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## FROTHING AGENTS FOR USE IN FROTH FLOTATION PROCESSES

Roger F. Powell, Gwelo, Southern Rhodesia, and Eric F. Martin, Germiston, Transvaal, Union of South Africa; said Martin assignor to said Powell

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This invention relates to froth flotation processes for the concentration of noble and base metal ores and their products and other material amenable to such processes and it has particular reference to frothing agents used in carrying out such processes.

A major feature of this invention is the provision of a wide range of frothing agents for use in place of the commonly employed steam-distilled pine oil and other frothing agents already known, from which range of frothers a selection may be made as may best suit the wide and variable nature and composition of the materials to be treated by flotation processes.

The invention provides improvements in processes of the above kind using as is well understood, any usual promoting reagents such as for instance xanthates, with if desirable, any usual well-known conditioning reagents such as acids, alkalis, salts and so forth, by replacing the well-known "frothers" such as pine oil, cresols, higher alcohols and so on, by a single member, a fortuitous mixture, or a pre-arranged blend, of a very wide range of related organic compounds (excluding sulphur or nitrogen) as hereinafter indicated.

In the said range of related compounds, there are very wide variations of properties, ranging from straight froth-producing substances, through frother-collectors, to collector-frothers. Because of the wide variation of properties, and because virtually all the individual compounds are mutually miscible, it has been found practicable to provide a single compound, or a blend, ideally suited to the particular requirements of any particular industrial flotation process.

The related compounds above referred to comprise firstly alkoxy substituted acyclic hydrocarbons, the unsubstituted hydrocarbon containing from 4 to 10 carbon atoms, being substituted with from 4 to 6 alkoxy groups, having no more than one disubstituted alkoxy grouping at a terminal carbon atom of said hydrocarbon, the alkoxy groups being connected to the hydrocarbon by a C—O—C ether linkage and being selected from the group consisting of methoxy, ethoxy, normal propoxy, isopropoxy, methoxy-ethoxy and ethoxy-ethoxy; secondly alkoxy substituted acyclic straight chain hydrocarbons containing from 4 to 10 carbon atoms in the hydrocarbon chain and substituted with from 3 to 5 alkoxy groups and one divalent oxygen, the alkoxy substituents being connected to the hydrocarbon chain by a C—O—C ether linkage, having no more than one disubstituted alkoxy grouping at a terminal carbon atom of said hydrocarbon, and being selected from the group consisting of methoxy, ethoxy, normal propoxy, isopropoxy, methoxy-ethoxy and ethoxy-ethoxy.

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To give one striking example in connection with the properties of such compounds, those compounds whose properties rate them as "pure frothers" are usually found to give excellent recoveries of easily floatable minerals such as chalcocite, but if such compounds are used on an ore-containing tarnished pyrite, or pyrrhotite, the froths are still of an excellent type, but only a small proportion of the latter minerals reports in the froth. On the other hand, those compounds whose properties rate them as "frother-collectors," are still found to give excellent recoveries of the chalcocite, but in the case of tarnished pyrite, it is found that a very large proportion of the latter mineral reports very rapidly in the froth, as is implied by the term "frother-collector."

Certain of the compounds have the "collecting" property very highly developed, at the expense of the straight frothing property. The mineral reports very rapidly but the froth "hangs back in the machine." A good example of this is the tetra-ethyl-ether of pentaerythritol. In such cases blending-in some of a straight-frothing compound overcomes the difficulty.

Certain of the compounds have a very pronounced collecting power, and give strong froths, but there is a tendency for the condition of "over-oiling" to appear; the remedy being to blend-in a compound of different characteristics. This tendency to "over oil" appears to be connected with an "unbalanced" molecular structure, where the hydrocarbon portion of the molecule is not sufficiently "balanced" by enough alkoxy substituents.

Contrasted with the latter, is the type represented by 1:2:3:4 tetramethoxybutane and 1:2:3:4:5:6 hexamethoxyhexane. Both of these tend to give rather shallow wattery brittle froths; and it is considered that the alkoxy substituents are here in excess. The compound of intermediate structure, 1:1:3:5 tetramethoxyhexane has much better properties.

Some of the compounds which may be used according to the present invention, are solids at room temperature. However, they function quite satisfactorily if the crystals are slowly added to the ore-pulp or the like. Where such method may be industrially impracticable, the crystals may be dissolved in a small quantity of one of the liquid compounds.

It has become clear that the possible permutations and combinations of flotation properties in the wide range of compounds comprised in the definition here given, are extremely numerous. Actual flotation examples hereinafter set forth are accordingly intended to demonstrate that:

(i) As widely different classes of compounds are herein proved it may be reasonably assumed that the whole range according to this invention has a distinct value in flotation processes; and

(ii) In one section namely the alkoxy-substituted straight-chain-paraffins, the gradation of flotation properties has been correlated in considerable detail with gradation in molecular structure from ethane to octane, and over the range of substituents methoxy-, ethoxy-, n-propoxy-, isopropoxy-, and methoxy-ethoxy-.

The structure, which is considered as bringing about molecule frothing or frothing-collecting properties of value, is comprised in the following, in which the symbol X denotes—

| | |
|---|---|
| Methoxy | $CH_3O-$ |
| Ethoxy | $C_2H_5O$ |
| Normal Propoxy | $CH_3.CH_2.CH_2.O-$ |
| Isopropoxy | $CH_3.\underset{\displaystyle O}{\underset{\vert}{CH}}.CH_3$ |
| Methoxy-Ethoxy | $CH_3O.CH_2.CH_2O-$ |
| Ethoxy-Ethoxy | $CH_3.CH_2O.CH_2.CH_2O-$ |

wherein symbol Y denotes double-bonded oxygen and symbol Z denotes hydroxyl:

(i) At least two monovalent substituents X shall necessarily be attached by the C—O—C (ether) linkage to at least one or more carbon atoms in any of the straight-chain, branched-chain or monocyclic structures set out below.

(ii) More than two substituents X are allowable; some very valuable compounds have four substituents and several have been tested that have six, and it is believed accordingly that more than six are admissible.

(iii) In addition to the substituents X, the divalent substituent Y above, may be attached to any single carbon atom. More than one substituent Y may be present.

(iv) In addition to the substituent X, the monovalent substituent Z above, may be attached to any single carbon atom. More than one Z substituent may be present.

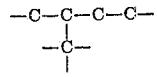
(v) Y and Z substituents may not be attached to the same carbon atom.

The molecular structures above referred to, are exemplified as follows, it being assumed that all free valencies on all carbon atoms are satisfied by hydrogen atoms except where the substituents as X, Y and Z are attached:

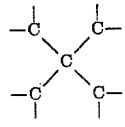
(i) *Straight chain.*—Four up to ten carbon atoms C—C—C—C— . . . &c.

