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PROCESS FOR CONCENTRATING MINERALS

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My present invention relates to an improved process for concentrating minerals by floating a siliceous mineral, such as quartz, from an oxidized mineral, such as bone phosphate of lime, or by the reverse of the noted flotation procedure, which in either instance obtains the desired result. This invention may be regarded as an improvement over the well known processes of froth flotation and of table agglomeration. It is also an improvement over my belt process as disclosed in Letters Patent No. 2,231,066. Accordingly, the invention may be carried out in a froth flotation cell, a Wilfley table, or the belt apparatus described in Letters Patent No. 2,047,-773.

The novel feature of the present invention resides in the provision and use of a primary flotation reagent not heretofore utilized in the concentration of minerals or ores.

Another feature of the discovery consists in the utilization in the connection desired of a reagent which when used alone cannot be considered a practical collector but which is available, with other reagents, to effect the flotation of either of the noted minerals.

The teaching of the prior art of concentrating ores by flotation primarily depends on the selective oiling of the mineral constituent which it is desired to float, while the other minerals in the ore are maintained in a wetted and non-floatable condition. The reagents which are now known to be effective for this purpose are all characterized by molecular structures made up of a polar and a non-polar part. The chemical and potential characteristics of the polar part of the molecule determine its specific properties as a collector for the flotation of particular minerals, and it is this part of the molecule which attaches itself to the surface of the ore mineral. The non-polar portion of the molecule has the general property of a hydrocarbon chain of being water repellent. This part of the molecule extends away from the mineral surface and represents the non-wettable oiled surface. Hydrocarbon oils which are incapable of collection if used alone, e. g., fuel oil, kerosene and the like, may be used in conjunction with the selective reagent to further fortify the oiled surface. Such oils have no inherent oiling properties for wet mineral surfaces until the surfaces of the minerals have been treated and at least partially oiled with the known selective reagents.

Substantially all of the selective reagents used heretofore have molecules in which the polar part is situated at the end of one or two non-polar hydrocarbon chains or groups. For the treatment of phosphatic sands, for example, the hydrocarbon groups are preferably characterized by eight or more carbon atoms.

This invention is concerned with reagents of a different type. In the present case, water-repellent hydrocarbon chains are attached through polar groups to large protein-like molecules of high molecular weight; one or more of these non-polar chains may be attached to a single molecule. The points of attachment are at the peptide linkages of the protein-like molecule. The protein-like molecule contains one or more polypeptide chains in which the peptide groups (CO.NH) alternate with straight or branching hydrocarbon chains or groups. It contains also additional polar groups as a result of an initial partial hydrolysis of a parent protein of still larger molecular weight. The hydrocarbon groups that are inherently a part of the protein-like molecule, in addition to those attached to it as described above, are thought to have some water-repellent properties that assist in attaching the treated mineral to oil and air; and the various polar groups are thought to have mineral-attaching properties. This is how I have come to understand the remarkable efficiency of this agent as a mineral collector in spite of its comparatively large molecular weight. The result may be represented as a large molecule containing a number of non-polar chains or groups and a number of polar groups in the same molecule. This is essentially different from the molecular structure of the reagents previously known to the art, in which one polar group is attached to one or two non-polar hydrocarbon parts.

Reagents having the flotation properties which I have discovered may be obtained by the reaction, under alkaline conditions, between high molecular split-off products of albumin and molecules containing an easily replaceable halogen atom. The high molecular split-off products of albumin are partial hydrolytic cleavages of the protein molecules obtained in their alkaline decompositions and have been referred to as lysalbinic acid and protalbinic acid. They may be prepared from protein wastes, egg albumin, milk albumin, blood, hides, horn casein, soya bean protein, fish albumin, vegetable albumin, animal albumin, gelatin, glue and the like. The reactant whose molecules contain an easily replaceable halogen atom may be acid chlorides of either saturated or unsaturated higher fatty, resin or naphthenic acids or mixtures thereof.

