

Chapter 2

Collectors for Nonsulfide Minerals

2.1 Fatty Acids and Soaps

Fatty acids and soaps are widely applied in the flotation of oxidized ores. In general, fatty acids are comprised of saturated and unsaturated carboxylic acids with C_{10} – C_{20} . The components of various fatty acids are listed in Table 2.1 [1]. Fatty acid collectors are usually insoluble in water. The solubilities of various fatty acid collectors are found in Table 2.2. Fatty acid soaps are prone to form micelle with the increase in its concentration. The *CMC*, *CDC*, and *HMC* had been discussed in Chap. 1. Based on the flotation testing of calcite, it can be obtained that $CDC \approx CMC$. It can be obtained that $HMC \approx 1/100CMC$ according to the flotation testing of quartz with fatty amine. The *CMC* of various fatty acid soaps is found in Table 2.3.

Fatty acids are weak electrolytes. The dissociation of fatty acids can be expressed as follows:



The dissociation constants of various fatty acids can be found from the former chapters.

2.2 Oxidation Products of Petroleum Paraffin

2.2.1 Brief Introduction to Synthetic Fatty Acids

In order to solve the problem that natural fatty acids are insufficient, they are usually substituted by oxidized paraffin soaps (synthetic fatty acids). Oxidized paraffin

Table 2.2 Solubilities of various fatty acid collectors (g/100 g water)

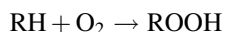
Fatty acid	Solubility		Fatty acid	Solubility	
	20 °C	60 °C		20 °C	60 °C
Capric acid	0.0150	0.0290	Pentadecanoic acid	0.0120	0.0020
Undecylenic acid	0.0039	0.0150	Palmitic acid	0.00072	0.0012
Lauric acid	0.0035	0.0087	Margaric acid	0.00042	0.00081
Tridecanoic acid	0.0033	0.0054	Stearic acid	0.00029	0.00050
Myristic acid	0.0020	0.0034			

Table 2.3 CMC and CDC of various fatty acid collectors

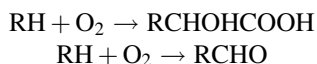
Fatty acid	CMC [2] (mol/L)	Fatty acid	CMC [3] (g/L)	CDC (g/L)
Sodium laurate	3.59×10^{-2} (20 °C)	Sodium linoleate	0.15	0.6
Potassium laurate	2.15×10^{-2} (25.8 °C)	Linolenic acid	0.20	0.9
Potassium palmitate	3.4×10^{-3} (70 °C)	Sodium oleate	0.25	1.0
Sodium oleate	2.7×10^{-3} (20 °C)	Sodium ricinoleate	0.45	2.0
Potassium oleate	7.12×10^{-4} (25.8 °C)	Tal oil soap	0.50	2.2
Sodium naphthenate	2.5×10^{-3}			

soaps have been successfully applied in the flotation of hematite, scheelite, and cassiterite.

Oxidized paraffin soaps can be synthesized by adopting petroleum paraffin as raw material. Because synthetic reaction of oxidized paraffin is relatively simple, oxidized paraffins are widely applied in industry. Synthetic methods of oxidized paraffin comprise air oxidation process and NO_2 oxidation process. Air oxidation process is widely applied. In general, petroleum paraffin is heated to 150 °C or above in the presence of O_2 and KMnO_4 . The oxidation reactions can be given by the following:



Side reaction:



2.2.2 Production Process of Oxidized Paraffin Soaps

The flowchart of oxidized paraffin soaps is shown in Fig. 2.1. The main production conditions of oxidized paraffin soaps are as follows.

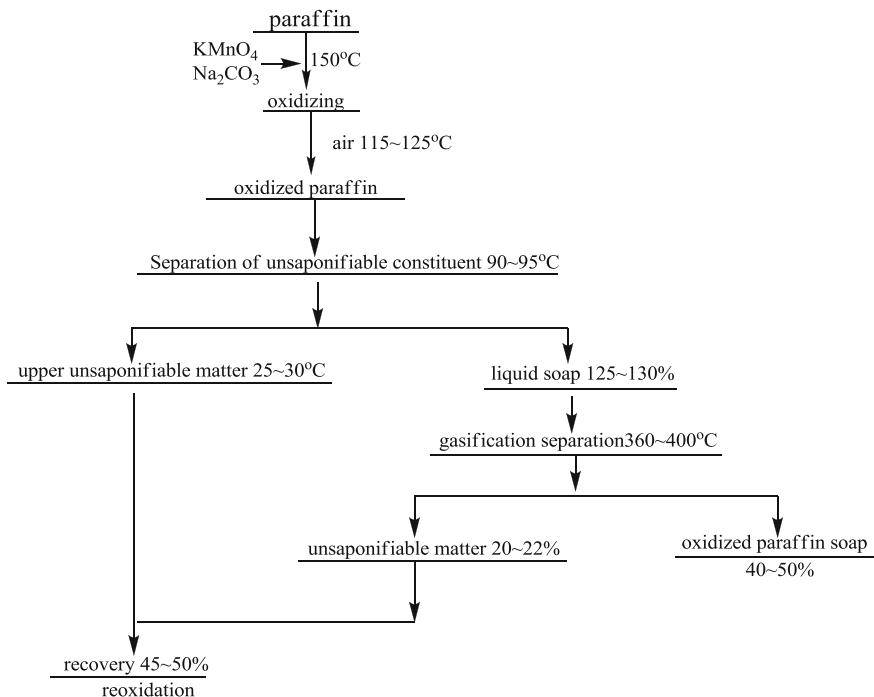


Fig. 2.1 Flowchart of oxidized paraffin soaps

(i) **Oxidizing condition**

The oxidizing reaction is motivated by the addition of KMnO_4 and Na_2CO_3 at a high temperature. Then, air is injected into the reaction tank at 150°C . The productivity of oxidized paraffin soaps can reach 95 % when the acid value of reactive liquid approaches a certain threshold.

(ii) **Separation of unsaponifiable constituent**

The reactive liquid of oxidized paraffin soaps is moved to soaping kettle. And oxidized paraffin soaps are separated by water dilution method when oxidized paraffin has been soaped at $90\sim 95^\circ\text{C}$ in the presence of NaOH . The upper unsaponifiable matter is separated out. The main ingredients of unsaponifiable matter are aldehyde, ketimine, and unreacted paraffin. The productivity of unsaponifiable matter is about 25–30 %.

(iii) **Gasification separation**

The liquid soap is first moved to gasification furnace. The upper unsaponifiable matter is separated out at $360\sim 400^\circ\text{C}$. The main ingredients of unsaponifiable matter are alcohols. The productivity of unsaponifiable matter is about 20 %.

The quality of oxidized paraffin soap varies with the production condition and raw material. The characteristics of two oxidized paraffin soaps can be seen from the following:

Product	Total fatty acid (%)	Fatty acid content (%)	Moisture content (%)	Carbon content (%)
Oxidized paraffin soaps	50–55	27–30	33–37	0.2–0.5
Oxidized paraffin soaps	60–70	56–60	12–16	–

2.2.3 Characteristics of Oxidized Paraffin Soaps

(1) Component of oxidized paraffin soaps

Oxidized paraffin soaps comprise saturated fatty acid, oxyacid (such as alcohol acid and ketonic acid), dicarboxylic acid, unsaponified oxides, and unoxidized hydrocarbons. Oxidized paraffin soaps that are used as collector are comprised of fatty acids because mostly unsaponified oxides and unoxidized hydrocarbons had been removed from the product. The proportion of saturated fatty acid in oxidized paraffin soaps is about 80 %. And the proportion of oxyacid is about 5–10 %. The proportion of unsaponified oxides is about 2–3 %.

(2) Hydrocarbon chain length of oxidized paraffin soaps

According to the reports, hydrocarbon chain lengths of fatty acids in oxidized paraffin soaps are given as follows [4]:

C ₄ –C ₁₀	Fatty acid	12 %
C ₁₀ –C ₂₀	Fatty acid	65 %
C ₂₀ –C ₂₈	Fatty acid	14 %
>C ₂₈	Fatty acid	9.0 %

Hydrocarbon chain lengths of saturated fatty acids in oxidized paraffin soaps prepared in a certain Chinese factory are given by the following:

C ₅ –C ₉	Fatty acid	10 %
C ₁₀ –C ₁₅	Fatty acid	23–25 %
C ₁₆ –C ₂₀	Fatty acid	23–25 %
>C ₂₀	Fatty acid	23–25 %

The flotation performances of fatty acids with different hydrocarbon chains had been discussed in Volume 1. The flotation performance of oxidized paraffin soap is the same with fatty acid. Generally speaking, the collecting capability of oxidized paraffin soap increases with the increase in the hydrocarbon chain length. In general, the collecting capabilities of oxidized paraffin soaps with C_{10} – C_{20} are relatively better. Meantime, the dosage and solubility of oxidized paraffin soap decrease with the increase in hydrocarbon chain length. The required flotation temperature increases with the increase in the hydrocarbon chain length. For example, the required flotation temperatures of oxidized paraffin soaps with different hydrocarbon chain lengths can be seen as follows:

Hydrocarbon chain length	Required flotation temperature
C_5 – C_9	30 °C
C_{10} – C_{20}	40 °C
$>C_{20}$	35 °C

The characteristics of the distillation products of oxidized paraffin soap can be seen as follows:

Product	Cut fraction (°C)	Melting point	Acid value	Saponification value
(1)	180	25 °C	144.00	209.63
(2)	180–235	–	125.27	155.20
(3)	235–275	29 °C	63.22	92.09

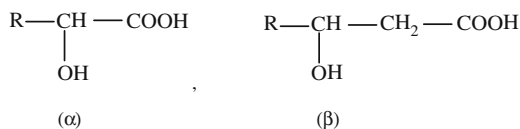
Based on the flotation results of hematite, the orders of flotation performances of these three distillation products are as follows:

$$(3) > (2) > (1)$$

The flotation results indicate that the collecting capability of distillation product obtained from high temperature is comparatively better.

(3) Hydroxy acids of oxidized paraffin soaps

Hydroxy acids mainly refer to α -hydroxy acids and partly β -hydroxy acids. The general expressions of α -hydroxy acids and β -hydroxy acids are as follows:



As mentioned before, the collecting capability of hydroxy acid is better than that of general fatty acid. Petroleum ether extracted from oxidized petroleum paraffin

includes carboxylic acids (1) and hydroxy acids (2). The characteristics of petroleum ether extracted from oxidized paraffin soap can be seen as follows:

Product	Acid value	Saponification value	Hydroxy value	Carboxyl value
Oxidized paraffin soap	72.55	165.6	109.3	65.52
(1)	55.47	107.5	99.25	56.31
(2)	82.48	210.5	107.3	—

Based on the flotation results of hematite, the collecting capability of product (2) is better than that of product (1).