(ii) *Branched chain.*—From four to ten carbon atoms.

(*a*) Such for instance as isopentane



(*b*) The type represented by neopentane



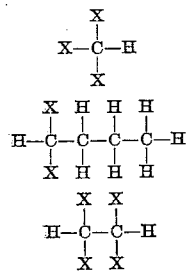
(*c*) And any intermediate types in which the chain is branched.

(iii) Any of the above structures (i) and (ii)

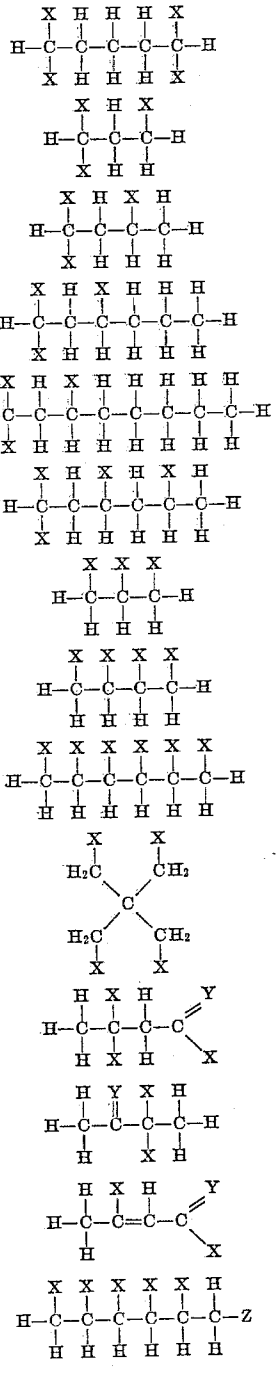


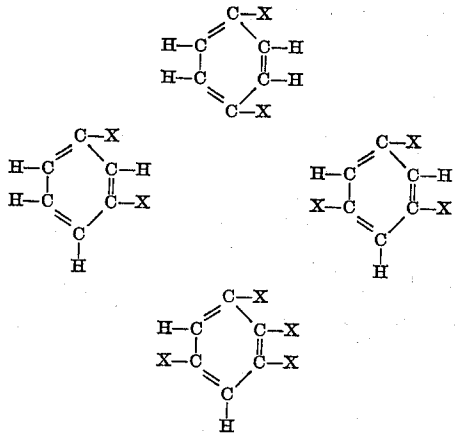
in which two adjacent carbon atoms are linked by an unsaturated double bond —C=C—.

The following examples of structural types, the subject of tests already made, illustrate the wide range of organic compounds which possess frothing or frothing-collecting properties:



through the series up to:





Before reference is made to tabulations of results of tests made with a wide variety of organic compounds, it is convenient to summarize the essential properties of frothers of interest in froth flotation processes, when used in conjunction with any of the commonly known promotors and/or conditioners, as follows:

i. That a small quantity of the frother per unit quantity of the ore or other material treated shall suffice to obtain the desired effect.

ii. Rate of dispersability of the frother in an aqueous ore or like pulp to which it is added.

iii. "Carrying or collecting power"—a term already understood in the art.

iv. Selectivity of the frother in its action upon the different minerals or other substances in association with one another in the pulp or the like, each of which having to be floated and, as far as possible, floated separately.

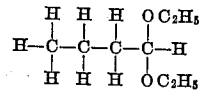
v. Selectivity of the frother in its action as between minerals or other materials which it is desired to float, and gangue or the like which it is desired not to float.

vi. Persistence of the frother in recirculation.

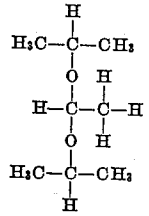
More particularly when straight-chain compounds are used such may be a polyalkoxyparaffin comprising from a single carbon atom to six carbon atoms in the paraffin chain (or up to 10 carbon atoms in the chain in certain cases) with from 4 to 6 or more alkoxy groups attached by the carbon-oxygen-carbon or "ether" linkage in any positions on the paraffin chain; the said alkoxy groups being methoxy, ethoxy, normal propoxy or isopropoxy, methoxy-ethoxy, ethoxy-ethoxy, or a mixture of said alkoxy groups.

*Dialkoxy paraffins.*—Although a number of these compounds are found to be technically effective, they are weaker frothers than pine oil, for example, the dialkoxyparaffins:

1:1 diethoxybutane

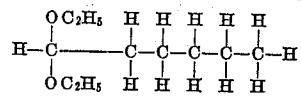


and 1:1 diisopropoxyethane





Dialkoxyparaffins containing upwards of 5 carbon atoms in the paraffin chain are frothers: for example the dialkoxyhexane:

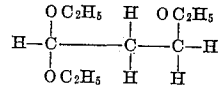


Trialkoxyparaffins other than 1:1:3 triethoxybutane as mentioned in my Patent No. 2,561,251, have shown marked differences in behaviour as for example 1:1:3 trimethoxybutane, 1:1:3 triethoxybutane, 1:1:3 tri-normal-propoxybutane, 1:1:3 tri-iso-propoxybutane, 1:1:3 tri-normal butoxybutane, and 1:1:3 tripentoxybutane. From the fact that the latter two compounds were found to be virtually useless, it appeared clear that the number of carbon atoms in the alkoxy groups should lie between 1 and 3, that is—

| | |
|---|---|
| Methoxy (—$OC_3$) | effective |
| Ethoxy (—$OC_2H_5$) | |
| Propoxy (—$OC_3H_7$) | |
| Methoxy-ethoxy | |
| Ethoxy-ethoxy | |
| Butoxy (—$OC_4H_9$) | ineffective |
| Pentoxy (—$OC_5H_{11}$) | |

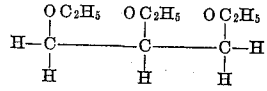
*Position of alkoxy groups*

It has been discovered that the position of the three alkoxy groups attached to the atoms of the paraffin chain is not of the utmost importance. Thus, 1:1:3 triethoxypropane of formula—

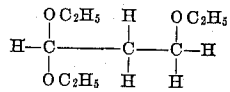


differing only from the 1:1:3 triethoxybutane by having one less carbon atom in the paraffin chain was investigated and proved highly effective, although other differences were found which render the selection of the butane as preferable.

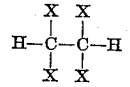
Compared to this 1:2:3 triethoxypropane displayed properties very close in all respects to those of 1:1:3 triethoxypropane, compare:



with

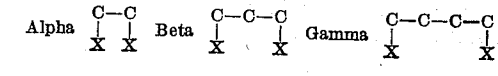


The above discovery coupled with another set out hereinafter regarding the effectiveness of polyalkoxy-paraffins in which the alkoxy groups are attached in the 1:1:2:2 position:



supports the conclusion that the positioning of the alkoxy groups on the carbon atoms of the paraffin chain is not a vital factor.