The general types of reagents with which this

invention is concerned are described, together with methods for their preparation, in Letters Patent No. 2,015,912 to Sommer. The reaction between the albumin products and the acid chloride is carried out under alkaline conditions. The molecule is a long protein-like chain of which the following is the preferred type:

R—CO.NH(R')—CO.NH(R') . . . CO.NH(R')—COOZ

in which R is the hydrocarbon radical of the fatty acid chloride and may also be attached to other peptide groups, and in which R' is a hydrocarbon group. These hydrocarbon groups may differ from one another, may be saturated or unsaturated, and may contain side chains. The number of CO.NH(R') groups is preferably in the neighborhood of five to eight. Z is preferably an alkali metal or an ammonium radical, but may also be hydrogen or metals other than alkalies, for example, calcium. In the specification of the Sommer patent the material is described as: "the products of the chemical reaction of high molecular split-off products of albumin of the type of lysalbinic and protalbinic acid with higher fatty acid chlorides."

The described reagents are clearly distinguishable from the proteins, the protalbinic-lysalbinic acids, and the amino acids. They differ from the proteins in that they have acid radicals produced by the hydrolysis of the parent proteins; and also by their smaller molecular weights. They differ from the protalbinic-lysalbinic acids in that they have a much smaller proportion of free amino-groups, if any. They differ from the amino acids in three respects: they have peptide lintages; they have much larger molecular weights; and they have a much smaller proportion of free amino groups, if any. The polypeptide chains of the primary reagent employed in the present process are not limited to the particular construction set forth above, but may vary with different protein raw materials and different degrees and conditions of their hydrolysis. Thus the hydrocarbon parts of these chains may be saturated or unsaturated and may contain side chains. These chains may have various polar groups and atoms attached to them, such as hydroxyl, carboxyl, halogen, and the like.

British Patent No. 413,016, issued July 12, 1934, describes the preparation of products within the class of the primary reagents employed in the disclosed process by reacting high-molecular cleavage products of albumin with either saturated or unsaturated acid chlorides or acid anhydrides. German Patent No. 670,096, issued January 11, 1939, extends the reacting reagent to include halogenated aromatic or aromatic-aliphatic hydrocarbons containing an easily exchangeable halogen atom. The products described by these noted patents are contained within the limits of the chemical classification of reagents employed in the present process, the same including high molecular protein like molecules containing a plurality of non-polar constituents attached through the peptide linkages either directly or through other polar groups.

The material with which the described partial hydrolytic cleavage products of the proteins are reacted or condensed may be any saturated or unsaturated aliphatic acid chloride or anhydride containing ring structures such as would be derived from naphthenic acids or resin acids.

It is well known that either the acid chlorides or acid anhydrides may be used in such reactions as those described above and these two types of compounds are known as "acylating agents," which term is used herein as including both types.

My experimental work has been done with a product of the described type made by the Chemical Marketing Company of New York, N. Y., under the trade name "Lamepon," which is normally supplied as a water solution of the active ingredient.

By experiment, I have ascertained that the "Lamepon" reagent, when used without other reagents, acts as a foaming agent. The voluminous foam carries mineral particles of all kinds, generally however, showing preference for the phosphatic particles. Lamepon may be a weak collector, but such property, if it exists, is masked by its tremendous foaming property. However, I have discovered that the collecting property of these reagents is much enhanced and controlled by other reagents. For instance, small amounts of barium chloride, calcium chloride, ferrous sulfate, aluminum nitrate, and similar salts activate the flotation of quartz with "Lamepon."

Example 1

As an example of the flotation of silica with the process of this invention a sample of fine Florida phosphate ore containing bone phosphate of lime (B. P. L.) and silica gangue was screened through a 20-mesh Tyler screen and largely deslimed. The wet ore, containing in the neighborhood of 25% water, was gently agitated for two minutes with a 10% solution of $FeSO_4.7H_2O$ in the proportion of 4.49 pounds of $FeSO_4.7H_2O$ to the long ton of dry ore. Then the "Lamepon" reagent was added as a 20% aqueous solution in the proportion of 0.90 pound of the active ingredient per long ton of ore, and mixed into the dense pulp for two minutes. The ore pulp was then diluted in a laboratory subaeration flotation cell of the impeller type and a float was removed for 0.7 minute. The float weighed 66.4% of the original ore, analyzed 86.84% insoluble and 9.63% B. P. L., and represented 85% of the silica in the original ore.