Therefore, the deep oxidation of petroleum paraffin is needed for improving the collecting capability of oxidized paraffin soap product. But it should be pointed out that the collecting capability of oxidized paraffin soap will decrease when the oxidation of petroleum paraffin is too deep. The reason lies in that the molecular weight decreases with the increase in the oxidation degree of petroleum. And the decrease in molecular weight of reagent is bad for flotation performance of oxidized paraffin soap.

2.2.4 Application of Oxidized Paraffin Soaps

Compared with oleic acids, the application characteristics of oxidized paraffin soaps in the flotation of oxide mineral can be given by the following:

- (1) Oxidized paraffin soaps are characterized by low price, abundance in resources, and wide application.
- (2) The collecting capabilities of oxidized paraffin soaps are worse than those of oleic acids when the pulp temperature is less than 40 °C. According to the flotation tests, the collecting capabilities of oxidized paraffin soaps become better than those of oleic acids when the pulp temperature approaches 70 °C. Therefore, the solubilities of oxidized paraffin soaps are improved by adopting emulsifier or other additives when reagents are used at the normal temperature level.
- (3) The frothing capabilities of oxidized paraffin soaps are not as strong as those of oleic acids.

2.3 Tar Oil and Paper Pulp Products

2.3.1 Paper Pulp Products

Paper pulp products refer to the sulfate soaps which are separated from the black liquor of paper pulping. The components of paper pulp products are unsteady. For instance, the components of domestic paper pulp product are listed as follows:

Fatty acids	14.11 %	Moisture content	31.75 %
Resin acids	18.49 %	Total alkalinity	7.18 %
Neutral substances	9.77 %	Mechanical impurity	15.18 %

In general, fatty acids and resin acids are the active ingredients. The content of fatty acids or resin acids is about 10–20 %. Fatty acids are mainly comprised of saturated acids such as oleic acids, linoleic acids, and linolenic acids, and a spot of unsaturated acids such as those with C_5 – C_{24} . Resin acids are mainly comprised of dehydroabietic acids, and dihydro- and terealin abietic acids.

In addition, some impurities such as cellulose and lignin exist in the product. Because these impurities perform depressing capability in the flotation of some minerals, these impurities are usually considered as detrimental impurities.

Compared with oleic acids, the application characteristics of paper pulp products in the flotation of oxide mineral can be given by the following:

- (1) Paper pulp products are characterized by unstable composition. Therefore, flotation performance of reagent obviously varies with the change of source.
- (2) The content of active ingredient of paper pulp product is too low. Therefore, the collecting performance of paper pulp product is not good. And the dosage is relatively higher.
- (3) Paper pulp products usually contain a specified volume of detrimental impurities.
- (4) The foam is too viscous when paper pulp product is used in industry.

By far, paper pulp products are rarely employed in industry.

2.3.2 Crude Tar Oils

Crude tar oils are the crude products of the sulfate soaps which are separated from the black liquor of paper pulping. The contents of fatty acids and resin acids are increased through the crude processing. For instance, the components of domestic crude tar oil are listed as follows:

Fatty acids	35.89 %	Mechanical impurity	0.76 %
Resin acids	42.89 %	Acid value	119.66
Neutral substances	17.75 %	Saponification value	129.68 %
Moisture content	3.38 %	Specific gravity	0.96–0.98 %

The components of several foreign crude tar oils are found in Tables 2.4 and 2.5. The flowchart of crude tar oils is shown in Fig. 2.2. The content of active ingredient of crude tar oils is twice as much as that of paper pulp products. And the component of crude tar oils is relatively steady. Therefore, the flotation performance of crude tar oils is relatively better. It should be pointed out that however, the contents of unsaturated fatty acids and resin acids are relatively higher. Therefore, the frothing capacity of crude tar oils is so high that crude tar oils are hard to be applied in industry.

Table 2.4 Components of crude tar oil [5]

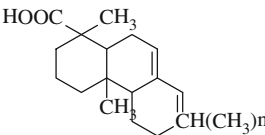
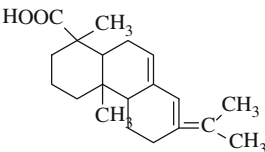
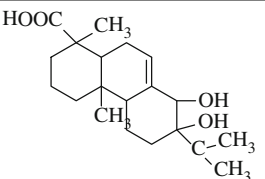
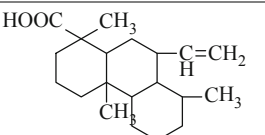
Category	Name	Structure	Content (%)
Resinolic acid	Abietic acid		20–25
	New abietic acid		22–27
	Dihydroxy abietic acid		4–5; 3–4
	Passang abietic acid		8–10; 29–43
Fatty acid		$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	46–48
		$\text{CH}_3(\text{CH}_2\text{CH}=\text{CH})_3\text{CH}_2(\text{CH}_2)_6\text{COOH}$	1–2
		$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	43–45
	Saturated acid		6–8
Unsaponifiable matter	Plant sterol		25–35
	Higher alcohols		5–15
	Hydrocarbons		35–60

Table 2.5 Components of crude tar oil

Product	Component (%)				Note
	Palmitic acid	Linoleic acid	Oleic acid	Resin acid	
Crude tar oil A	2.0	6.0	35.0	32.0	Linolenic acid 25.0 %
Crude tar oil B	2.0	36.0	33.0	29.0	No linolenic acid
Pure tal oil C	2.0	47.5	49.5	1.0	No linolenic acid

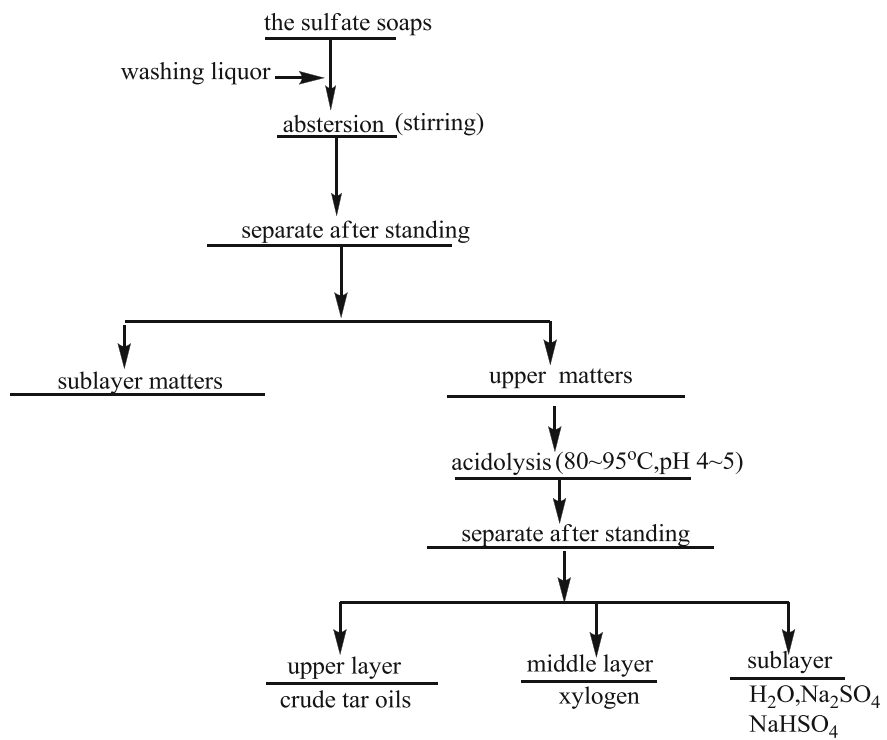


Fig. 2.2 Flowchart of crud tar oils

2.3.3 Essential Tar Oils

Essential tar oils refer to the fatty acids which are distilled from crude tar oils. The components of essential tar oil are found in Table 2.5. The content of unsaturated fatty acids is above 90 % in essential tar oils and related soaps. Therefore, essential tar oils and related soaps can be used as good collector.

2.4 Modified Products of Fatty Acids

Although fatty acids and related soaps have been widely applied in the flotation of oxidize minerals, their flotation performance is still bad. Because of their bad selectivities and solubilities, ore pulps must be heated when fatty acids and related soaps are used in the flotation process. Main methods for improving the flotation performances of fatty acids and related soaps lie in the following aspects:

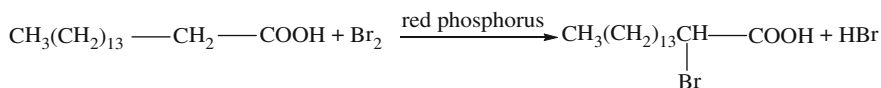
- (1) Improving the solubilities of fatty acids and related soaps:
It can be achieved by introducing high polarity groups or unsaturated bonds.
- (2) Increasing the selectivities of fatty acids and related soaps:
It can be achieved by introducing high selectivity groups.

Because the structures and characteristics of saturated and unsaturated fatty acids are diverse, their modification processing is different, too. In general, other groups are introduced into the α -position of saturated fatty acids. But other groups are usually introduced into unsaturated bond of unsaturated fatty acids.