On the foregoing reasoning it is considered that the polyalkoxyparaffin will be effective when the paraffin contains from 4 to 10 carbon atoms and is substituted with alkoxy groups in the alpha, beta, or gamma positions in relation to one another, e. g. where X represents an alkoxy group:



or in specific cases 1:1:4:4 gamma-tetra-methoxybutane, and 1:2:3:4 tetra-methoxybutane.

*Effect of nature of alkoxy group*

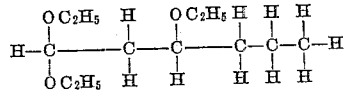
It was found by experiment on the following compounds namely:

Trimethoxypropane
Triethoxypropane
Tripropoxypropane
Trimethoxybutane
Triethoxybutane
Tripropoxybutane
Tributoxybutane
Tripentoxybutane
Tetra-ethoxyethane
Tetra-propoxyethane
Tetra-butoxyethane

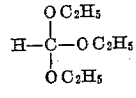
that the butoxy and pentoxy species were useless and so are excluded and that in each of the above sub-groups the properties varied in the ascending series methoxy→ethoxy→propoxy and there was a clear difference between the normal propoxy and the iso-propoxy cases. Tests have shown that the substituent methoxy-ethoxy- has properties very closely similar to those possessed by ethoxy-.

*Number of carbon atoms in the paraffin chain*

In the case of polyalkoxyparaffins having more than 4 carbon atoms in the paraffin chain it has been found from tests on (*a*) 1:1:3 triethoxyhexane of formula



and on (*b*) the substance 1:1:3 triethoxyoctane that these compounds are extremely effective with properties differing from the related triethoxypropane and triethoxybutane showing clearly the relationship between properties and the number of carbon atoms in the paraffin chain. Thus in the case of triethoxymethane of formula



it has been found that this extreme member of the series of triethoxyparaffins is weak but perfectly effective and its observed properties fall in the deducible place in the series from the single-carbon methane to the 6-carbon hexane.

GENERAL

Supported by results of further tests, the conclusion has been reached that all polyalkoxyparaffins within the range already indicated in an earlier part of this specification, and more particularly set out below, are effective flotation frothers with flotation properties varying in accordance with the following variables:

i. Number of carbon atoms in the paraffin chain from 4 to 10 or even more.

ii. Number of alkoxy groups attached to the paraffin chain from 4 to 6.

iii. Nature of the alkoxy group.

Limited to methoxy, ethoxy, normal propoxy, isopropoxy, methoxy-ethoxy and ethoxy-ethoxy.

Adverting to the question of properties of any frother, upon which depend its effectiveness in flotation processes, the following further observations are made in relation to the use of the polyalkoxyparaffins above discussed:

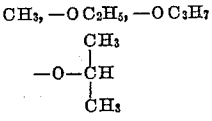


*No. 1.—Quantity needed per ton of ore or coal to produce desired effect*

(*a*) The greater the number of alkoxy groups the less is this quantity, other structure of the molecules being equal.

(*b*) The greater the number of carbon-atoms in the paraffin chain, other structure of the molecule being equal, the less is this quantity.

(*c*) The particular alkoxy group selected from the possibles, namely methoxy, ethoxy, normal propoxy and isopropoxy, very markedly affects this property; generally, increasingly smaller quantities are required per ton of ore or the like as the series is ascended:



but occasionally methoxy-ethoxy- behaves very much the same as ethoxy-.

*No. 2—Rate at which the ("water-insoluble") frother disperses in the aqueous ore-pulp*

The tetraalkoxyethanes have been observed to disperse extremely rapidly, and an increase in the number of alkoxy groups appears to have no appreciable effect on this property.

It appears that 6-carbon atoms in the chain determines the practical limit on this property. It has been observed also that this property appears not to be substantially affected by change in the nature of the alkoxy group employed.

1:1:3 triethoxyoctane (8-carbon) is rather slower-dispersing than 1:1:3 triethoxyhexane but is a practicable commercial substance when used alone.

*No. 3—"Carrying" or "collecting" power*

This property, which though nearly is not strictly the inverse property to property No. 1 above:

(*a*) Increases as the number of carbon-atoms in the paraffin chain, this increase being very clear and definite;

(*b*) Is affected only slightly by changes in number of alkoxy groups;

(*c*) Increases very definitely, other structure of the molecule being equal, in the series—

Methoxy, ethoxy, isopropoxy, and normal propoxy

*No. 4.—Selectivity as between two or more valuable minerals which are required to be floated as far as possible separately*

(*a*) This property, other structures of the molecule being equal, decreases very materially in the direction methoxy, ethoxy, n-propoxy, and isopropoxy, that is to say the property is in inverse ratio to property 3 above;

(*b*) This property is substantially unaffected by the number of alkoxy groups attached in the chain;

(*c*) This property depreciates, that is selectivity decreases, with increase in the number of carbon atoms in the paraffin chain.

*No. 5—The deleterious tendency to float valueless gangue with valuable minerals, or the like*

(*a*) This property seems to be especially troublesome when insufficient alkoxy substituents

are present on a long paraffin chain; ineffective in this regard are—

1:1:3 triethoxyhexane
and 1:1:3 triethoxyoctane

On the other hand, this property seems to be absent from 1:2:3:4:5:6 hexa-methoxyhexane, and we believe that in this latter case the effect of the 6 alkoxy groups has overcome it. On many ores this property is not very serious, but in the case of base metal flotation, it is an important one, so that a definite limit has to be set in selecting a suitable species of frother. As is well known the flotation of a relatively larger amount of gangue can be tolerated when treating sulphide gold ores for the reason that the gold content will be extracted not by smelting the whole concentrate but by wet lixiviation methods; so that the limit of five-carbon chains does not apply, in fact the six-carbon 1:1:3 triethoxyhexane has been proved by test to be an extremely effective frother on sulphide gold ores.

(*b*) The property again increases markedly as between the ethoxy and the isopropoxy groups, other structures of the molecules being equal, and decreases as between ethoxy and methoxy, but less markedly.

*No. 6.—Persistence of frother in water recirculated to head of circuit*

In commercial practice this is a very valuable property already recognised in the art. From visual and other observations the following conclusions are reached:

(*a*) Whereas this property is possessed in a marked degree by polyalkoxyparaffins containing methoxy or ethoxy groups it is possessed to a less marked degree in 1:1:3 triethoxyhexane than in the other ethoxy compounds; and it appears to become less marked when treating ores containing unusually high colloid contents. Polyalkoxyparaffins containing isopropoxy groups appear largely devoid of this property, while normal propoxy groups bring about a total deficiency in this property;

(*b*) 1:1:2:2 tetraethoxyethane possesses the property in a marked degree.