Example 2

In a similar test 0.45 pound of aluminum nitrate and the "Lamepon" reagent to the extent of 0.68 pound of active ingredient produced a silica float equal to 63% of the original weight of the heads.

I have ascertained that the use of small amounts of various oils with "Lamepon" converts it into a selective phosphate collector. These are such hydrocarbon oils as fuel oil, kerosene, mineral oil; or they may be oily materials such as pine oils, tar oils and hydrocarbon sulphonates. Some of my experiments have been conducted with a light gravity fuel oil. The admixture of small amounts of fuel oil into ore pulps along with the reagents primarily employed in the present process greatly reduces the foaming power of these reagents. To a certain extent this is desirable because the foaming power of "Lamepon" is abnormal and tends to produce too voluminous a foam. A small amount of a frothing oil such as pine oil may be added to restore the pulp to proper frothing characteristics if required.

Example 3

A sample of fine phosphate-silica ore was deslimed and mixed as a dense wet pulp for four

minutes with a 20% aqueous solution of "Lamepon" equivalent to 0.45 pound of active ingredient per long ton of dry heads, 0.47 pound of fuel oil, and 0.1 pound of pine oil. The pulp was then diluted in the flotation cell and both roughing and cleaning flotations were performed without further addition of reagents. This produced phosphatic floats and siliceous tailings and a middling as shown in the following table:

	Wt.	B. P. L.	Insol.	B. P. L. recovery
	Percent	*Percent*	*Percent*	*Percent*
Heads	100.0	25.42	67.87	
Concentrates	25.9	77.85	4.90	79.3
Tailings	74.1	7.13	89.86	
Middlings	5.3			

Example 4

The same phosphate ore described in Example 3 was mixed for 1 minute as a dense pulp with an amount of a 20% aqueous solution of "Lamepon" equivalent to 0.18 pound of active ingredient per long ton of heads. An oil solution of 10 parts by weight of mahogany sulfonate, 15 parts of fuel oil and 2.5 parts of pine oil was then added to the pulp in proportion to give 0.33 pound of mahogany sulfonate, 0.50 pound of fuel oil and 0.08 pound of pine oil per ton of ore. The mixing was continued for 3 minutes longer after which the pulp was diluted in a flotation cell. Agitation and aeration produced a rough phosphate concentrate of good grade amounting to 27.1% of the original ore weight.

In concentrating phosphate ores by procedures similar to that set forth in Example 4, in which the primary reagent of this invention is used in conjunction with oil soluble sulfonate such as mahogany sulfonate, I have found that small amounts of pine oil generally give the best results. The pine oil may be incorporated in the oil solution as described in Example 4 or it may be added to the pulp separately. However, I have obtained useful results with no pine oil. Similarly I have obtained good results both with and without small additions of pine oil when using the "Lamepon" reagent and fuel alone.

The addition of from 0.1 to 0.3 pound of an alkali such as sodium hydroxide has been found to have no beneficial effect when the concentration is carried out with "Lamepon" and fuel oil. However, I have found a beneficial effect on adding such quantities of caustic soda to pulps which are to be concentrated with the "Lamepon" reagent in conjunction with fuel oil solutions of mahogany sulfonates.

Example 5

In commercial operation at the Coronet Phosphate Company's Hopewell recovery plant, very satisfactory results have been obtained with the major reagent of my invention "Lamepon," in conjunction with a fuel oil solution of oil soluble sulphonates known as mahogany sulphonates together with small amounts of pine oil and caustic soda. The separating process used at this plant is that described in Patent No. 2,231,066 preceded by the usual desliming operations. Operating on a normal tonnage of deslimed phosphate feed of 30.5 tons per hour, the following reagents were added in proportion to give 0.26 lb. of "Lamepon," 0.73 lb. of fuel oil, 0.52 lb. of a mahogany sulphonate containing 50% of oil soluble sulphonates, .06 lb. of pine oil, and .24 lb. of caustic soda, all per ton of dry heads. This operation produced the results shown in the following table.