2.4.1 Modified Products of Saturated Fatty Acids

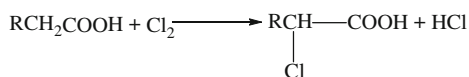
(1) Halogenated products of saturated fatty acids

Halogens such as Cl, Br, and I can be introduced into the α -position of saturated fatty acids. For instance, the halogenation of palmitic acid with Br can be expressed as follows:

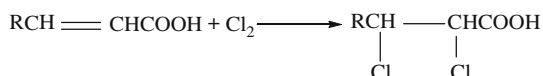


Fatty acid chloride has been used as collector in the flotation of hematite and apatite [6–8]. The main preparation method of fatty acid chloride is as follows:

- (1) Fatty acid chloride can be synthesized by adopting oxidized paraffin and Cl_2 as raw materials.
- (2) The halogenation reaction can be given as follows:



When some unsaturated fatty acids exist in the reaction system, addition reaction occurs as follows:



- (3) The halogenation conditions can be given as follows:

Photometric quantity: $\mu = 1800\text{--}5800 \text{ \AA}$

Reaction temperature: $60\text{--}70 \text{ }^\circ\text{C}$

Chlorine dose: $0.2\text{--}0.23 \text{ kg/t min}$

- (4) The halogenation procedures can be given as follows:

Dehydration Dry air is injected when the materials are heated to $80\text{--}90 \text{ }^\circ\text{C}$

Chlorination Cl_2 is injected when the materials are cooled to $60 \text{ }^\circ\text{C}$. And the chlorination time is $50\text{--}60 \text{ h}$

Dechlorination Dry air is injected to remove Cl_2 when the reaction finishes. The dechlorination time is $30\text{--}45 \text{ h}$

The quality of fatty acid chloride is as follows:

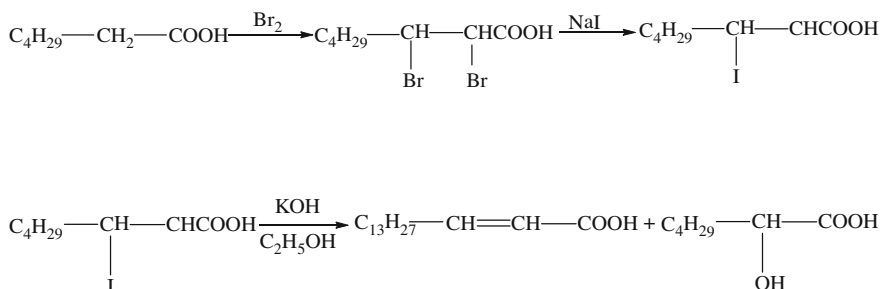
Combined chlorine content	16.21–19.97 %	Specific gravity	1.063–1.081
Acid value	160–180	Solidifying point	-1 to $+3 \text{ }^\circ\text{C}$
Moisture content	0.01–0.6 %	Viscosity	9.21–15.72
Free chlorine	0.089–0.18 %	Molecular weight	300–338

The application characteristics of fatty acid chloride in the flotation of hematite can be given by the following:

- (1) Fatty acid chloride is characterized by low melting point and high solubility. Therefore, fatty acid chloride can be applied at the normal temperature level.
- (2) Fatty acid chloride shows a good collecting performance in the flotation of fine-grained ores.
- (3) The dosage of fatty acid chloride is relatively lower.
- (4) Fatty acid chloride is unsteady. It is prone to produce Cl_2 and HCl which lead to hard operating environment in industry.
- (5) Fatty acid chloride is insoluble water. Condensing and filtering processes are hard to be achieved when kerosene is adopted as thinner.

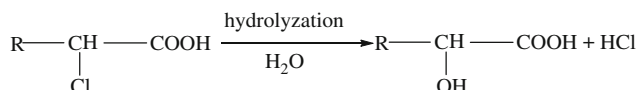
(2) α , β -unsaturated fatty acids and α -hydroxyl acids

According to R. S. Sweet, α -hexadecenoic acid can be produced by adopting α -bromopalmitic acid, NaI, and acetone as feeds. The synthetic reaction of α -hexadecenoic acid is given by the following:

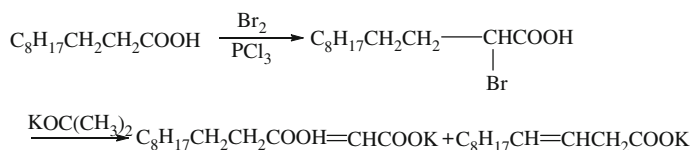


The synthetic products are comprised of 2-hexadecenoic acid and α -hydroxy acid. α -hydroxy acid can be extracted from petroleum ether. The raffinate is hexadecenoic acid. The proportion of hexadecenoic acid to hydroxy acid is 2:1.

It was reported that hydroxy acid can also be produced by the hydrolysis of α -chloroacid:



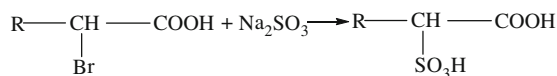
According to C.F. Allen, α -olefine acid and β -olefine acid can be produced by adopting lauric acid, Br_2 , K, and tributyl alcohol as feeds. The reaction of α -olefine acid and β -olefine acid is given by the following:

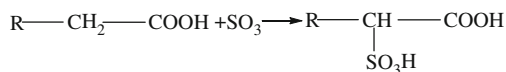


The solubilities of α -olefine acid and β -olefine acid are larger than those of saturated fatty acids.

(3) Sulfonated products of saturated fatty acids

The sulfonation reaction of saturated fatty acids is given by the following:

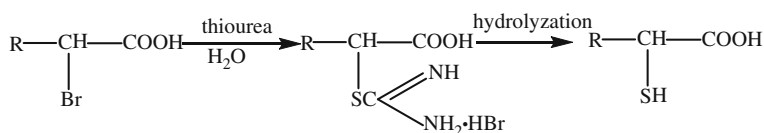




The flotation performances of sulfofatty acids had also been discussed in the former chapters. Based on our studies, sulfofatty acids are characterized by strong frothing capability and good water solubility. The solubility of sulfo-octadecanoic acid and sulfohexadecanoic acid is 13 g/100 g water and 25 g/100 g water, respectively.

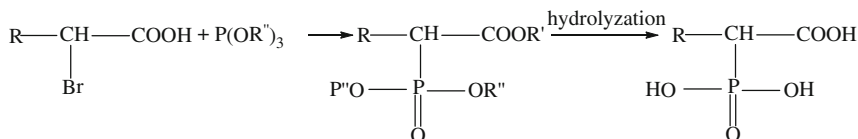
(4) Thiol fatty acids

Thiol fatty acids can be prepared from bromofatty acids and thiocarbamide. The synthetic reaction of thiol fatty acids can be given by the following:



(5) Phosphate esterification of saturated fatty acids

According to D. Swern, phosphate ester can be produced by adopting α -bromoacid esters and trialkyl phosphoric acid as feeds. The synthetic reaction can be given by the following:

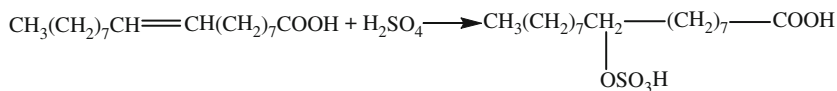


The flotation performances of various phosphate esters are found in Table 3.21 in Volume 1.

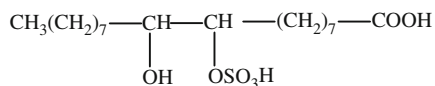
2.4.2 Modified Products of Unsaturated Fatty Acids

(1) Sulfation of unsaturated fatty acids

Sulfuretted unsaturated fatty acids can be prepared from unsaturated fats and concentrated sulfuric acid. For example, the sulfation reaction of oleic acid can be given by the following:



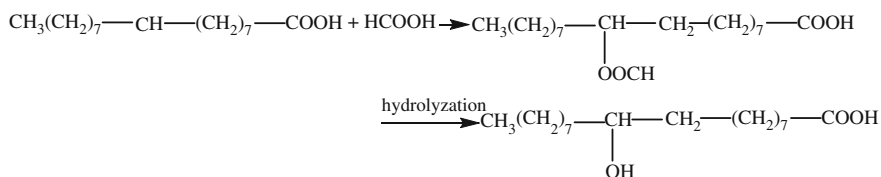
In addition, the sulfation reaction produces a little by-product as follows:



The flotation performances of unsaturated fatty acids are improved by the sulfation reaction.

(2) Hydroxylation of unsaturated fatty acids

According to K.B. Knight, hydroxyoleic acid can be prepared via addition hydrolysis reaction of methanoic acid using chloric acid or sulfuric acid as catalyst. The reaction can be given by the following:



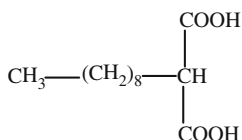
It is well known that 9,10-octadecanoic acid shows good flotation performance in flotation.

2.5 Carboxylic Acids and Derivative Collectors

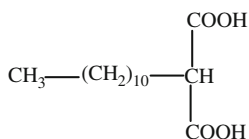
2.5.1 Polycarboxylic Acids

Polycarboxylic acids such as oxalic acid, dihydroxysuccinic acid, and citric acid have been used as depressant. It was reported that polycarboxylic acid collectors for cassiterite can be given as follows [9]:

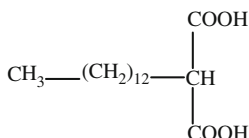
1,1-decyl dicarboxylic acid (DCA-10):



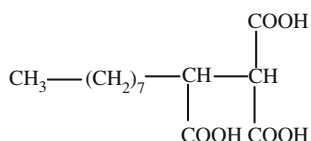
1,1-dodecyl dicarboxylic acid (DCA-12):



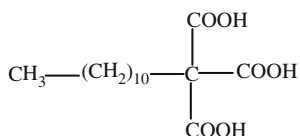
1,1-nonadecane dicarboxylic acid (DCA-19):



1,1,2-decyl tricarboxylic acid (TCA-10):



1,1,1-dodecyl tricarboxylic acid (TCA-12):

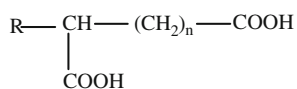


The molecular weights and the *CMC* of the above polycarboxylic acids are given as follows:

	Molecular weight	<i>CMC</i>
DCA-10	274	10^{-1}
DCA-12	302	10^{-2}
DCA-19	400	4.0×10^{-5}
TCA-10	340	—
TCA-12	368	—

The flotation results of cassiterite, quartz, and tourmaline using the above polycarboxylic acids are listed in Table 2.6.

In addition, some polycarboxylic acids are reported in East Germany and Britain. For example, one of the general expressions of polycarboxylic acids is as follows:



where R refers to the alkyl of $\text{C}_7\text{--C}_{20}$; n refers to 0, 1, and 3.

Table 2.6 Flotation results of cassiterite, quartz, and tourmaline using DCA and TCA

Collector	pH range of 100 % flotation	Optimum pH of cassiterite	Limit of inevitable metal ions		Flotation results of quartz (%)	Flotation results of tourmaline (%)
			Fe ³⁺ (mg/L)	Ca ²⁺ (mg/L)		
DCA-10	2.5–9.0	3.0–9.0	–	650	20	65
DCA-12	3.0–9.0	3.0–4.0	250	650	20	70
DCA-19	2.5–10.0	3.0–5.0	250	650	10	75
TCA-10	3.5–11.0	4.0–5.5	150	–	30	95
TCA-12	2.0–11.0	3.5–4.5	–	–	60	95

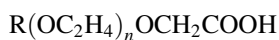
It was reported that the flotation performances of these polycarboxylic acids are good in the flotation of fluorite, barite, and cassiterite.