From the foregoing it appears that species which show this property do so by reason of a lesser degree of adsorption upon the minerals and gangue, compared with pine oil, for example, and that species containing isopropoxy groups and/or long paraffin chain species may be of little interest per se in processes of certain kinds.

The following three tabulations of data support the foregoing correlation of molecule structure within the range of this invention with the more important of the flotation properties above discussed which are briefly outlined for case of reference to the tables:

"Mineral selectivity" varies inversely as the molecular weight of the alkoxy group and inversely as the length of the paraffin chain.

"Mineral-carrying power" ("collecting-power") varies directly as the molecular weight of the alkoxy group. Isopropoxy confers very much increased "collecting-power" compared with normal-propoxy. It also varies directly as the length of the paraffin chain.

"Quantity needed, per ton of ore or coal, to produce desired effect," decreases very markedly as the number of alkoxy groups increases, as the number of carbon atoms increases from two to four, except when the four alkoxy groups are attached in the 1:2:3:4 position; and also as the alkoxy series rises through methoxy, ethoxy, isopropoxy.

Deleterious tendency to float valueless gangue varies directly both in the ascending series methoxy, ethoxy, to isopropoxy-n-propoxy and as the length of the paraffin chain.

TESTS

Fourteen tests were carried out in a 2,000-gram Denver-Fahrenwald Flotation Machine, under rigidly standardised conditions.

The only variable introduced was the different substance used as frother in each case; the quantity added was the same in each case, namely one standard capillary drop at the start of flotation, followed by four standard capillary drops after removing the primary concentrate for two minutes; an exception was made in two special tests, where only one drop was added after removing the primary concentrate.

The ore was of an ordinary type, largely quartzitic, with a natural alkalinity of pH 9.2; the two minerals present were a barren chalcopyrite and an auriferous pyrrhotite. Grinding was to 62% minus 200-mesh.

Earlier research had demonstrated that the pyrrhotite is peculiarly sensitive to adequate "carrying power" of the frother; accordingly the standard conditions for the tests were so selected that the "Control Test" just did not give optimum recovery of the pyrrhotite.

The results set out in Tables I, II and III, give full details of the tests carried out. It should be noted that the "Lbs. Pyrrhotite in Residue" are, under the standard test conditions inversely proportional to the "carrying-power," or "collecting-power" of the frother tested.

Additional to those shown in the tabulation, the following other polyalkoxyparaffins were tested, and found to have only slight value as frothers.

1:1:3 triisobutoxybutane
1:1:3 tri-n-butoxybutane
1:1:3 tripentoxybutane
1:1:2:2 tetra-n-butoxyethane

The tabulations I, II and III of data correlate the structure of the various polyalkoxyparaffins with the three most important flotation properties.

TABLE I.—MINERAL SELECTIVITY

| Test No. | Frother Used | Lbs per Ton of Ore, Floated in 1st Con. | | Ratio Pyrrhotite to Chalco pyrite |
|---|---|---|---|---|
| | | Pyrrhotite | Chalcopyrite | |
| 19 | 1:1:3 Trimethoxypropane | 40.9 | 69.2 | .59 to 1. |
| 20 | Triethoxymethane | 49.8 | 69.5 | .72 to 1. |
| 19 | 1:2:3 Triethoxypropane | 57.7 | 72.2 | .80 to 1. |
| 13 | 1:1:2:2 Tetraethoxyethane | 58.9 | 67.3 | .87 to 1. |
| 8 | Comml. Triethoxybutane | 63.5 | 70.1 | .90 to 1. |
| 14 | 1:1:3 Triethoxypropane | 60.8 | 66.4 | .91 to 1. |
| 21 | 1:1:3 Triisopropoxypropane | 79.4 | 75.5 | 1.05 to 1. |
| 16 | 1:1:2:2 Tetra-n-Propoxyethane. | 76.6 | 69.1 | 1.11 to 1. |
| 10 | 1:1:2:2 Tetraisopropoxyethane. | 88.2 | 62.2 | 1.31 to 1. |
| 12 | do | 84.8 | 70.1 | |
| 9 | 1:1:3 Triethoxyhexane | 91.7 | 68.1 | 1.39 to 1. |
| 11 | do | 98.3 | 68.8 | |

TABLE II.—MINERAL-CARRYING POWER

(Collecting Power)

| Test No. | Frother Used | Pyrrhotite | |
|---|---|---|---|
| | | Lbs. per ton ore, left in Residue | Percentage Recovery |
| 9 | 1:1:3 Triethoxyhexane | 14.5 | 92.3 |
| 11 | 1:1:3 Triethoxyhexane 40% of std. qty. | 25.0 | 86.0 |
| 10 | 1:1:2:2 Tetraisopropoxyethane | 15.0 | 91.8 |
| 12 | 1:1:2:2 Tetraisopropoxyethane 40% of std. qty. | 36.6 | 79.0 |
| 8 | Comml. Triethoxybutane | 33.5 | 81.7 |
| 14 | 1:1:3 Triethoxypropane | 33.5 | 82.1 |
| 15 | 1:2:3 Triethoxypropane | 34.2 | 80.9 |
| 20 | Triethoxymethane | 88.2 | 53.1 |
| 19 | 1:1:3 Trimethoxypropane | 91.6 | 50.0 |

TABLE III.—DELETERIOUS TENDENCY TO FLOAT VALUELESS GANGUE

| Test No. | Frother Used | Percent Gangue in— | | |
|---|---|---|---|---|
| | | First Con. | 2nd. Con. | |
| | | | Std. Qty. Frother | ¼ st. Qty. |
| 19 | 1:1:3 Trimethoxypropane | 13.1 | 20.6 | -------- |
| 15 | 1:2:3 Triethoxypropane | 13.2 | 27.6 | -------- |
| 20 | Triethoxymethane | 21.9 | 20.9 | -------- |
| 13 | 1:1:2:2 Tetraethoxyethane | 15.2 | 31.8 | -------- |
| 14 | 1:1:3 Triethoxypropane | 15.2 | 32.8 | -------- |
| 8 | Comml. Triethoxybutane | 18.3 | 31.7 | -------- |
| 10 | 1:1:2:2 Tetraisopropoxyethane | 23.8 | 60.9 | -------- |
| 12 | do | 25.8 | -------- | 41.1 |
| 9 | 1:1:3 Triethoxyhexane | 22.4 | 58.2 | -------- |
| 11 | do | 24.9 | -------- | 46.1 |

Adverting to the feature that organic compounds embraced within the wide range herein set forth and utilizable individually as effective frothing agents, are readily miscible with one another with the important result that means are thereby afforded in flotation practice enabling the frother by selective mixture to be varied in such a way as to combine in desired proportion essential properties each possessed by the individual substances in different degrees to suit special characterisation of a given ore, coal or other material to be treated, this aspect of the present invention will now be more fully discussed.

