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FLOTATION METHOD

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This invention relates to a novel process of concentrating minerals from their ores and to new flotation reagents for use in such a process which function as collecting and frothing agents, in that they assist in producing a better froth and effect the collection of the desired mineral values present in the ore in cooperation with other frothing and collecting agents, if the metallurgy of the particular ore under treatment makes the use of additional collecting or frothing agents advisable. The new reagents are useful in the beneficiation of ores, particularly metalliferous ores, such as copper, lead, zinc, silver, gold, and tungsten; and also nonmetallic ores, for example, talc. They are useful in the beneficiation of oxidized metalliferous ores as well as sulphide metalliferous ores.

The use of sulphonated soaps of alkali metals produced by saponifying a sulphonated fatty acid with sodium hydroxide, and the corresponding soaps of heavy metals, such as lead and copper, produced by reaction between the alkali soap and a heavy metal salt, such as lead acetate or copper acetate, as flotation reagents for the concentration of metalliferous ores and of ores of so-called non-metallic minerals, is now known. However, I have found that organo-metallic compounds or mixtures thereof can be rendered much more effective as flotation reagents if they, or the products from which they are derived, are produced by neutralization of sulphonated castor oil (the alkali salt of ricinoleo-sulphuric acid) with an alkali or an alkaline earth metal carbonate, instead of by saponification of the sulphonated castor oil with an alkali or alkaline earth metal hydroxide. An organo-metallic compound when so prepared is effective when the milling is carried out both in soft water and hard water. It offers increased advantages when the milling is conducted in hard water, and results have been attained with such a reagent when milling in sea water which heretofore it has been impossible to attain when using the usual frothers and collecting agents.

If sodium hydroxide, for example, is caused to react with sulphonated castor oil, saponification of the oil will take place with the production of a final product which, while being capable of operating as a collector in the concentration of minerals, possesses much less selectivity

and will not give as high recoveries of the desired mineral values as when the reagent is prepared by neutralization of the sulphonated castor oil with an alkali or an alkaline earth metal carbonate. Reagents formed by saponifying sulphonated castor oil with an alkali or alkaline earth metal hydroxide, regardless of the amount of alkali metal hydroxide used, produces a heavy, matted froth as distinguished from a relatively strong not-too-heavily mineralized froth in which the bubbles are of the desired size, such as is produced by the product resulting from the neutralization of the sulphonated castor oil with an alkali metal or an alkaline earth metal carbonate. However, in order to obtain the advantages resulting from the present invention, the castor oil must first have been sulphonated, as satisfactory results have not been obtained with a product resulting from the treatment of raw castor oil, either with an alkali metal or an alkaline earth metal carbonate.

Accordingly, the present invention relates to a flotation reagent which is the product, a derivative thereof, or a mixture of the products resulting from the neutralization of sulphonated castor oil with an alkali metal or an alkaline earth metal carbonate, and to a froth flotation method of concentrating minerals from their ores with such a product or mixture of products. While under certain conditions ammonium carbonate may be used, I prefer to use an alkali metal or an alkaline earth metal to neutralize the sulphonated castor oil, as the product resulting from neutralization of the oil with ammonium carbonate is relatively unstable and loses its frothing power more readily and produces a froth of poorer quality. The use of sodium carbonate as the alkaline neutralizing agent is preferred, and in the further description of the invention reference will be made to sodium carbonate as the neutralizing agent.

The flotation reagent of the present invention is prepared by the neutralization of castor oil which has been sulphonated by reaction with any appropriate sulphonating agent or in any well known manner, with sodium carbonate. When a reaction product of a heavy metal is desired, the product resulting from the neutralization of the sulphonated castor oil with the alkali metal carbonate, may be caused to react

with a salt of a heavy metal, such as lead acetate or copper acetate, whereupon the metal atom of the heavy metal salt will be substituted in the neutralization product in place of the alkali metal. Salts of various heavy metals, such as lead, iron, zinc, manganese, cobalt and copper, may be used to form the heavy metal product, as the resulting product of all of them shows characteristic powerful flocculation of slimed minerals, but ordinarily a lead salt is preferred.