	Tons/hour	B. P. L.	Insol.	B. P. L. recovery
		Per cent	*Per cent*	*Per cent*
Heads	30.5	30.70	62.01	
Concentrates	9.0	75.49	6.14	72.4
Tailings	21.5	12.02	85.02	

Also, I have found that the reagents of the class described herein can be used to effect a flotation of the finer part of the silica constituent, after which phosphate can be floated from the remaining coarser silica constituent with no further addition of the active collecting reagent but merely the addition of an inert oil such as fuel oil, kerosene and the like. For example, with a phosphate ore similar to those described in the examples above, the pulp was first treated with 4 to 7 pounds per ton of calcium chloride and 1.8 pounds of "Lamepon." On diluting, agitating and aerating the same in a flotation cell, a siliceous float, amounting to 31.9% of the original heads and analyzing 82.92% insoluble, was removed. The tailings from this operation were then treated with 0.52 pound of fuel oil and returned to the flotation cell. Agitation and aeration of the pulp then produced a phosphate float analyzing 78.82% B. P. L.

The overall recoveries of phosphate in the described operation were fair. Such operation may be improved by using other silica activating reagents such as mentioned previously in this specification, and also by the addition of further "Lamepon" reagent along with the fuel oil for the phosphate flotation step. While in the above noted example, there was very little tendency for the silica to float in the phosphate flotation step, the use of some inorganic salts for the silica flotation step tends to float too much silica in the second operation. In these cases, the pulp can be subjected to a slight scrubbing or attrition action before the fuel oil is added for the subsequent flotation of the phosphate constituent.

It is not to be supposed that all of the possible reagents coming within the classification set forth in this specification will act as flotation collectors in the manner described. It would be impossible in the lifetime of an individual to test the flotation properties of the vast numbers of possible molecular configurations in this classification. However, simple tests on any reagents of the class described along the lines set forth in this specification should readily establish their utility as mineral flotation reagents.

I claim as my invention:

1. The process for the concentration of phosphate ore containing silica which comprises, mixing an aqueous pulp of the ore with a reagent of the polypeptide class formed by the action in the presence of an alkali of an acylating agent containing a straight-chain hydrocarbon group of at least eight carbon atoms on a protein decomposition product of the class consisting of protalbinic and lysalbinic acids, and submitting the thus conditioned pulp to a concentration treatment to separate the phosphate from the silica.

2. The process for the concentration of phosphate ore containing silica which comprises, mixing an aqueous pulp of the ore with a reagent of the polypeptide class that formed by the ac-

tion in the presence of an alkali of an acylating agent containing a straight-chain hydrocarbon group of at least eight carbon atoms on a protein decomposition product of the class consisting of protalbinic and lysalbinic acids together with an unsaponifiable water-immiscible organic liquid, and subjecting the pulp to a concentration treatment to separate the phosphate as a concentrate.

3. The process of claim 2 in which the organic liquid is a petroleum hydrocarbon.

4. The process of claim 2 in which the organic liquid is fuel oil.

5. The process of claim 2 in which a mahogany sulfonate is used in addition to the reagents described therein.

6. The process of claim 2 in which concentration is effected by froth flotation of the phosphate.

7. The process for the concentration of phosphate ore containing silica which comprises, mixing an aqueous pulp of the ore with a reagent of the polypeptide class formed by the action in the presence of an alkali of an acylating agent containing a straight-chain hydrocarbon group of at least eight carbon atoms on a protein decomposition product of the class consisting of protalbinic and lysalbinic acids together with a silica activating agent consisting of ferrous sulfate, and subjecting the pulp to a concentration treatment to separate the silica from the phosphate.

8. The process of claim 7 in which concentration is effected by froth flotation of the silica.

9. The process for the concentration of phosphate ore containing silica which comprises, mixing an aqueous pulp of the ore with a reagent of the polypeptide class formed by the action in the presence of an alkali of an acylating agent containing a straight-chain hydrocarbon group of at least eight carbon atoms on a protein decomposition product of the class consisting of protalbinic and lysalbinic acids together with a silica activating agent, subjecting the pulp to froth flotation to separate a silicious float, thereafter adding to the unfloated remainder of the pulp an unsaponifiable water-immiscible organic liquid, and subjecting the pulp to a second froth flotation operation to remove a floating concentrate of phosphate.

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