From a knowledge of the particular flotation properties of individual species in the wide range of compounds herein set forth, blends of any two or more of these substances can be produced with predictable flotation properties.

Advantages accruing from the aforegoing are very substantial, as will appear from the following wherein, for convenience, straight-chain compounds alone are dealt with:

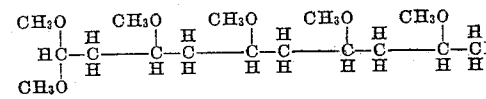
1. Large quantities of cheap species can be blended with smaller quantities of expensive species for economic reasons;

2. Species, one or other of whose properties exclude or substantially exclude them from the range of practical effectiveness when used alone, can be combined to bring such properties within the useful range by intelligent blending of such species with one another, for example:

(*a*) The six carbon polyalkoxyhexanes are so slow in dispersing in the ore-pulp or the like as generally to be unacceptable in practice. It is possible to blend a six-carbon hexane compound with a three carbon polyalkoxypropane compound so as to provide a blend better than the ingredients. The same remark applies to those species comprising more than six carbon atoms in the chain, which disperse at an even lower rate, appropriate blending overcoming this fault. Other properties, such, for instance, as strength of the polyalkoxyhexane constituent of the blend will not be destroyed by thus blending.

(*b*) The lower members of the series, such, for instance, as triethoxymethane and even some, at least, of the dialkoxyparaffins, which latter are comparatively cheap, can be brought into the range of practical utility by blending a suitable proportion of one of the more effective members of the series containing 4 or more alkoxy groups, and/or five or six or even more carbon atoms in the paraffin chain.

The possibilities arising from blending as explained may further bring into the range of practical utility as frothers, species up to decaalkoxydecanes, that is with carbon atoms up to 10, and with alkoxy groups up to 10 attached, for example, 1:1:3:5:7:9 hexamethoxydecane:



as well as intermediate members of the series, for instance trialkoxyheptane, tetraalkoxyoctane, and so on.

Adverting to the discussion of the principal practical properties of any frother as appearing earlier herein—

i. *Selectivity as between two or more valuable minerals which are required to be floated as far as possible separately*

This property of selectivity is substantially inversely proportional to "collecting-power," a fact which opens up wide possibilities in the result of blending suitably selected compounds.

ii. *Deleterious tendency to float valueless gangue with valuable minerals*

It has already been established that this tendency is proportional to the number of carbon atoms in the paraffin chain and is also specifically possessed by those species in which the alkoxy group is isopropoxy. Also there is little, if any, increase in this deleterious property as one increases the number of any specific alkoxy groups in the molecule.

For the flotation treatment of particular ores and the like, specific frothers may thus be produced by blending suitable members of the series having regard to the foregoing. As is well known, three main types of ore are met with, namely

(*a*) Gold ores in which a comparatively small percentage sulphides or arsenides individually rich in gold require to be concentrated by flotation, in which case the desideratum is maximum recovery of these auriferous minerals, while the floating of a little extra gangue can be tolerated.

(*b*) Bulk flotation of one or more minerals of one base metal, e. g. copper, in which case while maximum economic recovery is naturally highly

desirable it is absolutely essential that the minimum of siliceous gangue shall be present in the final concentrate.

(c) Ores in which minerals of two or more base metals are to be separated as far as possible from each other as well as from the gangue; in which case the desiderata are extreme selectivity coupled with deep and powerful froth while at the same time maximum "carrying-power" is desired in the second or final stage of flotation.

As regards coal separation the first desideratum is extreme selectivity to permit the separation of two or more basic types of coal, as for instance, "coking" and "non-coking" coal.

The following examples illustrate the advantages obtainable by the use of frothing agents obtained by selective admixture of two or more polyalkoxyparaffins in accordance with the present invention.

Tests were carried out in rigidly standardized conditions using the well known promoting reagent "301" at a natural pH of 8.0 in a standard 2,000 gram Denver-Farenwald flotation machine.

The ore used contained 150 lbs. per ton pyrrhotite and 13 lbs. per ton of chalcopyrite and contained a rather unusually large proportion of reactive true colloid.

Standard tests using pine oil as frother have given very poor results. It had been established by experience that each and all of the numerous tested polyalkoxyparaffins were completely miscible with each other.

The results set out in Tables IV, V and VI, are based upon two specific blends of frothers and they illustrate how (First test) 1:2:3 triethoxypropane whose properties used alone made it unsuitable for sulphide gold ores has been converted into a frother of great effectiveness for such ores by blending in the substance 1:1:3 triethoxyhexane in the proportion of 1 volume of the latter to 3 volumes of the former; and how (Second test) by mixing equal volumes of 1:1:3 triethoxybutane with 1:1:3 triethoxyhexane the resultant blend was such that three standardized volumes gave 76.9% recovery of the valuable mineral pyrrhotite while 4 standard volumes of 1:1:3 triethoxybutane only gave 61.3% recovery; while another test (test No. 3) using pure 1:1:3 triethoxyhexane gave the intermediate figure 67.1% using only two standard volumes.

TABLE IV.—MINERAL-CARRYING POWER

(Strength)

| Test No. | Frothers Used | No. of Drops | Lbs. per ton ore left in residue | Percentage Recovery |
|---|---|---|---|---|
| Test 2 | Comml. Triethoxybutane 1½ + 1:1:3 Triethoxyhexane 1½ (i. e. 1:1 vol. mix) | Total 3 | 33.6 | 76.9 |
| Test 3 | 1:1:3 Triethoxyhexane | 2 | 51.1 | 67.1 |
| Test 1 | 1:2:3 Triethoxypropane 3 + 1:1:3 Triethoxyhexane 1 (i. e. 3:1 vol. mix) | Total 4 | 55.4 | 62.9 |

TABLE V.—TENDENCY TO FLOAT VALUELESS GANGUE

| Test No. | Frothers Used | Nos. of Drops | | Percent Gangue in— | |
|---|---|---|---|---|---|
| | | 1st Con. | 2nd Con. | 1st Con. | 2nd Con. |
| Test 3 | 1:1:3 Triethoxyhexane | 1 | 1 | 28.7 | 42.4 |
| Test 1 | 1:2:3 Triethoxypropane 1½ + 1:1:3 Triethoxyhexane ½ (i. e. 3:1 vol. mix) | 2 | (1½) 2 | 29.8 | 41.3 |
| Test 2 | Comml. Triethoxybutane ½ + 1:1:3 Triethoxyhexane ½ (i. e. 1:1 vol. mix) | 1 | (1) 2 | 35.2 | 42.5 |

