for Sulfide Minerals

The applications of these collectors for sulfide minerals are mainly introduced in this chapter. According to structure characteristics, the categories of collectors for typical sulfide minerals can be given by the following.

Bonding atoms	Group	Dhio	Dithio	Esterifiable product	Disulfide
1. C—S C—S—C	Mercaptan Thioether	RSH RSR′	– –	– –	– –
2. C—S—C | O(S)	Thiocarbonic acid	ROCOSH	ROCSSH	ROC(S)OR′	ROC(S)SS(S)COR
	Thionocarboxylic acid	RCOSH	RCSSH	RC(S)OR	RC(S)SS(S)CR
	Thiosalicylic acid	RCH(SH)COOH 	–	–	
3. N—C—S	Thiocarbamic acid	RR′NCOSH	RR′NCSSH	RR′NC(S)SR″ SH	RR′NC(S)SS(S)NC RR′
	Sulfourea		–	–	–
4. C—P—S | O(S) O—P—S | O(S) N—P—S | O(S)	Thiohypophosphorous acid	RR′POSH	RR′PSSH	RR′PSS R″	$(RO)_2P(S)SS(S)P(RO)_2$
	Thiophosphoric acid (ester)	$(RO)_2POSH$	$(RO)_2PSSH$	$(RO)_2PSSR'$	
	Amino thiophosphoric acid	$(RR'N)_2POSH$	$(RO)_2PSSH$	$(RO)_2PSSR''$	

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1.1 Xanthates

1.1.1 Application of Xanthates

Xanthate was first prepared by Zeise in 1815. The general expression of xanthate can be given as follows:

where Me usually refers to Na or K ion, or ammonium sometimes; R refers to alkyl radical, alkylaryl, or alkoxy, but refers to the alkyl radical with C_2–C_6 in general.

The scientific name of xanthate is dithiocarbonate. The first application of xanthate in the flotation was dated from 1924. At present, xanthate is one of the most widely used collectors for sulfide minerals.

1.1.2 Preparation of Xanthates

The basic reaction in the preparation of xanthates can be expressed as follows:

$$ROH + MOH + CS_2 \rightarrow RO{\cdot}CS{\cdot}SM + H_2O$$

where M refers to alkali metal; R refers to the alcohol with nonpolar group.

But someone proposed that the reaction can be given by the following:

$$ROH + CS_2 \rightarrow RO{\cdot}CS{\cdot}SM$$

Based on the testing of O^{18} as labeled atom, it displayed that the O atom of NaOH entered into H_2O, with the O atom of ROH entering into the synthetical xanthates.

The reaction of preparation of xanthates is exothermic. In general, xanthates are synthesized under low temperature because xanthates are prone to break down under high temperature. The synthesizing technologies include direct synthesis technique, solution method, diluent method, partial diluent technique, superfluous alcohol method, steam technique, and alkali metal alcoholate technique. The differences of various synthesizing technologies mainly lie in the charging sequence, the sorts and amounts of solvent, and stirring strength.

The content of the active ingredient of xanthate is usually about 79–82 % in China. The quality guarantee period of xanthate is generally half-year. The technological parameter for the preparation of xanthates varies with experiment condition. Based on reports, the main technological parameters for various sodium xanthates can be given as follows:

Ethyl xanthate:

Burdening: $NaOH:C_2H_5OH:CS_2 = 1:1:1$;
The generating temperature of sodium alcoholate: 30–40 °C;
Etiolation temperature: 25–70 °C;

Butyl xanthate:

Burdening: $NaOH:C_4H_9OH:CS_2 = 1:1:1$;
The generating temperature of sodium alcoholate: 25 °C;
Etiolation temperature: 25–28 °C;
Drying temperature: 55–70 °C;

Pentyl xanthate:

Burdening: $NaOH:C_5H_{11}OH:CS_2:H_2O = 1.0:0.9:0.95:0.3$;
The generating temperature of sodium alcoholate: 30–36 °C;
Etiolation temperature: 15–38 °C;
Drying temperature: 30–40 °C;

Meantime, some side reactions occur during the preparation of xanthates.