Ordinarily a mixture of the product resulting from the neutralization of sulphonated castor oil with sodium carbonate and the heavy metal product derived therefrom will be used. The alkali metal or alkaline earth metal product of the neutralization, supplemented by a small amount of pine oil or cresylic acid, forms an excellent frothing agent, while the heavy metal product derived therefrom is a powerful collecting and flocculating agent. However, either product may be used without the other.

In one example, the reagent of the present invention was prepared by dissolving 75 parts by weight of sodium carbonate in 1000 parts of water, after which 50 parts of sulphonated castor oil was added slowly, with stirring, to the solution of sodium carbonate. The resulting product was the sodium neutralized ricinoleo-sulphuric acid.

In another example, 400 grams of lead acetate in solution was added to 20 lbs. of a solution of the neutralized product prepared as set forth above to form the lead salt of the neutralized ricinoleo-sulphuric acid.

In preparing the alkali metal product in the manner set forth, it is preferred to use an amount of alkali carbonate sufficient to neutralize substantially all of the sulphonated castor oil. Ordinarily, the amount of the alkali carbonate will be between 1.1 and 2 times the amount of sulphonated castor oil. The amount of water may be varied but the amount given above, as well as the relative amounts of sulphonated castor oil and alkali metal carbonate are preferred.

When it is desired to produce a reagent including a mixture of the sodium carbonate neutralized product and the heavy metal product derived therefrom, the amount of heavy metal salt added to the product resulting from the neutralization of the sulphonated castor oil with the alkali metal carbonate will depend upon the relative amount of heavy metal product, as a collecting or flocculating agent, desired in the final product. Accordingly, the amount of lead acetate which may be added in the first example referred to above may vary from a relatively small amount, such as 100 grams, if the above parts are computed in pounds, to a sufficient amount to react with and convert a large part of the alkali metal compound to the corresponding lead compound. If the reagent is to be used only for frothing, no heavy metal salt will be added thereto, while if a collecting or flocculating agent alone is desired the amount of heavy metal salt added may be sufficient to convert all of the alkali metal product into the corresponding heavy metal product.

While either the alkali metal product prepared as described or the heavy metal product derived therefrom will give improved results in the concentration of ores, I usually prefer to use a mixture of the alkali metal and heavy metal products in order to obtain the benefits of the collecting and flocculating properties of the heavy metal product on slimed mineral, and increase the re-

covery of that difficult fraction, and the benefit of the frothing properties of the alkali metal product. The relative extent of collection and flocculation, and frothing, produced by the reagent will depend upon the amount of the heavy metal salt added to the neutralized product and consequently upon the relative amounts of the heavy metal product and alkali metal products present.

The alkali metal product prepared in the manner set forth and the heavy metal product derived therefrom will function as collecting and flocculating, and frothing agents, respectively, with all types of ores and they have been found to be particularly useful with ores producing a high slime content when pulped, such as ores containing sericite and chlorite, which when pulped produce colloidal slimes.

In the concentration of certain ores, the heavy metal product as prepared above may be the only flocculating and collecting agent used, but with most ores it will be found desirable to use the present reagent along with some of the standard collecting agents, such as the xanthates and the "Aerofloats." However, when the heavy metal product is used, such additional collecting agents may be used in lesser amounts. Also, in froth flotation it is desirable to use the usual frothing agents along with the alkali metal product as it ordinarily has insufficient frothing power when used alone, but when used with proper proportions of standard frothing agents, such as pine oil or cresylic acid, improved metallurgical results and lowered total reagent costs are obtained. In froth flotation, it is only necessary to use about 30 to 40% of the amount of pine oil, cresylic acid or other frother ordinarily used, and to add sufficient of the alkali metal product to produce the required volume of froth. In that way, greater selectivity control is obtained as well as the more rapid and effective emulsification, and the production of froth of smaller bubble structure which offers improved facilities for mineral flotation.

In the concentration of minerals from their ores, the present reagents may be used in the form of the crude mixtures obtained in the manner described above or the sodium compound or the heavy metal compound or mixtures thereof, as the case may be, may be separated and used alone.

The amount of reagent which will be used will, in accordance with the usual practice, depend upon the particular ore being treated, the exact chemical and mineralogical nature thereof, the chemical character of the mill water and the temperature and physical characteristics of the particular pulp being treated; it being well understood that each batch of material may present its own problems with respect to the amount of flotation reagents which should be used to obtain the optimum results. It is also to be understood that subsequent to the mixing of the reagents with the ore pulp, the actual step of separating the mineral values may be effected in any desired type of flotation machine or even by tabling.