TABLE VI

| Test No. | Frothers Used | No. of Drops | Lbs. per ton of ore, floated in 1st Con. | | Ratio Pyrrhotite to Chalcopyrite |
|---|---|---|---|---|---|
| | | | Pyrrhotite | Chalcopyrite | |
| Test 2 | Comml. Triethoxy-butane. ½ + 1:1:3 Triethoxyhexane. ½ | 1 | 28.34 | 10.77 | 2.63 to 1. |
| Test 1 | 1:2:3 Triethoxypropane. 1½ + 1:1:3 Triethoxyhexane. ½ | 2 | 38.96 | 11.20 | 3.48 to 1. |
| Test 3 | 1:1:3 Triethoxyhexane. | 1 | 44.75 | 11.70 | 3.82 to 1. |

Further test results embracing the use of numerous representative organic compounds within the scope of this invention are now appended as Tables VII to X inclusive.

TABLE VII

Standardised, strictly comparative, flotation tests in a 2,000-gram Denver-Fahrenwald machine, on a gold, chalcopyrite, pyrrhotite, ore assaying approximately 16.8 dwts. Acc. Grind 45 minutes with 4 grams lime and 0.30 gram copper sulphate. 0.10 gram Sodium-sec-butyl xanthate and the Frother as stated, at start. 2 minutes froths designated as "First Cons." Then 0.25 gram of the same xanthate, and the Frother as stated. 5 minutes froths designated as "Second Cons." Residual pulp washed out of machine, designated as "Tailings."

| Test No. | Products Percent Weight | | | Assays of Products | | | | Units of Sulphur (Percent × assay) | | | | Percentage of Total Sulphur | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Percent Sulphur | | | Dwt. Gold | | | | | | | |
| | 1st Cons. | 2nd Cons. | Tailings | 1st Cons. | 2nd Cons. | Tailings | Tailings | 1st Cons. | 2nd Cons. | Tailings | Cal. Ore | 1st Cons. | 2nd Cons. | Tailings |
| PXX 1 | 7.03 | 6.22 | 86.75 | 30.65 | 23.62 | 0.86 | 5.0 | 215.5 | 146.9 | 74.6 | 437.0 | 49.3 | 33.6 | 17.1 |
| PXX 2 | 8.74 | 3.62 | 87.64 | 28.28 | 20.32 | 1.41 | 5.0 | 246.0 | 73.6 | 123.6 | 443.2 | 55.4 | 16.7 | 27.9 |
| PXX 3 | 7.75 | 3.22 | 89.03 | 27.19 | 17.57 | 1.96 | 6.0 | 210.7 | 56.6 | 174.5 | 441.8 | 47.7 | 12.8 | 39.5 |
| PXX 4 | 7.13 | 6.27 | 86.60 | 30.07 | 20.87 | 0.96 | 4.6 | 214.4 | 130.9 | 83.1 | 428.4 | 50.0 | 30.6 | 19.4 |
| PXX 6 | 7.00 | 6.25 | 86.75 | 29.66 | 21.01 | 1.02 | 4.65 | 207.6 | 131.3 | 89.0 | 427.0 | 48.5 | 30.7 | 20.8 |
| PXX 9 | 6.92 | 6.37 | 86.71 | 27.05 | 20.60 | 0.80 | 4.75 | 187.2 | 131.2 | 69.0 | 387.4 | 48.3 | 33.9 | 17.8 |
| PXX 10 | 6.16 | 6.72 | 87.12 | 19.88 | 29.38 | Not assayed. | Not assayed. | 122.5 | 197.4 | Not assayed. | | | | |

| Test No. | Substance used as Frother | Quantity of Substance added | | | Remarks |
|---|---|---|---|---|---|
| | | 1st Con. | 2nd Con. | Total | |
| | | cc. | cc. | cc. | |
| PXX 1 | Commercial 1:1:3 Triethoxybutane | .028 | .042 | .070 | Control test: Froth a little water, but active. Persistent. |
| PXX 2 | 1:1:3 Trimethoxybutane | .056 | .084 | .140 | Extremely active and strong. Highly persistent. A smaller quantity would have sufficed. |
| PXX 3 | 1:2:3:4 Tetramethoxybutane | .064 | .096 | .160 | Weak, watery and shallow. Clearly larger quantity needed. Persistent. |
| PXX 4 | 1:2:3:4:5:6 Hexamethoxyhexane + 1:2:3:4:5 Hexamethoxyhexanol | .056 | .084 | .140 | A mixture of 71% of the First Substance and 29% the second. All characteristics very similar to "Control Test." |
| PXX 6 | A high molecular-weight highly ethoxylated paraffin of unknown detail composition. | .032 | .048 | .080 | Froths tough and gummy: non-persistent. Intense flocculation of mineral. "Resins" present. |
| PXX 9 | Ethyl-Beta-Ethoxy-Crotonate | .030 | .045 | .075 | Just liquid at room temperature. Conditioning time about as for Pine Oil. Very strong, deep, active froths. Very persistent. |
| PXX 10 | 1:1:3 Triethoxyoctane | .014 | .028 | .042 | Conditioning time rather longer than for Pine Oil. Intensely mineralized small-bubble froths, with a tendency to "over-oil" even in this very small quantity. |

