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CONCENTRATION OF NONSULFIDE ORES

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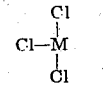
No Drawing. Application April 9, 1945, Serial No. 587,442

10 Claims. (Cl. 209—9)

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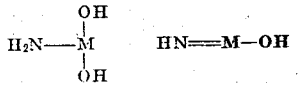
This invention relates to the concentration of ores. Particularly, it relates to separating the components, with a view to recovering the valuable constituents, of a wide variety of non-sulfide ores and minerals. More particularly it relates to those in which non-sulfide non-silicate minerals are admixed with silicious gangue, or in which silicate minerals are admixed with quartz, or in which potash minerals occur in their soluble ores. Among such ores and minerals, to the beneficiation of which the invention is particularly adapted, are phosphate, iron ore, barite, calcite, feldspar, fluorspar, kyanite, industrial sands and the constituents of soluble ores such as sylvinite.

The invention resides in the discovery of a new type of collector belonging to the group of amides and imides of trivalent metallic elements. Structurally they derive from the salts, hydroxide, oxides, etc., of trivalent metals, for example.



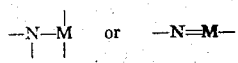
(Where M represents a trivalent metallic element.)

by substitution on one or more of the valences with one or more NH_2 or NH groups, the simplest being, for example, metal mono-amide hydroxide and metal mono-imide hydroxide



mono-amide mono-imide

All of the collectors of this invention are characterized, and chemically differentiated from collectors previously known to the art, by the fact that they contain the fundamental groups



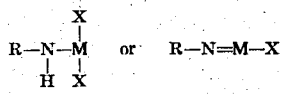
Included in this newly discovered class of collectors are the alkyl, alkylene, phenyl, cyclo-alkyl, naphthyl, abietyl and urea substituted trivalent metal amides and imides, their salts and halides.

However, to enable these compounds to function as collectors it is necessary that they contain at least one hydrocarbon group which is herein defined for convenience as a "functioning hydrocarbon group." This group may be: (*a*) an aliphatic group containing 7 or more carbon atoms at least 5 of which must be in a single straight chain; or (*b*) a hydrocarbon group such as is present in abietic acid; or (*c*) an alicyclic hydrocarbon such as is present in naphthenic acids; or (*d*) a naphthalene or substituted benzene group.

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Examples of functioning hydrocarbon groups are octyl, lauryl, myristyl, stearyl, oleyl, 7-ethyl-2-methyl-undecane and abietyl groups and the naphthenyl groups having the empirical formulas $C_nH_{2n-2}O_2$ where n is 8–13 and $C_nH_{2n-4}O_2$ and $C_nH_{2n-6}O_2$ where n is 14–25.

The collectors of the invention are, therefore, those compounds which contain at least one of the above described fundamental groups and at least one functioning hydrocarbon group. The general structural formula for these compounds may be represented as



wherein M is a trivalent metallic element; R is a functioning hydrocarbon group; X is OR, NRH, OY, or a halogen; Y being a salt-forming group or element and at least one R in the molecule being a functioning hydrocarbon group.

These compounds are readily prepared by methods well known to those skilled in the art. For example, they may be prepared by condensing trivalent metal salts or hydroxides or their amides with the proper amines or their hydrohalides, or by reacting anhydrides of acid forming trivalent metallic elements with amines or by reacting the ammonium salts of trivalent metal elements with suitable organic halides. Certain compounds of the invention may be prepared by reacting a substituted trivalent metallic acid with urea. Ammonium, amine, metal and alkali metal salts of the compounds may be formed by well known procedures.

The collectors of this invention have cationic activity and function as collectors for quartz, other silicious materials and sylvite. This is surprising, as heretofore cationic collectors have been considered to be basic compounds or the salts thereof, yet many of the compounds of this invention are acids and form salts with basic substances. Nevertheless these compounds as well as their salts, function as cationic active agents.