Another two general expressions of polycarboxylic acids are as follows:



2.5.2 Ether Acids

The general expression of ether acids is as follows:

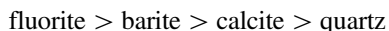


where R refers to the alkyl of C₈–C₁₈; *n* refers to 0–16.

Ether acids are usually used to flotite fluorite, barite and dolomite. Meanwhile, they also perform a certain collecting capability in the flotation of malachite, ilmenite, pyrite, and towanite. Compared with general carboxylic acids, the application characteristics of ether acids can be given by the following:

- (1) Ether acids are characterized by good solubility and low melting point.
- (2) The collecting performances of ether acids are not influenced obviously by Ca and Mg ions.
- (3) The dissociation degrees of ether acids are relatively higher. They can exhibit their collecting performances at pH 2–6. And optimal pH for the flotation of fluorite using ether acids is pH 4–5.

- (4) The orders of collecting performances of ether acids toward several minerals are as follows:



Based on the difference in collecting performances of ether acids toward several minerals, flotation separation of fluorite and calcite can be obtained with the help of depressant (such as dextrine and water glass).

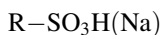
- (5) The collecting capabilities of ether acids are relatively stronger. The dosages of ether acids are relatively smaller. For example, the dosage of myristyl ether acid is 75–120 g/t in the flotation of fluorite. However, the dosage of sodium oleate is 300–1000 g/t.
- (6) The functional mechanism of ether acids is different from that of oleic acids. The adsorption of ether acids on mineral is reversible. Therefore, ether acids adsorb on mineral via physical adsorption. Or the chemisorption product is water-soluble. The adsorption reversibility of ether acids on mineral surface is given as follows:

Mineral	Oleic acids		Ether acids	
	Recovery rate (%)	After washing (%)	Recovery rate (%)	After washing (%)
CaF ₂	87	80	93	27
FeS ₂	81	69	73	3

2.6 Alkyl Sulfonates and Sulfates

2.6.1 Alkyl Sulfonic Acids and Sulfonates

The general expression of alkyl sulfonates is as follows:



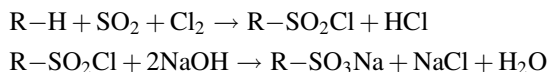
where R refers to alkyl, alkylaryl, and cycloalkyl.

Compared with sulfate, the S atom of alkyl sulfonate is directly linked with the C atom of alkyl.

The main synthetic routes of alkyl sulfonic acids and sulfonates are introduced as follows:

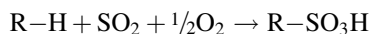
- (1) Sulfonation–chlorination of hydrocarbon

For example, alkyl sulfonate can be synthesized under ultraviolet radiation by adopting saturated hydrocarbon, SO₂, and Cl₂ as raw materials. The reactions can be given by the following:



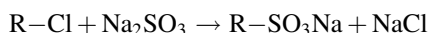
(2) Sulfonation oxidation of hydrocarbon

Sulfonation oxidation of hydrocarbon is similar to sulfonation–chlorination of hydrocarbon. Alkyl sulfonic acid can be synthesized under ultraviolet radiation by adopting saturated hydrocarbon, SO_2 , and O_2 as raw materials. The reaction can be given by the following:



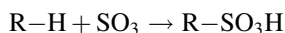
(3) Sulfonation of chloroalkane with sodium sulfite

The reaction can be given by the following:



(4) Sulfonation of hydrocarbon

Alkyl sulfonic acid can also be directly synthesized by adopting saturated hydrocarbon, SO_2 , and ClSO_3 as raw materials. The reaction can be given by the following:



2.6.2 Alkyl Sulfates

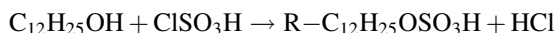
The general expression of alkyl sulfates is as follows:



where R refers to alkyl.

Compared with sulfonate, the polar group of alkyl sulfates connects with the C atom via O atom.

Synthetic routes of alkyl sulfates are diverse. In general, alkyl sulfates are prepared by sulfating higher alcohol. For example, dodecyl sulfate can be synthesized by adopting lauryl alcohol and chlorosulfonic acid as raw materials. The reaction can be given by the following:



In addition, concentrated sulfuric acid, chlorosulfonic acid + urea and naphthyridines-sulfur trioxide can also be used as sulfating reagent.

2.6.3 Flotation Characteristics of Alkyl Sulfonates and Sulfates

Compared with fatty acids, alkyl sulfonates and sulfates are strong electrolytes. Therefore, alkyl sulfonates and sulfates appear in the form of ions. The solubilities and the *CMC* of alkyl sulfonates and sulfates are found in Table 2.7.

Compared with fatty acids with the same alkyls, the flotation characteristics of alkyl sulfonates and sulfates can be given by the following:

- (1) Good solubility;
- (2) Good water hardness resistance;
- (3) Strong frothing capability;
- (4) Good selectivity.

Alkyl sulfonates make more sense in industry application. The reason is that the raw alcohols of sulfates are costly. Meanwhile, the hydrolysis reaction of alkyl sulfates often takes place in water:

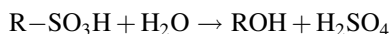


Table 2.7 Solubilities and *CMC* of alkyl sulfonates and sulfates

Alkyl radical	Sulfonate		Sulfate	
	Solubility [10] (g/100 g water)	<i>CMC</i>	Solubility [10] (g/100 g water)	<i>CMC</i>
C ₈	74.4 (25 °C)	0.15 (25 °C)		
C ₁₀	4.55 (25 °C)	0.012 (25 °C)		
C ₁₂	0.253 (25 °C), 48 (60 °C)	0.0011 (35 °C)	>280 (25 °C)	0.0066 (40 °C)
C ₁₄	0.041 (25 °C), 38.8 (60 °C)	0.0032 (45 °C)	160 (35 °C)	0.0015 (40 °C)
C ₁₆	0.0073 (25 °C), 6.49 (60 °C)	0.0012 (50 °C)	525 (55 °C)	0.0033 (40 °C)
C ₁₈	0.001 (25 °C), 0.131 (60 °C)		50 (60 °C)	0.000156 (40 °C)
α -naphthyl	13			
β -naphthyl	13			

Functional mechanisms of alkyl sulfonates and sulfates had been discussed in Volume 1. It can be concluded that the functional mechanisms of alkyl sulfonates and sulfates can be given by the following:

- (1) Electric double-layer adsorption of $R-SO_3^-$ and $R-SO_4^-$ on mineral surface;
- (2) van der Waals force or hydrophobic association of ions and neutral molecules;
- (3) Chemical adsorption.

Based on H.L. Shergold, chemical adsorption starts to take place at low pH (2.6–3.0) in the flotation of hematite using dihexylsulfate. Adsorption isotherm shows that adsorption amount of dihexylsulfate increases obviously after the reagent dosage approaches *HMC*. The maximal adsorption density of dihexylsulfate is about $6 \mu\text{mol cm}^{-2}$.

2.6.4 Industry Application of Alkyl Sulfonates and Sulfates

Alkyl sulfonates can be used as oxide collector, sulfide collector, frother, and emulsifier. It is reported that petroleum sulfonates are widely applied in the flotation of oxide minerals [10]. The foreign collectors such as Aero Promoter 800 and Reagent 800 are both petroleum sulfonates. The characteristics of various sulfonates had been discussed in the former chapters. Based on their characteristics, sulfonates can be divided into two varieties:

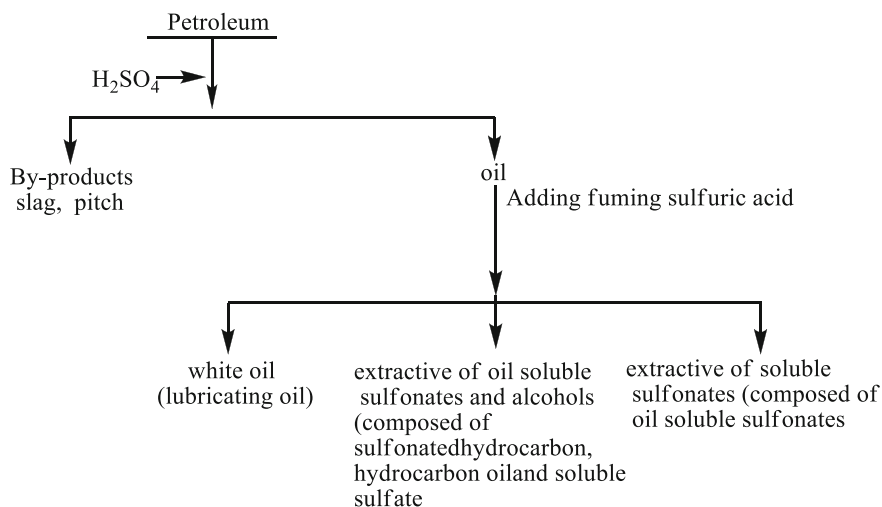
- (1) Water-soluble sulfonates

Water-soluble sulfonates are characterized by low molecular weight and highly branched hydrocarbon chain. The collecting capabilities of these reagents are not good. Because of strong frothing performance, these reagents can be used as frother. Meanwhile, they can replace xanthate to float sulfide minerals, as well as oxide minerals with high floatability.

- (2) Oil-soluble sulfonates

Oil-soluble sulfonates are characterized by high molecular weight. The number of C atoms of hydrocarbon chain exceeds 20 when hydrocarbon chain is alkyl. The collecting capabilities of these reagents are strong. And these reagents can be used as the collector for oxide minerals and nonmetallic minerals (such as fluorite, beryl, and apatite).

Petroleum sulfonates are also called as green acids which are the by-product when lubricant is produced from petroleum. The flowchart of petroleum sulfonates is given as follows:



Aerofloat 801 and 899 are water-soluble sulfonates. Aerofloat 825 is oil-soluble sulfonate. They are usually used with fuel oil. It should be pointed out that petroleum sulfonates have been widely used to flotage iron ores in industry because of extensive sources. Some examples for the flotation of iron ores using petroleum sulfonates are shown in Table 2.8.