TABLE VIII.—A CHALCOPYRITE-PYRRHOTITE ORE

| Substance tested as Frother | Product | Product Percentage Weight of Ore | Mineral Grade of Product | | | Lbs. Valuable Mineral Per Ton Ore | | Percent Recovery Mineral | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Percent Chalcopyrite | Percent Pyrrhotite | Percent Valueless Gangue | Chalcopyrite | Pyrrhotite | Chalcopyrite | Pyrrhotite |
| 1.1.5.5 Tetra-Ethoxy-Pentane (Pure), 0.028 cc. | 1st Conc. | 4.15 | 13.1 | 55.5 | 31.4 | 10.9 | 46.1 | 83.1 | 35.5 |
| | 2nd Conc. | 5.22 | 0.8 | 64.5 | 34.7 | 0.8 | 67.4 | 6.5 | 52.0 |
| | Combined Concs. | 9.37 | 6.2 | 60.5 | 33.3 | 11.7 | 113.5 | 89.6 | 87.5 |
| | Residue | 90.63 | 0.08 | 0.81 | | 1.4 | 16.2 | | |
| | Calculated Ore | 100.00 | 0.65 | 6.49 | | 13.1 | 129.7 | | |
| Pine Oil (Steam Distilled), 0.076 cc. | 1st Conc. | 3.85 | 13.9 | 50.7 | 35.4 | 10.7 | 39.1 | 81.5 | 28.8 |
| | 2nd Conc. | 5.28 | 1.3 | 63.7 | 35.0 | 1.4 | 67.3 | 10.5 | 49.5 |
| | Combined Concs. | 9.13 | 6.6 | 58.2 | 35.2 | 12.1 | 106.4 | 92.0 | 78.3 |
| | Residue | 90.87 | 0.06 | 1.62 | | 1.1 | 29.5 | | |
| | Calculated Ore | 100.00 | 0.66 | 6.79 | | 13.2 | 135.9 | | |
| 1.1.2.2 Tetra-Ethoxy-Ethane, .051 cc. | 1st Conc. | 3.24 | 19.1 | 51.4 | 29.6 | 12.4 | 33.3 | 86.2 | 22.6 |
| | 2nd Conc. | 5.15 | 1.6 | 66.5 | 31.9 | 1.6 | 68.5 | 11.2 | 46.7 |
| | Combined Concs. | 8.39 | 8.3 | 60.7 | 31.0 | 14.0 | 101.8 | 97.4 | 69.3 |
| | Residue | 91.61 | 0.03 | 2.53 | | 0.4 | 45.6 | | |
| | Calculated Ore | 100.00 | 0.71 | 7.37 | | 14.4 | 147.4 | | |

NOTE.—In all three tests the froths were excellent, though the pine oil frother was less persistent than the other two. Note the "collecting" property, on the mineral pyrrhotite, of the 1:1:5:5 tetra-ethoxy-pentane, as compared to the lack of "collecting" property of the 1:1:2:2 tetra-ethoxy-ethane.

TABLE IX.—STANDARD FLOTATION TESTS ON A CHALCOPYRITE-PYRRHOTITE ORE IN A 2,000 GRAM LAB. MACHINE

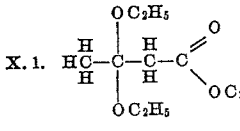
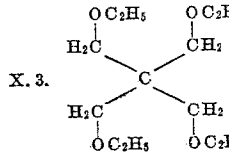
| Substance used as Frother | Product | Percent Weight of Ore | Mineral Grade of Products | | | Lbs. Mineral Per Ton Ore | | Froth type |
|---|---|---|---|---|---|---|---|---|
| | | | Chalcopyrite | Pyrrhotite | Gangue | Chal. | Pyr. | |
| X. 1.  beta beta diethoxy butyrate (0.042 cc.). | 1st Conc. | 3.87 | 14.0 | 38.7 | 47.3 | 10.9 | 29.9 | 0.014 cc. for 1st. con. was slightly too little. Mids very deep, active and persistent. |
| | 2nd Conc. | 5.94 | 0.5 | 61.1 | 38.4 | 0.5 | 72.6 | |
| | Comb. Conc. | 9.81 | 5.8 | 52.3 | 41.9 | 11.4 | 102.5 | |
| | Residue | 90.19 | 0.09 | 1.86 | | 1.5 | 33.6 | |
| | Calc. Ore | 100 | 0.64 | 6.80 | | 12.9 | 136.1 | |
| X. 3.  tetra ethyl ether of pentaerythritol (0.060 cc.). | 1st Conc. | 3.15 | 15.6 | 49.8 | 34.6 | 9.8 | 31.4 | A dead type hanging back in cell. "Collecting" power is, however, there. |
| | 2nd Conc. | 3.25 | 1.8 | 68.8 | 29.4 | 1.2 | 44.7 | |
| | Comb. Conc. | 6.40 | 8.6 | 59.5 | 31.9 | 11.0 | 76.1 | |
| | Residue | 93.60 | 0.08 | 3.27 | | 1.4 | 61.2 | |
| | Calc. Ore | 100 | 0.62 | 6.87 | | 12.4 | 137.3 | |
| A blend of 80% of the latter with 20% of Commercial Triethoxybutane (0.060 cc.). | 1st Conc. | 3.86 | 13.1 | 48.7 | 38.3 | 10.1 | 37.6 | Normal. |
| | 2nd Conc. | 2.94 | 1.3 | 71.5 | 27.1 | 0.8 | 42.1 | |
| | Comb. Conc. | 6.80 | 8.0 | 58.5 | 33.5 | 10.9 | 79.7 | |
| | Residue | 93.20 | 0.09 | 3.25 | | 1.7 | 60.6 | |
| | Calc. Ore | 100 | 0.63 | 7.01 | | 12.6 | 140.3 | |
| Steam-distilled Pine Oil (0.076 cc.) | 1st Conc. | 3.85 | 13.9 | 50.7 | 35.4 | 10.7 | 39.1 | Do. |
| | 2nd Conc. | 5.28 | 1.3 | 63.7 | 35.0 | 1.4 | 67.3 | |
| | Comb. Conc. | 9.13 | 6.6 | 58.2 | 35.2 | 12.1 | 106.4 | |
| | Residue | 90.87 | 0.06 | 1.62 | | 1.1 | 29.5 | |
| | Calc. Ore | 100 | 0.66 | 6.79 | | 13.2 | 135.9 | |

TABLE X.—RESULTS OF THREE STANDARDISED LABORATORY TESTS IN 2,000-GRAM FLOTATION MACHINE UPON A REFRACTORY GOLD-COPPER ORE

| Product | Grade of Product | | | | | | Percent Valueless Gangue | | |
|---|---|---|---|---|---|---|---|---|---|
| | Percent Chalcopyrite | | | Percent Pyrrhotite | | | | | |
| | Test 9 | Test 16 | Test 17 | Test 9 | Test 16 | Test 17 | Test 9 | Test 16 | Test 17 |
| 7-minute Concentrate | 7.48 | 8.69 | 8.32 | 53.93 | 62.27 | 60.66 | 38.59 | 29.04 | 31.02 |
| Residue | 0.038 | 0.038 | 0.029 | 2.970 | 1.892 | 2.533 | | | |
| Calculated Ore Feed | 0.677 | 0.753 | 0.717 | 7.343 | 6.851 | 7.372 | | | |

| | Test 9 | Test 16 | Test 17 |
|---|---|---|---|
| Gold left in Residue: per ton ore feed | 1.21 | 1.15 | 1.15 |