Concentrating processes of known types in which the collectors of this invention are useful include froth flotation, agglomeration with separation by means of shaking tables, underwater screens, moving belts, pneumatic launders, revolving perforated cylinders, etc. Other reagents may be used in conjunction with the collectors, appropriate to the particular process used, such as frothers, conditioners and modifiers. Of particular benefit are the water-insoluble, non-frothing hydrocarbon oils such as fuel oil, kerosene, etc.

Alkalies and acids or other pH adjusters may also be employed, their utility being readily ascertained by simple experimentation with the particular ore being treated, in a manner well known in the art. In concentrating soluble ores such as potash, the process should be carried out in a saturated aqueous solution of the soluble ore constituents.

The present invention may advantageously be utilized in step procedures, in one of the steps of which the collectors described are used. Thus, in the case of phosphate ores, the phosphate may be first partially concentrated by the use of the well known methods utilizing an alkali, fatty acids and a hydrocarbon oil; after which these reagents are inactivated or removed from the concentrate, for example by agitation with sulfuric acid, and then the residual quartz is removed by means of the collectors of the present invention. Or a portion of the quartz may be first removed by the agents of the present invention, followed by flotation of the phosphate with an alkali, fatty acids and a hydrocarbon oil. Purer products are obtainable by such combination methods.

Particular advantages of the collectors of this invention are the wide variety of ores to which they are applicable and the fact that in flotation they usually act immediately after being distributed in the pulp, at the most a short conditioning period being all that is required. Those compounds substantially insoluble in water may advantageously be dissolved in an organic solvent before being added to the pulp.

In such concentration processes as froth flotation, agglomeration tabling and the like, it is essential that there shall be selectively imparted to one of the ore constituents an air-adherent water-repellent quality. It is the functioning hydrocarbon group, as above defined, that gives to the reagents of this invention these essential qualities. It has been found by experiment that the functioning hydrocarbon group, whether it be aromatic, arylalkyl, alicyclic or aliphatic, may permissibly contain such constituents as halogens, low-molecular weight hydrocarbon groups, or ether, thioether, ester, imino and amido linkages, without impairing its capacity for imparting air-adherence and water-repellency.

The following specific examples are given by way of illustration of various embodiments of the invention and will illustrate to those skilled in the art how it is to be practiced. Examples 1–6 illustrate the effectiveness of various members of the class of compounds described on phosphate ore, in the concentration of which the collectors of the invention make it possible to float or agglomerate silicious gangue, showing these various members of the class to be qualitatively similar in their function. In examples 7–16 a variety of ores and minerals were concentrated or purified, using typical amides and imides of trivalent metallic elements of the invention, illustrating its general applicability to ores of the classes referred to above.

Example 1

Anhydrous aluminum chloride 33.3 g. (0.25 mol) and laurylamine 37.0 g. (0.2 mol) were dissolved in separate vessels in benzene, the aluminum chloride in a flask fitted with a reflux condenser. The solution of amine was added and the mixture refluxed for 16 hours at which time a red color had developed in the solution, which, when the solvent was evaporated, left a reddish residue. This residue was heated to 180° C. for 5 minutes and recrystallized from butyl ether in white

monoclinic crystals. These crystals, a mixture of lauryl aluminum amide and imide chlorides, were made up as a 2.5% solution in water and tested as a quartz collector in the froth flotation concentration of phosphate ore. Phosphate ore comprising from 35–37% B. P. L. (bone phosphate of lime) admixed with silicious gangue material was made into an aqueous pulp of 70% solids agitated, deslimed and screened to pass through a 28 mesh screen. It was then made into a pulp of 10% solids in a laboratory flotation machine and conditioned for 15 seconds with 2.0 pounds per ton of feed of the collector reagent above described and a quartz froth product removed. The machine discharge comprising the phosphate concentrate contained 69.5% B. P. L. with a recovery of 90.4%.