The advantages of the reagents of the present invention in the concentration of minerals will be better understood from the following examples of its use, in all of which the reagent proportions are given on the basis of pounds per ton of dry material treated, and the assays of the gold-bearing ores are given in gold value per ton of dry material.

Example I

Old stamp mill tailings from the Chicagof district of southeastern Alaska assaying \$3.10 in gold and consisting mainly of auriferous pyrite, free gold, and a small amount of amalgam, along with quartz and considerable quantities of sericite, calcite, chlorite and graphite were ground so that all of it passed through a 65 mesh screen and 68% passed through a 200 mesh screen. The ground product was made into a pulp containing 22% solids and to it was added in a conditioning tank:

	Pounds
The reagent as prepared above and containing the sodium and lead products.....	0.4
Amyl xanthate.....	0.15
Pine oil.....	0.02
Starch.....	0.1

The starch was added as a depressant for the graphite, the amyl xanthate as an additional collecting agent, and the pine oil as a frothing agent.

The addition of reagents required one minute, after which agitation was continued for another minute. The pulp thus conditioned was transferred to a froth flotation machine of the mechanical type, where it was agitated for eight minutes, during which time a rougher concentrate was floated and collected. Upon removal of the tailings, the rougher concentrate was returned to the flotation machine where, without further addition of reagents, it was again treated for four minutes to float a finished concentrate. The tailings of this cleaning treatment constituted a middling which was returned for further treatment. The finished concentrate assayed \$176.40, the middlings \$5.07 and the tailings \$0.44. With similar tests made with the same ore and under the same conditions, except that 0.03 lbs. of Aerofloat #31 was used instead of the reagent of the present invention, the concentrate assayed \$141.10, the middlings \$3.32 and the tailings \$1.05.

Example II

The metallurgy of certain gold-bearing ores involves the recovery of elementary gold, galena, and very small amounts of argentite and chalcopyrite, with the rejection of pyrite, pyrrhotite and graphite in the tailings. The heads of the slime flotation circuit in the treatment of such ores assaying \$0.40 were made into various pulps containing from 12 to 30% solids (averaging about 20%) to which were added in a conditioning tank:

	Pounds
The reagent as prepared above and containing both the sodium and heavy metal compounds.....	0.03 to 0.07
Amyl xanthate.....	0.006 to 0.012
Pine oil.....	0.03 to 0.07
Starch.....	0.04

The pulps thus conditioned were treated in a froth flotation machine for a period of three minutes. As the action of the frother on the ore treated was very rapid, the usual time for emulsification needed by pine oil or cresylic acid was not necessary and greater volumes of froth were produced. Therefore, it was possible to successfully use a relatively short period of treatment of the conditioned pulp in the froth flotation machines.

The finished concentrate assayed on an average \$300.00 and the tailings \$0.15. The average

reagent cost was \$0.013. The recovery of lead in the slime size was high.

Example III

The heads of the slime flotation circuit in the treatment of ores of the kind referred to in Example II were prepared and treated in a similar manner with the same reagents used in Example II, except that the reagent was the sodium product as prepared above, no heavy metal product being present. The finished concentrate assayed \$300.00, and the tailings \$0.17. The reagent cost was \$0.015 per ton treated. The recovery of lead in the slime size was also high.

In tests on the heads of the slime flotation circuit in the treatment of ores of the kind referred to in Examples II and III but using standard reagent, the finished concentrate assayed \$200.00 and the tailings \$0.20 with a reagent cost of \$0.035 per ton treated.

Example IV

In another test, old stamp mill tailings which had been under sea water for 24 years and which assayed \$3.00 were ground so that 92% passed through a 100 mesh screen and 65% passed a 200 mesh screen. The ground tailings were made into a pulp containing approximately 20% solids, using one half sea water and one half fresh water. To the pulp thus prepared there was added in a conditioning tank:

	Pounds
The reagent as prepared above and containing both the sodium and lead products.....	0.05
Amyl xanthate.....	0.15
Cresylic acid.....	0.02
Reagent #637.....	0.02
Diesel oil.....	0.01

The Diesel oil was used to prevent an excessive amount of light unstable foam which otherwise would be produced when milling in sea water, thereby enabling the use of the regular frothers.