| Product | Lbs. Mineral/Ton Ore in Product | | | | | | Percentage Recovery of Mineral | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Chalcopyrite | | | Pyrrhotite | | | Chalcopyrite | | | Pyrrhotite | | |
| | Test 9 | Test 16 | Test 17 | Test 9 | Test 16 | Test 17 | Test 9 | Test 16 | Test 17 | Test 9 | Test 16 | Test 17 |
| 7-minute Concentrate | 12.84 | 14.36 | 13.97 | 92.54 | 102.87 | 101.79 | 94.8 | 95.3 | 92.4 | 63.0 | 75.1 | 69.0 |
| Residue | 0.70 | 0.70 | 0.37 | 54.32 | 34.15 | 45.64 | 5.2 | 4.7 | 2.6 | 37.0 | 24.9 | 31.0 |
| Calculated Ore Feed | 13.54 | 15.06 | 14.34 | 146.86 | 137.02 | 147.43 | 100 | 100 | 100 | 100 | 100 | 100 |

| | Test 9 | Test 16 | Test 17 |
|---|---|---|---|
| Sodium-sec-butyl Xanthate added: grams | 0.35 | 0.35 | 0.35 |
| Frother added: | | | |
| Drops | 4 | 3 | 4. |
| cc | 0.058 | 0.051 | 0.052. |
| Grams | 0.052 | 0.051 | 0.047. |
| Composition of Frother | Commercial Trieth-oxybutane. | 1:1:2:2 Tetra-(Methoxy-Ethoxy)-Ethane. | 1:1:2:2 Tetra-Ethoxy-Ethane. |
| Actual weight Concentrate | 169. | 162 | 166. |
| Percent Weight concentrate | 8.55 | 8.26 | 8.39. |
| Actual weight Residue | 1807 | 1800 | 1812. |
| Percent Weight Residue | 91.45 | 91.74 | 91.61. |
| Actual weight Ore Feed | 1976 | 1962 | 1978. |
| Percent Weight Ore Feed | 100 | 100 | 100. |

REMARKS

1. Clearly the (methoxy-ethoxy)- substituent in a paraffin confers properties very close to those conferred by ethoxy-.
2. This is remarkable, seeing that differences between methoxy-, ethoxy-, isopropoxy-, and butoxy- have been found to be very great.
3. In spite of the fact that the molecular weight of the (methoxy-ethoxy)-compound is 326, vs. 206 for the corresponding ethoxy-compound, the "strengths" of the two are very similar (i. e. quantity needed to give same flotation results).
Yet 1:1:5:5. tetra-ethoxy-Pentane is quite three times as strong as either, though its molecular weight is only 248. Obviously the "strength" is proportional to the length of the paraffin chain.
4. Both viscosity and density are clearly greatly increased by the presence of the (methoxy-ethoxy)-substituent.

We are aware that the use of certain alkoxy-paraffins in flotation processes forms the subject of one or other of Union of South Africa patent applications Nos. 2,197/48 and 2,709/48, these applications corresponding to U. S. Patents Nos. 2,561,251 and 2,591,289 in the joint names of the applicant R. F. Powell herein, and others.

What we claim is:

1. A method for concentrating minerals by flotation comprising the steps of adding to the mineral pulp a small quantity of an alkoxy substituted acyclic hydrocarbon as a frother, the unsubstituted hydrocarbon containing from 4 to 10 carbon atoms, being substituted with from 4 to 6 alkoxy groups, having no more than one di-substituted alkoxy grouping at a terminal carbon atom of said hydrocarbon, the alkoxy groups being connected to the hydrocarbon nucleus by a C—O—C ether linkage and being selected from the group consisting of methoxy, ethoxy, normal propoxy, isopropoxy, methoxy-ethoxy and ethoxy-ethoxy, and thereafter subjecting the resulting mixture to a flotation operation.

2. A method for concentrating minerals by flotation comprising the steps of adding to the mineral pulp a small quantity of a frother which is an alkoxy substitute acyclic straight chain hydrocarbon containing from 4 to 10 carbon atoms in the hydrocarbon chain and substituted with from 3 to 5 alkoxy groups and one divalent oxygen, the alkoxy substituents being connected to the hydrocarbon chain by a C—O—C ether linkage, having no more than one di-substituted alkoxy grouping at a terminal carbon atom of said hydrocarbon, and being selected from the group consisting of methoxy, ethoxy, normal propoxy, isopropoxy, methoxy-ethoxy and ethoxy-ethoxy and thereafter subjecting the resulting mixture to a flotation operation.

3. A method for concentrating minerals by flotation comprising adding a frother to a mineral pulp, said frother being a member of the class consisting of an alkoxy substituted acyclic hydrocarbon, the unsubstituted hydrocarbon containing from 4 to 10 carbon atoms, being substituted with from 4 to 6 alkoxy groups, having no more than one di-substituted alkoxy grouping at a terminal carbon atom of said hydrocarbon, and an alkoxy substituted acyclic straight chain hydrocarbon containing from 4 to 10 carbon atoms in the hydrocarbon chain and substituted with from 3 to 5 alkoxy groups and one divalent oxygen, the alkoxy substituents being connected to the hydrocarbon chain by a C—O—C ether linkage, having no more that one di-substituted al-

koxy grouping at a terminal carbon atom of said hydrocarbon, and being selected from the group consisting of methoxy, ethoxy, normal propoxy, isopropoxy, methoxy-ethoxy and ethoxy-ethoxy and thereafter subjecting the resulting mixture to a flotation operation.

4. A method for concentrating minerals by flotation comprising adding to a mineral pulp a small quantity of beta,beta diethoxy ethyl butyrate as a frother and thereafter subjecting the resulting mixture to a flotation operation.

5. A method for concentrating minerals by flotation as claimed in claim 1 comprising adding to a mineral pulp a small quantity of hexa methoxy decane as a frother and thereafter subjecting the resulting mixture to a flotation operation.

6. A method for concentrating minerals by flotation as claimed in claim 1 comprising adding to a mineral pulp a small quantity of an alkyl ester of a diethoxy substituted fatty acid as a frother and thereafter subjecting the resulting mixture to a flotation operation.



7. A flotation method as in claim 3 wherein a blend of different frothers each in accordance with the frother formulation of claim 3 is employed.

8. A method as in claim 7 wherein one of said frothers in the blend is a solid substance and the other of said frothers is a liquid substance.

9. A method as in claim 3 wherein the frother is a tetra alkyl ether of pentaerythritol.

10. A method as in claim 3 wherein the frother is a 1,2,3,4 tetra alkoxy butane.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,902,070 | Halbig | Mar. 21, 1933 |
| 2,561,251 | Van Aardt | July 17, 1951 |
| 2,591,289 | Powell et al. | Apr. 1, 1952 |

OTHER REFERENCES

Milling Methods for 1930, © by American Institute of Mining and Metallurgical Engineers, pp. 307 to 357. (Copy in Div. 25.)