(i) When the reaction temperature or the content of H_2O is too large, the decomposition reaction of xanthates occurs as follows:

$$ROCSSNa + H_2O \rightarrow CS_2 + NaOH + ROH$$

(ii) CS_2 can also react with NaOH to produce the impurity of xanthates:

$$CS_2 + 2NaOH \rightarrow NaOCSSNa + H_2O$$
$$NaOCSSNa + 2H_2O \rightarrow 2NaHS + H_2CO_3$$
$$2NaHS + 2NaOH \rightarrow 2Na_2S + 2H_2O$$
$$Na_2S + CS_2 \rightarrow NaSCSSNa$$

1.1.3 Property of Xanthates

The melting points and the solubilities of several common xanthates are given by the following:

	Melting points of potassium xanthates						
Nonpolar group	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9	i-C_5H_{11}
Melting point (°C)	182–186	226	233–239	278–282	255–265	260–270	260–270

	Solubilities of xanthates (g/100 g)									
Nonpolar group	n-C_3H_7		i-C_3H_7		n-C_4H_9		i-C_4H_9		i-C_5H_{11}	
	K	Na	K	Na	K	Na	K	Na	K	Na
Solubility (0 °C)	43.0	17.6	16.6	12.1	32.4	20.0	10.7	11.2	28.4	24.7
Solubility (35 °C)	58.0	43.3	37.15	37.9	47.9	76.2	47.67	33.37	53.3	43.5

Xanthates convert rapidly to xanthic acids in water:

$$ROCSSNa \leftrightarrow ROCSS^- + Na^+$$
$$ROCSS^- + H_2O \leftrightarrow ROCSSH + OH^-$$

Xanthic acids are weak acid, and their dissociation constants had been given in Chap. 3 (Volume 1). Ethyl xanthic acid appears in the form of oil emulsion. The melting point of ethyl xanthate is −53 °C.

The stabilities of xanthates are weaker than those of carbonates because the stability of C—S bond in xanthate is weaker than that of C—O bond in carbonate. Xanthates are prone to break down into ROH, CS_2, and NaOH. In the presence of free alkali, the breakdown process of xanthates can be expressed as follows:

$$ROCSSNa + NaOH \rightarrow NaOCSSNa + ROH$$
$$ROCSSNa + 2NaOH \rightarrow NaOCOSNa + NaHS + ROH$$
$$ROCSSNa + NaHS \rightarrow NaSCSSNa + ROH$$
$$NaOCSSNa + NaOCOSNa \rightarrow NaSCSSNa + Na_2CO_3$$

Take ethyl potassium xanthate for example, the following reactions also occur in the presence of H_2O:

(i) $6C_2H_5OCSSK + 3H_2O \rightarrow 2K_2S + K_2CO_3 + 5CS_2 + 6C_2H_5OH$
(ii) $2C_2H_5OCSSK + CO_2 + H_2O \rightarrow CS_2 + C_2H_5OH + KHCO_3$
(iii) $4C_2H_5OCSSK + O_2 + H_2O \rightarrow 2C_2H_5OCSS—SSCOC_2H_5 + 4KOH$
(iv) $2C_2H_5OCSSK + H_2O + CO_2 + ½O_2 \rightarrow C_2H_5OCSS—SSCOC_2H_5 + 2KHCO_3$

The variations of decomposition rate constant (K_0) with the magnitude of hydrocarbon chains of xanthates are as follows:

Nonpolar group	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9	n-C_5H_{11}
K_0 (1/min mol)	213	226	214	207	209	202	211

The decomposition rate constants of xanthates are not only related to O_2, but metal ions. It had been found that the decomposition rate constants of xanthates are relatively small in the presence of Fe^{3+}. Under the condition of pH 8, the decomposition rate constant of potassium xanthate can be seen as follows:

Metal ions	Zn^{2+}	Mn^{2+}	Ba^{2+}	Al^{3+}	Pb^{2+}	Ni^{2+}	Hg^{2+}
Half-life of decomposition	520	520	450	435	435	373	352
Metal ions	Cu^{2+}	Sn^{2+}	Co^{2+}	Fe^{3+}	–	–	–
Half-life of decomposition	335	310	310	326	–	–	–

1.1.4 Brief Introduction of Various Xanthates

(1) **Alkyl xanthates**

Alkyl xanthates that are currently used in flotation industry mainly include ethyl xanthate and propyl xanthate in China. But propyl xanthate and *i*-butyl xanthate are employed mostly in other countries. The main reason lies in that is propyl xanthate and *i*-butyl xanthate have the advantage of low price and broad source.