The pulp thus conditioned was treated in a froth flotation machine in the manner set forth in the preceding examples to produce a finished concentrate. The concentrate assayed \$175.00, and the tailings \$0.70. The values were in the form of exceedingly fine pyrite, a small amount of free gold, and amalgam.

In this example the reagents of this invention were found to have the ability to form a stable froth, to flocculate and assist in the recovery of minerals that could not be recovered with the standard reagents under the difficult water, mineral surface conditions, and the low temperature at which the operations were carried out. With standard reagents, the same ore gave concentrates which assayed from \$105.00 to \$140.00 while the tailings assayed from \$1.20 to \$1.50.

Example V

In this example, ore from a small gold property in southeastern Alaska where flotation followed amalgamation, fine regrinding and tabling was ground, formed into a series of pulps and treated, in both fresh water and salt water, in the presence of the following reagents:

	Pounds
The lead product as prepared above.....	0.20
Aerofloat #25.....	0.10
Reagent #301.....	0.12
Reagent #208.....	0.10
Reagent #637.....	0.05
Copper sulphate.....	0.12

The assays under salt water and fresh water conditions were as follows:

With salt water circuit			With fresh water circuit		
Heads	Conc.	Tails	Heads	Conc.	Tails
\$13.00	\$335.00	\$3.75	\$9.25	\$175.00	\$3.15
10.60	250.30	2.75	10.85	195.30	3.50
10.85	235.20	3.45	9.70	250.00	2.97
10.50	270.20	3.35	9.50	163.85	2.55
11.20	225.00	3.35	13.40	205.40	3.45
9.45	225.00	3.00	12.90	350.00	3.75
9.05	270.00	3.50	12.60	250.40	3.50
10.60	258.67	3.31	Averages 11.17	228.56	3.27

In a series of comparative tests made under similar conditions except that the lead product was not used as the collecting and flocculating agent, the assays were as follows:

With salt water circuit			With fresh water circuit		
Heads	Conc.	Tails	Heads	Conc.	Tails
\$12.95	\$492.10	\$4.55	\$10.25	\$212.30	\$4.20
9.45	387.10	4.55	11.25	237.40	3.50
11.20	204.40	4.20	8.70	140.70	3.35
10.85	196.00	4.02	10.30	150.30	4.53
11.55	158.90	6.30	10.60	185.00	3.67
12.95	280.70	4.90	10.30	200.00	4.02
11.20	308.70	4.90			
11.45	289.70	4.77	Averages 10.23	187.61	3.88

Example VI

In another test on gold-bearing ores the reagents used were as follows:

	Pounds
The lead product as prepared above	0.08
The sodium product as prepared above	0.40
Pine oil	0.04
Starch	0.04

The assays were as follows:

Heads	\$ 0.44
Concentrates	249.90
Tails	0.17

In this example the test was of four hours duration. It is to be noted that the lead product of the invention was the only collecting and flocculating agent present.

Example VII

In this example a gold-bearing ore was treated in the usual manner with the following reagents:

	Pounds
Zinc product as prepared above	0.08
Sodium product as prepared above	0.40
Pine oil	0.04
Minerac "B"	0.003
Starch	0.04

The Minerac "B" was used along with the zinc product of the invention as a collecting and flocculating agent. The assays were as follows:

Heads	\$ 0.44
Concentrates	256.30
Tails	0.17

Example VIII

In this example a gold-bearing ore similar to

that used in Examples VI and VII was treated with the following reagents:

	Pounds
Iron product as prepared above	0.08
Sodium product as prepared above	0.40
Pine oil	0.04
Minerac "B"	0.003
Starch	0.04

The assays in this example were as follows:

Heads	\$ 0.44
Concentrates	298.20
Tails	0.17

In the above examples the tests were run primarily for the recovery of the gold content of the ore. However, the ores contained traces of copper as the sulphide, chalcopyrite, and lead as galena. The final concentrates were found to run about 3% in copper and about 40% in lead, thereby demonstrating the effectiveness of the reagents in the recovery of those metals. The flotation heads assayed from 0.05% to 0.07% lead.