Example 2

The ore, reagent and procedure were identical with Example 1 except that only 1 pound per ton of feed was used and with the addition of 1.1 pounds of kerosene per ton of feed. Results were as follows:

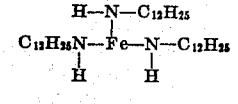
Product	Per Cent Wt.	Per Cent B. P. L.	Per Cent B. P. L. Rec.
Feed	100.0	39.5	100.0
Machine Discharge	54.5	70.7	97.5
Froth Product	45.4	2.7	2.5

Example 3

The ore and procedure were the same as in the foregoing examples. The collector reagent was prepared by reacting 30 g. (.11 mol) $CrCl_3.6H_2O$ dissolved in isopropanol with 18.5 g. (.1 mol) lauryl amine. The solution containing the two reactants was heated to the boiling point and the solvent allowed to evaporate off and the residue then heated to 180° where voluminous fumes came off indicating completion of the reaction. This reaction product, N-dodecyl chromic imide chloride, a dark green solid, was made up as a 2.5% solution and tested as quartz collector in the froth flotation concentration of phosphate. The machine discharge comprising the phosphate concentrate contained 74.3% B. P. L. with a recovery of 88.3%.

Example 4

Into a large evaporating dish was weighed 0.1 mol $FeCl_3.6H_2O$ and this warmed just to melting, into this melt was dropped with constant stirring 0.3 mol of lauryl amine, the addition of amine being very slow to avoid loss by spattering. When addition was complete, heating was continued until there was no further evolution of HCl and the reaction mixture had become quite viscous. This viscous sirup was taken up in butyl ether treated with aqueous HCl to remove unreacted amine and washed several times with water. The butyl ether was evaporated leaving a residue which we believe to be trilauryl tri-amino iron



as a thick semisolid which defied further purification. This product was soluble in isopropanol and was made up as a 2.5% solution in this solvent for the following froth flotation concentration test on phosphate, using 5 pounds per ton of feed. The ore and procedure were identical with Example 1 except that 2 pounds H_2SO_4 per ton

of feed were used as auxiliary. The results were as follows:

Product	Per Cent Wt.	Per Cent B. P. L.	Per Cent B. P. L. Rec.
Feed	100.0	38.9	100.0
Froth Product	48.8	3.84	4.8
Machine Discharge	51.2	72.3	95.2

Example 5

The ore, reagent and procedure were identical with Example 4 but as auxiliaries there were used 1.0 pound per ton of feed of H_2SO_4 and 1.0 pound per ton of feed of a reagent of the polypeptide class obtained by reaction, under alkaline conditions, between high molecular split-off products of albumin and molecules containing an easily replaceable halogen, as described in U. S. Patent 2,015,912. The collector reagent was used in a quantity of 5 pounds per ton of feed. The results were as follows:

Product	Per cent Wt.	Per cent B. P. L.	Per cent B. P. L. Rec.
Feed	100.0	38.2	100.0
Froth Product	66.5	18.14	32.2
Machine Discharge	33.5	77.54	67.8

Example 6

Example 4 was repeated decreasing the collector reagent to 4 pounds per ton of feed, all other conditions being identical. The results were as follows:

Product	Per cent Wt.	Per cent B. P. L.	Per cent B. P. L. Rec.
Feed	100.0	39.2	100.0
Froth Product	47.4	2.94	5.1
Machine Discharge	52.6	71.9	94.9

It will be noted here that in decreasing the reagent by one-fifth, the recovery and grade suffered by only 0.3% and 0.4% respectively while the per cent weight increased by 1.4%.

The foregoing examples showed the efficiency of the compounds of this invention in the concentration of phosphate ores. The following examples demonstrate the applicability of the compounds of this invention on other ores including soluble ores, such as sylvinite.

Example 7

Sylvinite ore received from Carlsbad, New Mexico, was crushed to pass a 10 mesh screen, and was then deslimed and ground in saturated brine so that it would pass a 35 mesh screen, after which it was made into a pulp of about 20% solids with a saturated brine of ore constituents. The reagent, 0.5 pound per ton of feed of a mixture of lauryl aluminum imino chloride and lauryl aluminum amino chloride, as a 2.5% water solution, made as described in Example 1, was added to the pulp. The pulp was agitated for 15 seconds to distribute the reagents and flotation was then effected. The froth product, which was the KCl concentrate, contained 86.5% KCl with a recovery of 73.2%.