Table 2.8 Examples for the flotation of iron ores using petroleum sulfonates

Mineral processing plant	Mineral type	Flotation plan	Collector	Dosage (g/t)	pH	Concentrate grade (%)	Recovery rate of Fe (%)
Groveland, America	Hematite	Cationic flotation	Petroleum sulfonate; tal oil; fuel oil	730–910	6.6	60	85.8
Annix, America	Hematite	Cationic flotation	Petroleum sulfonate; tal oil; fuel oil	–	Neutral	60–63	80.0
Dearborn, America	Hematite	Cationic flotation	Petroleum sulfonate; tal oil; fuel oil	–	Neutral	61.7	63.9
Krivoy Rog, Soviet Union	–	Cationic flotation	Petroleum sulfonate; tal oil Soap	2300	–	48	–

Table 2.9 Reagent systems of petroleum sulfonates in various flotation processes

Reagent	Dosage (g/t)			
	Spiral tailing flotation	Whole raw ore flotation	Pilot test of spiral tailing flotation	Industrial tests
Petroleum sulfonate	900	900	970	580
Fatty acid–fuel oil	250	200	400	–
Fatty acid or soap	–	1300	–	180
Fuel oil	540	670	480	320
Frother	–	–	70	–
H ₂ SO ₄	1800	1800	850	1000
Na ₂ SiO ₃	900	900	450	310
Starch	–	700	–	–
Ca(OH) ₂	–	2500	–	–

Petroleum sulfonates have been used for a long time in Groveland, America. The grain constitution of iron ore is 28–200 mesh. And the iron ores are comprised of 75 % hematite and 25 % magnetite. The flotation results with various reagents are found in Table 2.9.

Petroleum sulfonate was used to directly flotote the raw ore in laboratory. Meanwhile, fatty acid was used to reversely flotote quartz in the flotation of the raw ore. Comparison between direct and reverse flotation separations is given as follows:

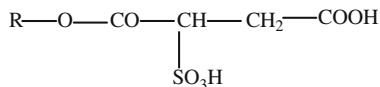
Direct flotation with petroleum sulfonate		Quartz reverse flotation with fatty acid	
Fe (%)	Recovery rate of Fe (%)	Fe (%)	Recovery rate of Fe (%)
58.4	73.7	54.6	70.8
61.1	84.7	52.3	85.9
56.3	85.2	51.6	89.1

It can be seen that the flotation performance of petroleum sulfonate is better than that of fatty acid.

According to M. C. Frankenstein, sodium alkylbenzene sulfonate can be used to flotote beryl [11]. The molecular weight of sodium alkylbenzene sulfonate is 450–470. The number of C atoms of hydrocarbon chain is 25–30. And the melting point of sodium alkylbenzene sulfonate is 250–260 F.

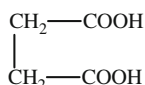
2.6.5 Other Sulfonic Acid Derivatives and Sulfosuccinic Acids

According to the foreign report, the structure of another sulfofatty acid is as follows [12]:

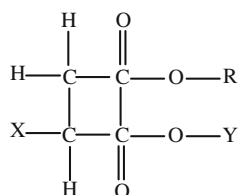


This sulfofatty acid is usually used to float fluorite.

Succinic acid can be used in the flotation of cassiterite and some oxide minerals. Succinic acid is also called as butanedioic acid. The structure of succinic acid is as follows:

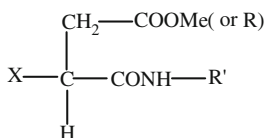


The general expression of the derivatives of sulfosuccinic acid can be given as follows:



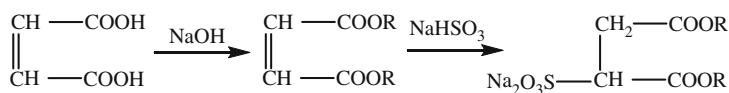
where R refers to the alkyl with C₅–C₂₀; X refers to SO₃Me; Me refers to K, Na, or NH₄; and Y refers to R, Me, or amide group.

When Y is amide group, the structure of the derivatives of sulfosuccinic acid is as follows:

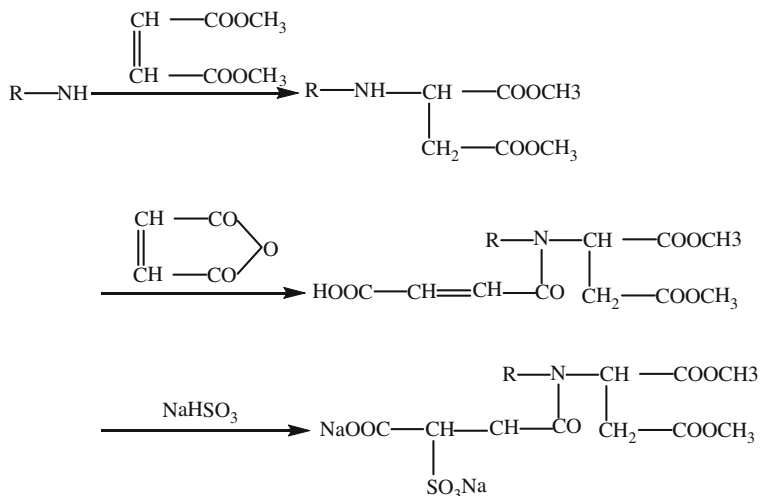


The above reagent is called as *N*-alkyl sulfo amidosuccinic acid. Aerosol surfactants belong to the series of *N*-alkyl sulfo amidosuccinic acid, like Aerosol 107.

Sulfosuccinic acid can be synthesized by adopting butenedioic acid as main raw material. The synthetic reaction is achieved by heating alcohol, butenedioic acid, and NaHSO₃. The synthetic reaction can be given by the following:



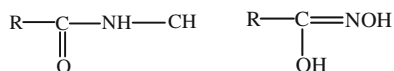
Sulfo amidosuccinic acid can be synthesized by adopting amine, butylene diacidic ester, and maleic anhydride as raw materials. The synthetic reaction can be given by the following:



The flotation performance of this reagent is good in the flotation of cassiterite at pH 7–9.

2.7 Hydroxamic Acids and Their Salts

Hydroxamic acids involve in the formation of the following two tautomers:

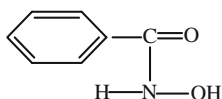


Hydroxamic acids can be synthesized from fatty acids and hydroxylamine. The reaction can be given by the following:



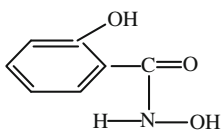
Hydroxamic acids mainly include the following compounds:

Benzoyl hydroxamic acid:



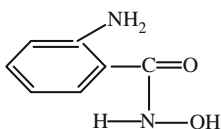
The solubility of benzoyl hydroxamic acid is 2.25 g/100 mL at 25 °C.

Salicyl hydroxamic acid:



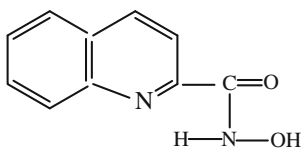
The solubility of salicyl hydroxamic acid is 0.5 g/100 mL at 25 °C.

Anthranil hydroxamic acid:

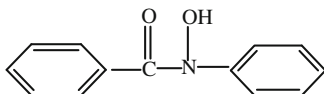


The solubility of anthranil hydroxamic acid is 0.4 g/100 mL at 23 °C.

Quinolyl hydroxamic acid:

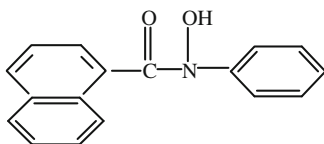


N-benzoyl-*N*-phenylhydroxylamine:



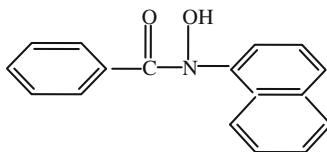
The solubility of *N*-benzoyl-*N*-phenylhydroxylamine is 0.04 g/100 mL.

N-1-naphthoyl hydroxylamine:



The solubility of *N*-1-naphthoyl hydroxylamine is 0.04 g/100 mL.

N-benzoyl-1-naphthoyl hydroxylamine:



The solubility of *N*-benzoyl-1-naphthoyl hydroxylamine is 0.013 g/100 mL.

Hydroxamic acids and related salts are initially used to flotite malachite and hematite. Subsequently, they are used in the flotation of various minerals of rare

metals [13–15]. Octyl hydroxamic acid and its potassium salt are used to float hematite and goethite. Because hydroxamic acid is characterized by slow adsorption and long stirring time, the flotation performance of hydroxamic acid or its potassium salt is relatively better when it is used to float fine-grained ore ($-15\ \mu\text{m}$). The grade of iron ore concentrate becomes 61–69 % when the dosage of octyl hydroxamic acid or its potassium salt is 0.18 kg/t.

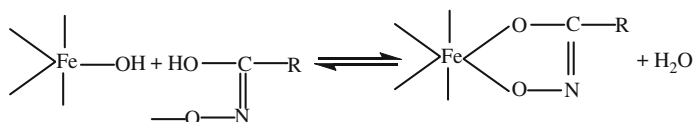
According to H.D. Peterson, the concentrate grade and recovery rate were, respectively, 31.6 and 76 % when potassium octyl hydroximate was applied in the flotation of malachite under the condition of reagent dosage 0.18 kg/t, pH 6.5, and temperature 58 °C.

Meanwhile, the hydroxamic acid with C_7 – C_9 (ИМ-50) shows good flotation performance when it is used in the flotation of pyrochlore, loparite, perovskite, cassiterite, yttrantalite, and various rare earth minerals.

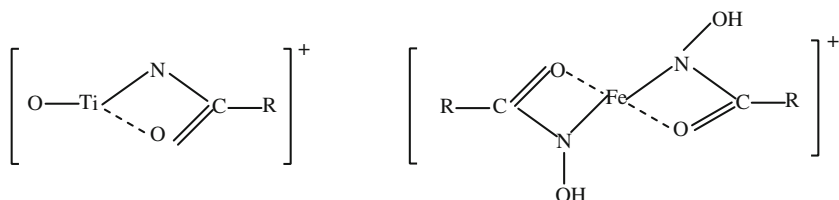
As mentioned above, hydroxamic acids adsorb on the mineral surface via chemical adsorption. According to M.C. Frankenstein, the FTIR testing results can be given as follows:

Hematite	1620, 3430 cm^{-1}
Octyl hydroxamic acid	1625, 1550, 1465, 1330, 1300, 1120 cm^{-1}
Fe^{3+} precipitation of hydroxamic acid at pH 3.0	1518, 1583 cm^{-1}
Fe^{3+} precipitation of hydroxamic acid at pH 9.0	1500, 1700 cm^{-1}

Based on these, adsorption mechanism of hydroxamic acid on hematite was proposed as follows:



According to the FTIR analysis of Polkin, the structures of Fe and Ti complexes of hydroxamic acid can be given as follows:



In general, the appearances of absorption bands at 1538 and 1690 cm^{-1} show that both the complex and the free acid generates on the mineral surface.