The synthetic technology of isomerous xanthate is similar to that of normal xanthate. For example, the synthesis conditions of isobutyl xanthate with direct synthesis technique are as follows:

Burdening:	*i*-C_4H_9OH:NaOH:CS_2 = 1:1:1;
Reaction temperature	20–30 °C;

The collecting capability of isobutyl xanthate is equal to or higher than that of *n*-butyl xanthate. Two examples for the flotation of copper ore using butyl xanthates as collectors can be seen as follows:

Mine	Reagent	Dosage (g/t)	Raw ore grade (%)	Concentrate grade (%)	Recovery rate (%)
A	*i*-butyl xanthate	120–130	1.47	15.19	94.31
	n-butyl xanthate	120–130	1.46	14.95	94.18
B	*i*-butyl xanthate	65–75	0.56	16.41	93.91
	n-butyl xanthate	65–75	0.56	16.16	93.60

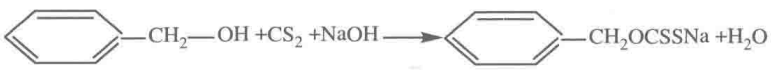
For those long-chain alkyl xanthates such as*n*-amyl and *i*-amyl xanthates, they are able to be applied in the flotation process of the presulfied CuO, PbO, and ZnO.

For those long-chain alkyl xanthates with C_{10} or above, they have not been used in flotation because their water solubilities are not good. Someone proposed that eicosane xanthate can be used as depressant in the flotation of fine blende [1].

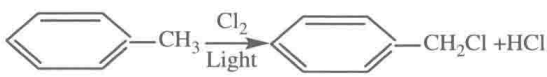
The performance of xanthate with aliphatic unsaturated hydrocarbon is close to that of normal alkyl xanthate. It was reported that those aliphatic xanthates include propylene-propyl and propylene-butyl xanthates [2].

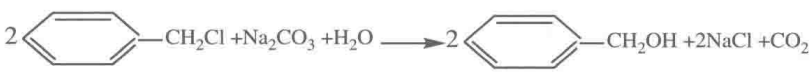
(2) **Aryl xanthates**

Aryl xanthates mainly comprise phenmethyl and cinnamyl xanthates. Benzyl alcohol xanthate can be prepared from benzyl alcohol:



Benzyl alcohol can be prepared from toluol:





The performance of phenmethyl xanthate is equal to those of propyl and butyl xanthates. Cinnamyl xanthate is prepared from cinnamyl alcohol. According to the results of laboratory tests, the synthesis conditions of cinnamyl xanthate with partial water dilution method are as follows:

$$\begin{aligned} &\text{Burdening :} && \text{KOH : ROH : } CS_2 = 1 : 0.9 : 0.95; \\ &\text{Water dosage :} && 6 - 14\,\% \text{ alcohol;} \end{aligned}$$

Flotation results show that the performance of cinnamyl xanthate is worse than those of butyl and phenmethyl xanthates. However, the selectivity of cinnamyl xanthate appears best. The flotation results of copper ore with various xanthates are shown in Tables 1.1 and 1.2.

The adsorption amounts of several xanthates on the galena surface are listed in Table 1.3. As shown in Table 1.3, the adsorption amount of xanthate is consistent with the collecting capability. For example, the adsorption amount and the collecting capability of phenmethyl xanthate are both largest.

Table 1.1 Flotation results of copper ore with aryl xanthates (reagent dosage 100 g/t)

pH	Phenmethyl xanthate		Cinnamyl xanthate	
	Concentrate grade of Cu (%)	Recovery rate (%)	Concentrate grade of Cu (%)	Recovery rate (%)
8	4.36	86.70	8.18	70.22
9	4.18	87.70	8.34	79.41
10	4.15	89.62	8.31	80.31
11	3.88	89.00	8.13	71.47

Table 1.2 Comparison of aryl xanthate and alkyl xanthate in the flotation of copper ore

Dosage (g/t)	Phenyl xanthate			Cinnamyl xanthate			Butyl xanthate			*i*-amyl xanthate		
	Concentrate grade of Cu (%)	Recovery rate (%)	pH	Concentrate grade of Cu (%)	Recovery rate (%)	pH	Concentrate grade of Cu (%)	Recovery rate (%)	pH	Concentrate grade of Cu (%)	Recovery rate (%)	pH
80	4.07	88.62	10	5.10	74.00	10	3.67	78.77	10.2	3.68	87.96	9.8
100	4.20	92.30	10.2	6.08	80.30	10.2	4.00	90.99	10.2	3.35	88.73	10
120	4.45	95.32	10	5.91	85.92	10	3.50	91.89	10	3.30	87.61	10.2
140	3.50	93.21	9.8	5.59	83.00	9.6	3.32	83.17	10	3.22	87.20	9.8