Example 8

The ore and procedure were identical to that of Example 7. The reagent N-dodecyl chromic imide chloride, prepared as described in Example 3 was added as a 2.5% solution in isopropanol in a quantity of 1 pound per ton of feed. The plup and reagent were conditioned by agitation for 15 seconds and a KCl froth product removed which contained 81.3% KCl and a recovery of 52.1%.

Example 9

A sample of Minnesota iron ore of a fineness to pass a 35 mesh screen was deslimed by hand. The deslimed feed analyzed 27.8% Fe. This feed was made into a pulp of 20% solids and conditioned with 0.1 pound per ton of feed of a mixture of lauryl aluminum imino chloride and lauryl aluminum amino chloride for 15 seconds and a silica froth removed. The results were as follows:

Product	Per cent Wt.	Per cent Fe	Per cent Fe Rec.
Feed	100.0	28.8	100.0
Froth Product	35.4	55.9	68.6
Machine Discharge	64.6	14.0	31.4

Example 10

N-dodecyl chromic imide chloride was used as collector reagent in a test in which the ore and procedure were identical with Example 9. The amount of reagent used was 0.25 pound per ton of feed as a 2.5% solution in isopropanol. The results were as follows:

Product	Percent Wt.	Percent Fe	Percent Rec.
Feed	100.0	27.8	100.0
Froth Product	58.0	12.6	25.4
Machine Discharge	42.0	51.3	74.6

Example 11

The ore, procedure and reagent were identical to Example 10 except that 0.4 pound per ton of feed of the reagent was used and 1.0 pound per ton of feed of NaOH was used to adjust the pH of the pulp. The following results were obtained:

Product	Percent Wt.	Percent Fe	Percent Rec.
Feed	100.0	27.8	100.0
Froth Product	57.7	12.9	24.9
Machine Discharge	42.3	52.9	75.1

Example 12

A sample of barite ore was agitated for 3 minutes at 70% solids and deslimed, dried and screened to pass a 28 mesh screen. This was made into a pulp of 10% solids with 0.4 pound per ton of feed of lauryl chromic imino chloride described in Example 3 as a collector. The machine discharge yielded 76.7% $BaSO_4$ with a recovery of 59.7%.

Example 13

The ore and procedure were identical to Example 12. The reagent was 0.25 pound per ton of feed of tri-lauryl tri-amino iron as a 2.5% isopropanol solution and prepared as described in Example 4. The machine discharge yielded 80.7% $BaSO_4$ with a recovery of 80.1%.

Example 14

The test of Example 13 was repeated using 0.75 pound per ton of feed of the collector reagent

and 2.0 pounds per ton of feed of NaOH as auxiliary. Results were as follows:

Product	Per Cent Wt.	Per Cent $BaSO_4$	Per Cent $BaSO_4$ Rec.
Feed	100.0	70.2	100.0
Froth Product	55.0	58.8	46.1
Machine Discharge	45.0	84.4	53.9

Example 15

Feldspar ore was agitated as 70% solids pulp for 3 minutes and deslimed. Then it was dried and screened to pass through a 35 mesh screen. This feed was made into a 70% solids pulp, conditioned for 15 seconds with 0.02 pound per ton of feed of a mixture of lauryl aluminum amino chloride and lauryl aluminum imino chloride, diluted and mica removed. The pulp was dewatered to 70% solids, 4 pounds of HF and 0.1 pound of the collector reagent added, (both weights per ton of feed) conditioned for 15 seconds and a feldspar froth product removed which analyzed 19.7% Al_2O_3 with a recovery of 81.4%.

Example 16

The ore, procedure and reagent quantities were identical with Example 15. The reagent used was trilauryl triamino iron as described in Example 4. The results were as follows where froth product No. 1 is the mica float and froth product No. 2 is the feldspar froth. Collector reagent quantities are combined for both froth products, the mica float requiring 0.02 pound and the feldspar float 0.1 pound, both per ton of feed.