2.8 Phosphonic Acids and Arsonic Acids

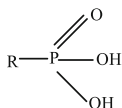
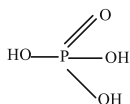
2.8.1 Preparation of Phosphonic Acids and Arsonic Acids

Phosphonic acids and arsonic acids are initially used to flotat cassiterite. Subsequently, they are gradually used for the flotation of various oxide minerals [16–18]. High selectivity is the preponderant characteristic of phosphonic acids and arsonic acids. Phosphonic acids and arsonic acids are not sensitive to Ca^{2+} in the flotation process.

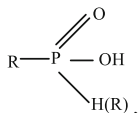
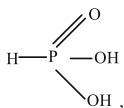
According to organic chemistry, the structures of various phosphonic acids and arsonic acids can be given as follows:

(I) Phosphonic acids and arsonic acids

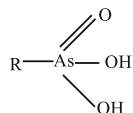
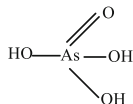
Phosphonic acids:



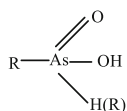
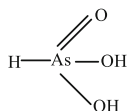
Hypophosphorous acids:



Arsonic acids:

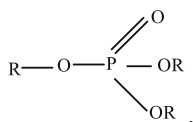
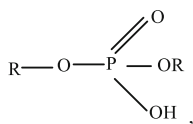
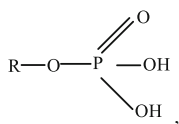


Arsenious acid:

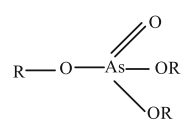
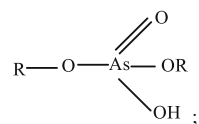
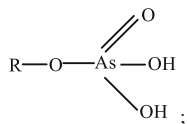


(II) Phosphates and arsenates

Phosphates:



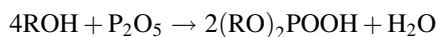
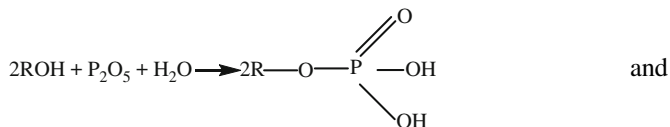
Arsenates:



The difference in the structures of phosphonic acid and phosphate lies in the following aspects:

- (1) The P atom of phosphate indirectly connects with the C atom of alkyl via O atom;
- (2) The P atom of phosphonic acid directly connects with the C atom of alkyl.

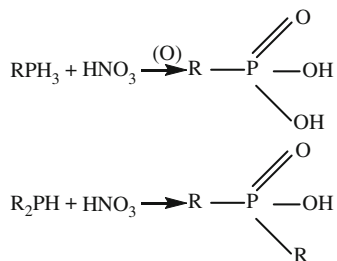
Phosphates can be synthesized from alcohols. The reaction can be given by the following:



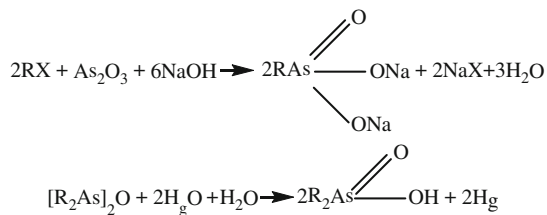
The preparation methods of phosphonic acids and arsonic acids can be given by the following:

(I) Fatty phosphonic acids and arsonic acids

Fatty phosphonic acids can be synthesized by the following:

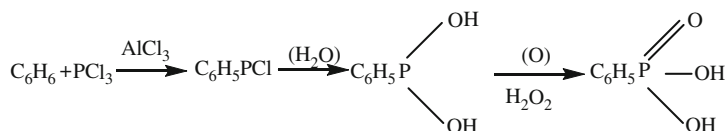


Fatty arsonic acids can be synthesized from arsenious acids and haloalkanes. The reaction can be given by the following:

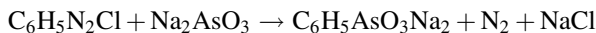


(II) Aryl phosphonic acids and arsonic acids

Aryl phosphonic acids can be synthesized by the following:



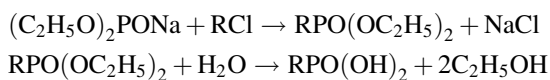
Aryl arsonic acids can be synthesized by the following:



According to the related reports, some specific preparation methods of various phosphonic acids used as flotation reagent are as follows:

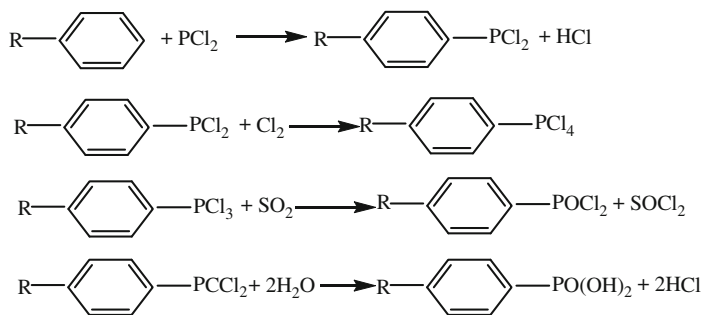
(1) Alkyl phosphonic acids

Alkyl phosphonic acids can be synthesized by the following:

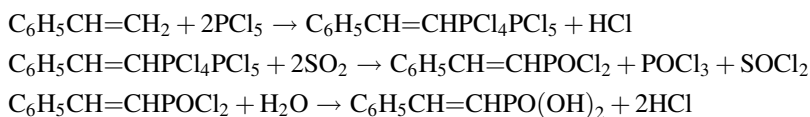


(2) Aryl phosphonic acids

Aryl phosphonic acids can be synthesized by the following:



The specific preparation process of styrene phosphoric acid can be expressed as follows:



2.8.2 Flotation Performance of Phosphonic Acid

It was reported that organic phosphonic acids with the alkyl of C₆–C₈ perform good flotation performance in the flotation of cassiterite. For the flotation of cassiterite, the orders of flotation performances of various phosphonic acids are as follows:

Recovery rate:

p-ethyl phenyl phosphonic acid > ethyl phosphonic acid > *p*-tolyl phosphonic acid > dodecyl phosphonic acid > butyl phosphonic acid

Concentrate grade:

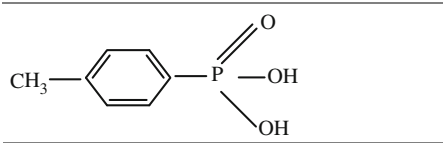
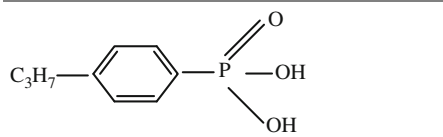
p-tolyl phosphonic acid > *p*-ethyl phenyl phosphonic acid > dodecyl phosphonic acid > ethyl phosphonic acid

Comparison between phosphonic acid, phosphorous acid, and pyrophosphoric acid was reported subsequently. The comparison of the above reagents can be summarized as follows:

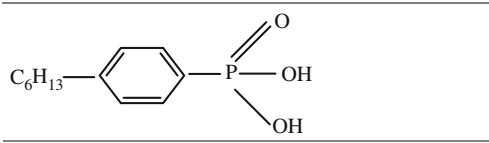
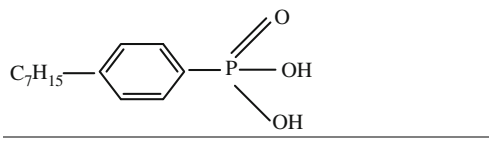
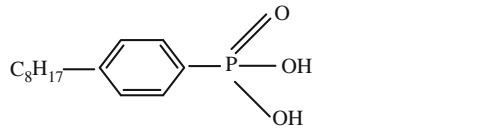
- (1) Alkyl or aryl phosphorous acids have no collecting capability.
- (2) The collecting performance of pyrophosphoric acid is worse than that of phosphonic acid.

- (3) Phosphonic acid can generate phosphomonoester, phosphodiester, and phosphotriester because phosphonic acid contains three $-OH$. Phosphotriester has no collecting performance. Dialkyl and aryl phosphonates also have no collecting performance. The flotation performances of decoyl and octyl phosphomonoesters are relatively better in the flotation of cassiterite.

For alkylaryl phosphonic acids, the flotation performances of *p*-methyl and *p*-propylphenyl phosphonic acids are relatively better.

	<i>p</i> -methyl phosphonic acid
	<i>p</i> -propylbenzene phosphonic acid

For alkyl phosphonic acids, the flotation performances of decoyl, heptyl, and octyl phosphonic acids are relatively better.

	Decoyl phosphonic acid
	Heptyl phosphonic acid
	Octyl phosphonic acid

Comparatively speaking, the concentrate grade is relatively higher when aryl phosphonic acid is applied in the flotation process; the recovery rate is relatively higher when alkyl phosphonic acid is applied in the flotation process. The related flotation results of cassiterite are given as follows:

	Tolyl arsonic acid	Ethyl phenyl phosphonic acid	Heptyl phosphonic acid
Dosage (g/t)	410	295	100
The content of Sn in original ore (%)	0.37	0.39	0.39
The content of Sn in concentrate (%)	5.90	6.18	2.79
Recovery rate (%)	63.60	72.90	83.90

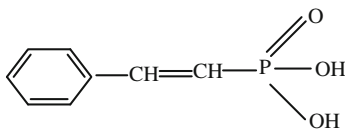
Among the phosphonic acid collectors, the collecting capability of styryl phosphonic acid is best in the flotation of cassiterite. And the collecting capability of styryl phosphonic acid is not influenced by Ca^{2+} or Mg^{2+} . The flotation results of Edinburgh's cassiterite using various phosphonic acid collectors are shown in Table 2.10.