Example IX

In a test run on a high grade silver-lead ore from the Mayo district of Yukon Territory in which the silver carrying minerals present were tetrahedrite, proustite, argentite and galena, and which also contained zinc, pyrite cerussite and anglesite, a pulp of the ore was treated in the usual manner with the following reagents:

	Pounds
Sodium product as prepared above	0.50
Pine oil	0.05
Amyl xanthate	0.12
Sodium carbonate	0.30
Sodium cyanide	0.40

The sodium carbonate and sodium cyanide were added to depress zinc and iron sulphide. The assays were as follows:

Heads	\$137.94 oz. ag.
Concentrates	1164.62 oz. ag.
Tails	7.38 oz. ag.

The silver loss was due to the presence of anglesite and cerussite.

In a test made on an ore containing tungsten as well as copper, where the usual mill practice is to float copper and table flotation tailings for recovery of tungsten, the addition of a small amount of a mixture of the sodium and lead products of the invention caused the tungsten to be floated along with the copper.

From the foregoing it will be apparent that the product of the neutralization of sulphonated castor oil with an alkali or alkaline earth metal carbonate, and the corresponding heavy metal product, are particularly useful as frothing and collecting agents in the concentration of metals by the froth flotation method, and possess advantages in such a method over similar collecting agents prepared by saponifying the sulphonated castor oil with an alkali metal hydroxide such as sodium hydroxide.

In the accompanying claims, the term "alkali carbonate" is used as a generic term to include an alkali carbonate such as ammonium carbonate, alkali metal carbonates and alkaline earth metal carbonates.

I claim:

1. A process of beneficiating metalliferous ores which comprises admixing ground ore with a reagent prepared by reacting sulphonated castor

oil with at least 1.1 times its weight of an alkali carbonate and separating in an aqueous pulp the mineral values from the ore.

2. A process of beneficiating metalliferous ores which comprises admixing ground ore with a reagent prepared by reacting sulphonated castor oil with at least 1.1 times its weight of sodium carbonate and separating in an aqueous pulp the mineral values from the ore.

3. A process of beneficiating metalliferous ores which comprises admixing ground ore with a heavy metal compound prepared by reacting a salt of a heavy metal with the product of neutralization of sulphonated castor oil with an alkali carbonate, and separating in an aqueous pulp the mineral values from the ore.

4. A process of beneficiating metalliferous ores which comprises admixing ground ore with a lead compound prepared by reaction of a lead salt with the product of the neutralization of sulphonated castor oil with sodium carbonate, and separating in an aqueous pulp the mineral values from the ore.

5. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of a reagent prepared by reacting sulphonated castor oil with at least 1.1 times its weight of an alkali metal carbonate, and separating in an aqueous pulp the mineral values from the ore.

6. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of a heavy metal compound prepared by reacting a salt of a heavy metal with the product of the neutralization of sulphonated castor oil with an alkali metal carbonate, and separating in an aqueous pulp the mineral values from the ore.

7. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of a lead compound prepared by reacting a lead salt with the product of the neutralization of sulphonated castor oil with an alkali metal carbonate.

8. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of the product resulting from the neutralization of sulphonated castor oil with an alkali carbonate and in the presence of a heavy metal compound formed by the reaction of a heavy metal salt with such neutralization product.

9. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of the product of the neutralization of sulphonated castor oil with an alkali metal carbonate and in the presence of a lead compound produced by reacting such a neutralization product with lead acetate.

10. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of a lead compound prepared by reacting a lead salt with the product of the neutralization of sulphonated castor oil with from 1.1 to 2 times its weight of an alkali metal carbonate.

11. A process of beneficiating metalliferous ores which comprises admixing ground ore with a reagent prepared by reacting a salt of a heavy metal with the product of the neutralization of sulphonated castor oil with sodium carbonate.

12. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of a lead compound prepared by reacting lead acetate with the product of the neutralization of sulphonated castor oil with sodium carbonate.

13. A process of beneficiating metalliferous ores which comprises subjecting ground ore to froth flotation in the presence of the product resulting from the neutralization of sulphonated castor oil with an alkali carbonate and in the presence of a lead compound prepared by reacting such a neutralization product with a lead salt.

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