Product	Per Cent Wt.	Per Cent Al_2O_3	Per Cent Al_2O_3 Rec.
Froth Product No. 1	23.7	16.8	25.0
Froth Product No. 2	44.0	20.8	57.5
Machine Discharge	32.3	8.7	17.5
Feed	100.0	16.0	100.0

Summarizing some of the points illustrated by the foregoing examples, it will be observed that it has been shown that a wide range of compounds containing the fundamental trivalent metal amide and imide groups and at least one functioning hydrocarbon group function as collectors. The examples include compounds in which the functioning hydrocarbon group or groups are aliphatic, alicyclic and aromatic; in which they are attached to nitrogen; and in which three such groups are attached to three different nitrogens. They also show that the compounds may have all of their OH groups replaced by a halogen.

The compounds of the examples and the particular procedures and ores therein set forth are to be taken as illustrative merely and not as limitations of the invention which is to be construed broadly within the purview of the claims.

What is claimed is:

1. The process of separating the components of ores of the class consisting of non-sulfide non-silicate minerals admixed with silicious gangue and silicate minerals admixed with quartz and soluble potash minerals occurring in their soluble ores, which comprises admixing an aqueous pulp of the ore in a suitably divided state with a collector selected from the group consisting of: the amides and imides of trivalent iron, chromium and aluminum and salts of their amides and imides which contain at least one functioning hydrocarbon group from the class of aliphatic groups containing 7 or more carbon atoms at least 5 of which are in a single straight chain, hydrocarbon groups present in abietic and naphthenic acids, and naphthalene and substituted benzene groups; and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

2. The process of claim 1 wherein a mixture of said metal amides and metal imides is used.

3. The process of separating the components of ores of the class consisting of non-sulfide non-silicate minerals admixed with silicious gangue and silicate minerals admixed with quartz and soluble potash minerals occurring in their soluble ores, which comprises admixing an aqueous pulp of the ore in a suitably divided state with a collector selected from the group consisting of the amides and imides of trivalent iron, chromium and aluminum and salts of their amides and imides which contain a functioning hydrocarbon group which is an aliphatic group containing at least 7 carbon atoms at least 5 of which are in a single straight chain, and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

4. The process of separating the components of ores of the class consisting of non-sulfide non-silicate minerals admixed with silicious gangue and silicate minerals admixed with quartz and soluble potash minerals occurring in their soluble ores, which comprises admixing an aqueous pulp of the ore in a suitably divided state with N-monolauryl chromic imide chloride, and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

5. The process of separating the components of ores of the class consisting of non-sulfide non-silicate minerals admixed with silicious gangue and silicate minerals admixed with quartz and soluble potash minerals occurring in their soluble ores, which comprises admixing an aqueous pulp of the ore in a suitably divided state with a collector selected from the group consisting of the amides and imides of trivalent iron, chromium and aluminum and salts of their amides and imides containing at least one functioning hydrocarbon group which is a lauryl group, and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

6. The process of separating the components of ores of the class consisting of non-sulfide non-silicate minerals admixed with silicious gangue and silicate minerals admixed with quartz and soluble potash minerals occurring in their soluble ores, which comprises admxing an aqueous pulp of the ore in a suitably divided state with trilauryl triamino iron, and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

7. The process of claim 1 in which the concentration operation is a froth-flotation treatment in a froth-flotation machine.

8. The process of concentrating phosphate minerals from their ores containing silicious gangue which comprises admixing an aqueous pulp of the ore in a suitably divided state with trilauryl triamino iron and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

9. The process of concentrating phosphate minerals from their ores containing silicious gangue which comprises admixing an aqueous pulp of the ore in a suitably divided state with N-monolauryl chromic imide and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

10. The process of concentrating phosphate minerals from their ores containing silicious gangue which comprises admixing an aqueous pulp of the ore in a suitably divided state with a mixture of N-monolauryl aluminum amide chloride and N-monolauryl aluminum imide chloride and subjecting the thus conditioned pulp to a concentration operation to separate the ore constituents.

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