Table 2.10 Flotation results of Edinburgh's cassiterite using various phosphonic acid collectors

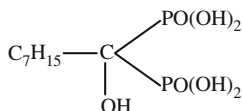
Collector	Dosage (g/t)	Sn grade of raw ore (%)	Sn grade of concentrate (%)	Recovery rate of Sn (%)	Ore grain size
Cinnamene phosphoric acid	270	0.32	4.33	85.4	Coarse fraction
Cinnamene phosphoric acid	240	0.33	9.85	79.4	
Heptyl phosphoric acid	85	0.37	5.55	84.7	
Tolyl arsonic acid	415	0.25	4.47	65.3	
Alkyl phosphomonoester	160	0.31	0.79	77.6	
Hydroximic acid	105	0.43	0.88	87.5	
Oleic acid	760	0.32	1.15	75.4	Fine fraction
Cinnamene phosphoric acid	390	0.23	4.67	57.8	
Cinnamene phosphoric acid	375	0.21	4.77	63.0	
Heptyl phosphoric acid	190	0.24	4.06	61.5	
Tolyl arsonic acid	510	0.22	2.30	53.0	
Alkyl phosphomonoester	195	0.22	0.89	28.1	
Hydroximic acid	126	0.28	2.15	31.6	

The functional mechanism and the structure–activity relationship of styryl phosphonic acid and similar phosphonic acids had been studied. It was reported that the selectivity of phosphonic acid has the relation with the quantity of polar groups. Take the following reagents for example:

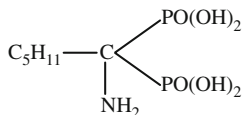
(1) Styryl phosphonic acid



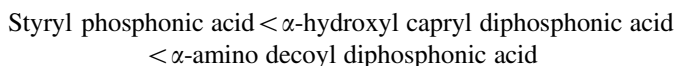
(2) α -hydroxyl capryl diphosphonic acid



(3) α -amino decyl diphosphonic acid

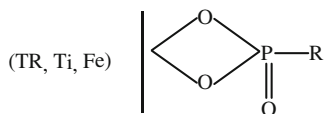


The collecting capability of styryl phosphonic acid is further improved with the addition of another phospho group. The collecting capability of amino decyl diphosphonic acid is stronger than that of hydroxyl capryl diphosphonic acid. The orders of collecting capabilities of the above phosphonic acids are as follows:



Based on these differences in collecting capabilities of the above phosphonic acids, the cassiterite with granularity—44 μm —is flotated through roughing using styryl phosphonic acid, and flotated subsequently using α -amino decyl diphosphonic acid choicely. It can be obtained that the concentrate grade and the recovery rate are, respectively, 11 and 56–60 %.

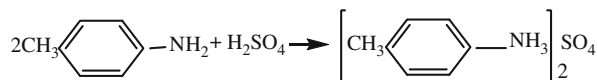
Phosphonic acids adsorb on mineral surface mainly via chemical adsorption and partly hydrogen bond and electrostatic force. The bonding graph between phosphonic acid and mineral can be expressed as follows:



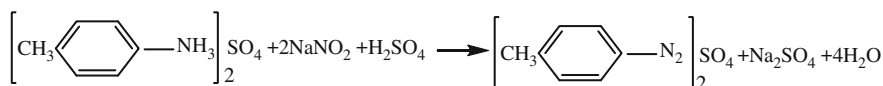
2.8.3 Flotation Performance of Arsonic Acid

It was reported that the collecting capability of *p*-tolueneearsonic acid is best among the arsonic acid collectors. The preparation methods of arsonic acid can be given by the following:

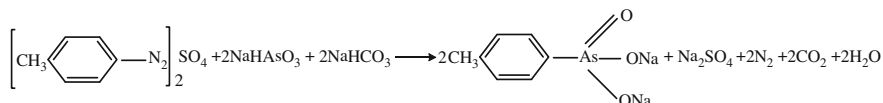
(1) Acidification



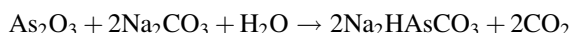
(2) Diazotization



(3) Arsonic acidification



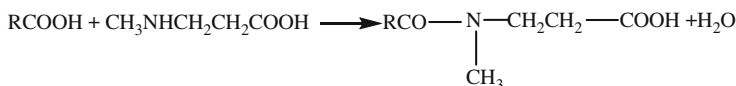
Sodium arsenate is prepared from white arsenic. The reaction is as follows:



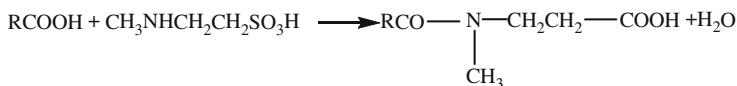
2.9 Amino Acids and Amphoteric Collectors

As discussed above, amino acids are amphoteric collectors. Various amino acids are used in the flotation of oxide minerals [2, 19, 20]. Take the following reagents for example:

(1) The condensation products of fatty acids and amino acid:



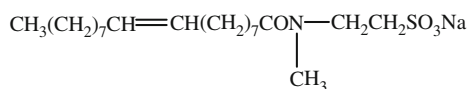
(2) The condensation products of fatty acids and sulfamic acid:



These above reagents can be used to flotite hematite, scheelite, and wolframite.

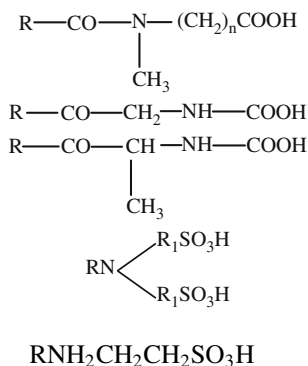
Various amino acids can be produced using various raw materials. The sodium aminocarboxylate (Medialan A) and sulfamic acid (Hostapon T) are both synthesized using oleic acid as raw material. The sodium aminocarboxylate (Medialan KA) and sulfamic acid (Hostapon T) are both synthesized using lauric acid as raw material.

Igepon type collectors also belong to sulfamic acids. For instance, the structure of Igepon T is as follows:

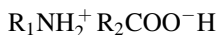


Igepon T is synthesized via the condensation reaction of $\text{C}_{17}\text{H}_{33}\text{COCl}$ and $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{SO}_3\text{Na}$.

The structure of synthetic product varies with the structure of raw material. For example, the following synthetic products can be obtained when the lengths of $-\text{CH}_2-$ and the positions of $-\text{NH}_2-$ are different in raw amino acids.



As mentioned before, amino acids are dissociated into neutral dipole at a certain pH:



The changes of flotation performance of amino acid in the vicinity of the zero charge point had been discussed. The flotation results of white mica, hematite, and quartz using sodium *N*-alkyl- β -aminopropanoate are found in Fig. 3.3 (Volume 1).

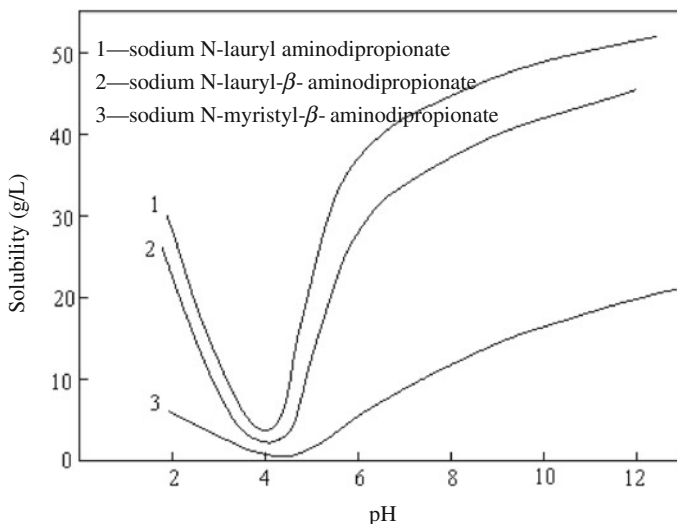


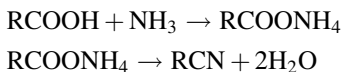
Fig. 2.3 Influence of pH on the solubility of amino acid

The influence of pH on the solubility of amino acid is shown in Fig. 2.3. As shown in Fig. 2.3, the solubility of amino acid appears to be smallest when the solution pH approaches the zero charge point.

2.10 Cationic Collectors

Cationic collectors are mainly comprised of primary amine and alkyl naphthyridines. For manufacturing reason, secondary amine usually exists in the primary amine. The synthetic routes of primary amine are divided into nitrile reduction process and aliphatic nitrile reduction process. The main synthetic reactions are given by the following:

- (1) Synthesis of nitrile from fatty acid



- (2) Catalytic hydrogenation of fatty nitrile

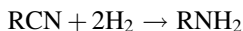
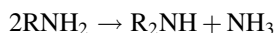


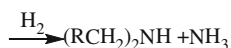
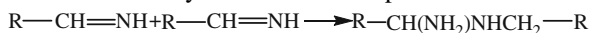
Table 2.11 Solubilities and *CMC* of various amines [2, 19]

Amine	Solubility (mol/L)	<i>CMC</i> (mol/L)	
		Ref. Dobjas	Ref. Tamamushj
Decyl amine	5×10^{-4}	5.4×10^{-2}	
Laurylamine	2×10^{-5}	9.38×10^{-2}	0.0130 (20 °C), 0.0133 (40 °C)
Tetradecyl amine	1×10^{-6}	2.8×10^{-3}	0.0034 (40 °C)
Cetylamine		8.0×10^{-4}	0.0012 (40 °C)
Octadecylamine		3.0×10^{-4}	
Bromlauryl pyridine			0.0012 (40 °C)

side reaction:



Fatty nitrile can be reduced to primary amine in the presence of Raney Ni. The reaction of secondary amine can be expressed as follows:



The solubilities and *CMC* of various amines are shown in Table 2.11.

The orders of solubilities of the salts that are generated by arylamine and various acids can be given as follows:

molybdate, vanadate, silicate $< 2.5 \times 10^{-4}$ mol/L

$\text{S}_2\text{O}_3^{2-} < \text{HCO}_3^-$, SO_3^{2-} , $\text{HAsO}_4^{2-} < 1.25 \times 10^{-4}$ mol/L

$\text{SO}_4^{2-} < 25 \times 10^{-4}$ mol/L $< \text{F}^-$, boric acid, Cl^- , S^{2-} , $\text{H}_3\text{PO}_4^{2-}$

The confecting methods of two amine solutions are listed in Table 2.12 [10].

These amine collectors include Alamine, Alamac, Armac, Armeen, and Ninol in other countries. Amine collectors are mainly used to flotat quartz, aluminosilicate, phosphate, carbonate, and soluble salt. Meanwhile, they can be applied in the reverse flotation of hematite.

In recent years, fatty amines have been used as the collector of quartz in the reverse flotation of hematite in laboratory and industry. For example, using starch and dextrine as depressant, the flotation results of Canadian Knob iron ore using various amine collectors in laboratory can be given as follows:

Table 2.12 Confecting methods of two fatty amine solutions

Solution	Confecting method	Mass concentration of amine	Neutralization degree of amine	Temperature
Amine/water	(1) Water (60–100 %)	2.5–5 %	25–48 %	Blending: (1) Water 100–120 F (2) Amine 100–150 F (3) Acetic acid Storing: 80–100 F
	(2) Amine			
	(3) Acetic acid			
	(4) Diluting			
Amine–kerosene/water	(1) Water (60–100 %)	2.5–5 %	25–35 %	Blending: (1) Water 100–120 F (2) Amine–kerosene 80–120 F (3) Acetic acid Storing: 80–100 F
	(2) Amine–kerosene			
	(3) Acetic acid			
	(4) Diluting (cold water)			

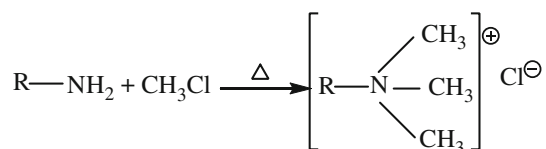
Amine collector	Concentrate grade (%)		Recovery rate of Fe (%)
	Fe	SiO ₂	
RADA	61.2	5.6	93.9
AL-11	67.3	4.6	93.4
DL-11	62.4	4.6	94.1
Alamine 21	61.4	5.6	94.4
Diamine 21	62.1	5.3	95.3
Diamine 26	57.3	12.7	98.0
Arosurf MG83	67.7	4.3	94.2

Using wheat dextrine as depressant, the flotation results of Canadian Knob iron ore using Arosurf MG83 at pH 10–10.5 can be given as follows:

Milling capability	Raw ore grade (%)		Concentrate grade (%)		Recovery rate of Fe (t/h)
	Fe	SiO ₂	Fe	SiO ₂	
890	55.6	16.5	62.8	6.2	89.6
1020	56.0	14.7	63.3	5.4	91.6

Arosurf MG83 is comprised of *N*-tridecyloxy-propyl-1, 3-propylene diamine acetate. It belongs to ether amine collector. Ether amine refers to the nonpolar hydrocarbon chain containing the O atom of ether. Based on the flotation results of hematite using various ether amines and fatty amines [21], it can be obtained that the collecting performance of octadecyl ether amine is as same as that of tetradecyl amine. The collecting performance of tetradecyl ether amine is as same as that of dodecyl amine. The collecting performance of dodecyl ether amine is relatively weak.

Quaternary amine with short hydrocarbon chain is mainly used in the flotation of soluble salt ores. Quaternary amine can be synthesized by adopting primary amine and methyl chloride as raw materials. The synthetic reaction can be given by the following:



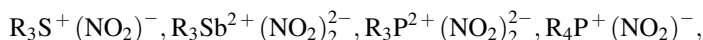
It was reported recently that quaternary amine salts had been used as the collector of copper oxide ore [22]. Those quaternary amine salts include propyl, butyl, amyl, and trimethyl hexadecyl quaternary amine salt.

Diamines were also used as the collector of copper oxide ore and scheelite [22]. The length of the hydrocarbon chain of these diamine collectors is relatively large. When butanediamine is substituted by the R group with C_{14} – C_{18} :



The flotation performance of this modified diamine is better than that of monoamine in the separation of scheelite from calcite. The selectivity of diamine is better than that of monoamine in the separation of feldspar from quartz.

In addition to organic amine collectors, cationic collectors also involve in the surfactants containing S, P, and Sb atoms. These other cationic collectors can be given as follows:



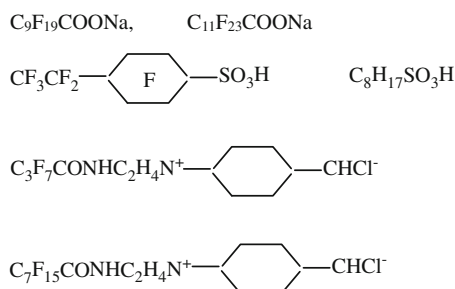
where R refers to the alkyl with C_1 – C_8 .

It was reported that these cationic collectors were mainly used to flotage Cu, Ni, and Co oxide ores, as well as some sulfide minerals.

2.11 Other Collectors

2.11.1 Organofluorine Collector

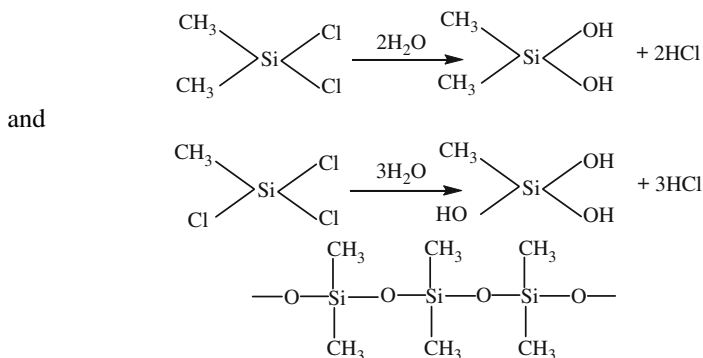
It was reported that organofluorine compounds could also be used as flotation collector [23]. The synthetical organofluorine collectors are given as follows:



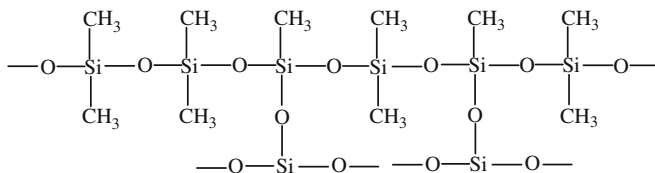
Meanwhile, potassium ethyl xanthate and potassium butyl xanthate that contain organofluorine are also used as collector. The flotation performances of organofluorine collectors are as same as those of fatty acids, amines, and xanthates in the flotation of hematite and pyrite. Because of their unstable characteristics, these organofluorine collectors are rarely used in flotation industry.

2.11.2 Organosilicone Collector

It was reported that organosilicone compounds could also be used as flotation collector [24, 25]. Organosilicone collector can be synthesized by adopting methylsilane and H_2O as raw materials. The reactions can be given by the following:



and



The recovery rate of silica sand is 92–95 % in the flotation of fluorite under the condition of fumigating time 10 min and pine oil dosage 50 g/t.

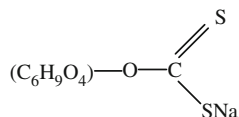
The flotation characteristics of organosilicone collector can be given by the following:

- (1) Raw ore must undergo pre-desliming process.
- (2) Raw ore must be dried.
- (3) Not suitable for flotating the polyporous and frangible ore.

2.11.3 Macromolecule Collector

It had been discovered very early that macromolecule compounds can be used as flotation collector. For example, gelatin is the collector of quartz. Casein can be used as the collector of feldspar and quartz. The main ingredients of gelatin and casein are proteins and amino acids. The flotation results of feldspar and quartz using amino acid are shown in Fig. 2.4.

Cellulose xanthate can be used as flotation collector, too. The structure of cellulose xanthate can be expressed as follows:



It was reported that cellulose xanthate was used to flotata silicate mineral from hematite. And it was a substitute for xanthate in Japan during World War II. The flotation performance of cellulose xanthate is worse than that of xanthate in the flotation of copper sulfide ore.

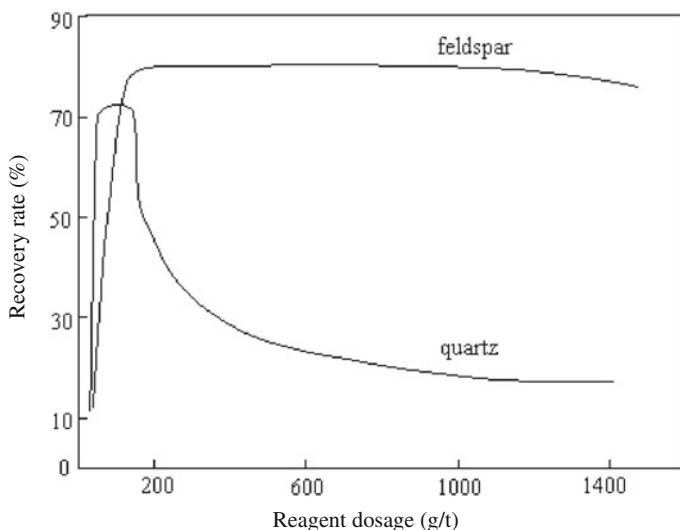
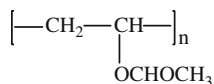


Fig. 2.4 Flotation results of feldspar and quartz using amino acid

2.11.4 Polymer Complexes Collector

Polymer complexes collector refers to the mixture of water-insoluble macromolecular polymer and general oxide collector. Therefore, polymer complexes collector is characterized by water-soluble and good collecting performance. For example, two polymer complexes solutions are obtained when polyvinyl acetate (PVAC) is, respectively, mixed into laurylamine hydrochloride (LAHCL) and sodium dodecyl sulfonate (NaLS). The structure of PVAC can be expressed as follows:



It is reported that the molecule of LAHCL gets adsorbed on the hydrocarbon chain of PVAC via van der Waals force.

For the following two polymer complexes collectors:

- (1) NaLS-PVAC polymer complexes collector
The mass ratio of NaLS to PVAC is 1:5.
- (2) LAHCL-PVAC polymer complexes collector
The mass ratio of LAHCL to PVAC is 1:1.

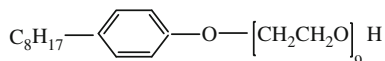
The flotation results of magnetite using the above two polymer complexes collectors are given as follows:

- (1) The separation indexes of magnetite using the above two polymer complexes collectors are better than those using individual NaLS or LAHCL.
- (2) The flotation processes are characterized by wide flotation pH and no limit of PZC of mineral when the above two polymer complexes used as collector.
- (3) The flotation of magnetite using LAHCL as collector is depressed when BaCl_2 is used as depressant. However, the flotation of magnetite using LAHCL-PVAC as collector is not influenced when BaCl_2 is used as depressant.

It can be seen that the collecting performance of polymer complexes collector is relatively stronger.

2.11.5 Nonionic Collector

Some nonionic collectors such as alkenes can also be used as flotation collector although they do not contain the strong polar groups. It was recently reported that octylphenol polyoxyethylene ether can be used to flot quartz and cassiterite [26]. The structure of octylphenol polyoxyethylene ether can be expressed as follows:



Octylphenol polyoxyethylene ether can be synthesized by adopting octylphenol and epoxyethane as raw materials.

Flotation results of quartz and cassiterite show that the flotation processes are influenced obviously by pulp pH. The flotation performance of octylphenol polyoxyethylene ether is good in the flotation of quartz when pulp pH is under 3. And octylphenol polyoxyethylene ether shows no flotation performance when pulp pH is above 9. As far as I know, octylphenol polyoxyethylene ether gets adsorbed on mineral surface via hydrogen bond. Hydroxyls appear on the mineral surface when pH is above pH_{PZC} . Therefore, flotation cannot take place because hydrogen bond weakens.

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