Patented July 16, 1940 2,208,143

UNITED STATES PATENT OFFICE

2,208,143

PROCESS OF TREATING CALCAREOUS MATERIALS

Arthur J. Weinig, Golden, Colo., assignor to Riverside Cement Company, Los Angeles, Calif., a corporation of Delaware

No Drawing. Application August 10, 1937, Serial No. 158,339

28 Claims. (Cl. 209—166)

This invention relates to a method for the separation of calcareous materials used in cement manufacture from other constituent materials of the natural products. More particularly, the invention relates to the separation of brucite or other magnesium compositions, from the constituents of limestone.

Objects

It is a primary object of the present invention to separate from limestone and similar compositions, brucite and/or other magnesium-containing constituents, in a simple, effective and economical operation, and thereby render the limestone or similar compositions, after separation, suitable for the manufacture of Portland cement.

Another object of the invention is to provide a froth flotation operation in which reject material, usually constituting a small percentage of the entire mass treated, is floated and removed as a froth concentrate while the useful product of the operation, which usually comprises a large percentage of the mass treated, is collected as a non-floated residue of the operation.

A further object of the invention is to provide a sufficiently large group or class of reagents to render the process efficient and economical under varying market conditions in the treatment of materials of various compositions.

Froth Flotation

In the practice of the froth flotation process, it is customary to grind ores or other earthy materials to a suitable degree of fineness, then add water thereto in sufficient quantities to produce a free flowing pulp, in which certain flotation reagents are introduced. The pulp is then subjected to aeration and agitation whereby a froth is formed, which carries certain constituents of the pulp to the surface where they are removed by suitable means.

The reagents added to the pulp will vary with the nature of the material being treated and also must be varied in accordance with the properties of the specific minerals which are to be collected in the froth.

One function of a reagent is to produce a froth and reagents possessing this property are called frothers. Another function is to cause certain minerals to adhere and collect in the froth, and reagents possessing this property are known as collectors. Sometimes it is necessary to prevent a given mineral from collecting in the froth, and reagents performing this function are depressors or inhibitors. Other reagents may modify the volume, toughness or other characteristics of the froth, and are designated regulators or modifiers.

In some instances, a single reagent will possess more than one of the above properties, and a given flotation treatment may be performed successfully with one reagent composition. Other treatments will require two or more reagent compositions, and in some instances, a different reagent composition will be required for each function utilized in the operation.

In performing the process, a two-stage operation is frequently employed in which the first separation is known as a "rougher" operation, followed by what is termed a "cleaner" operation, in which the rougher froth is treated to improve the flotation separation.

Advance in the Art

The present invention utilizes standard procedures to a large degree and may be performed in various apparatus designed for the froth flotation process, generally. The invention resides in the discovery that magnesium minerals may be removed collectively, as an impurity, from materials which otherwise would not be adapted for use in the manufacture of cement, by floating the impurity off in froth, and recovering the valuable constituents as a non-floated residue.

To make the process workable under varying conditions of reagent cost, and chemical and physical characteristics of the material treated, a relatively large group of preferred reagents has been provided for the froth flotation separation.

Suitable frothers for such a treatment are pine oils, cresylic acid or compositions of cresylic acid. Collectors which may be used with good results in the treatment are hydrocarbons, like gas fuel oil, mineral oils, or mineral oil fractions, as well as aromatic hydrocarbons like dipentine, which also possess certain qualities of modifier reagents, particularly in floating finely divided magnesia minerals.

It has been observed that under certain circumstances, particularly when sufficient gas oil and cresylic acid are used to produce flotation without other collector reagents, the volume of froth may become excessive and difficult to control under these conditions.

Reagents which may be used for controlling froth are the alkaline earth soaps, such as calcium oleate and magnesium oleate. Such reagents are best prepared by precipitating a warm

(but not boiling) solution of sodium oleate with soluble calcium or magnesium salts, and then washing and drying the resulting soaps, which are insoluble in water.

After drying, these soaps are soluble in warm gas oil, and a solution in this form is preferably added to the pulp for froth control, although other means satisfactory for this purpose may be employed. The alkaline earth soaps also function as a collector for the flotation of magnesium minerals.

While the above-described reagents are effective in causing finely-divided magnesum minerals like brucite and some forms of olivine to collect in the froth, and at the same time reject the desired constituents for cement manufacture, namely, those containing lime, alumina, iron or silica; there are coarser grains of magnesia minerals, such as brucite, which will not be so effectively collected in the froth.

Where it is necessary to collect these coarser sizes in the froth, soluble salts of metals, such as lead or thallium, when added to the pulp with xanthates, thiocarbanalide or cresylic acid compositions heated with phosphorus pentasulphide, which are commonly known in the flotation art as phosphocresylic acids, will effectively float the coarser sizes of brucite or other magnesium minerals. Where flotation of this type is employed, the lead and thallium salts are preferably added to the pulp before the addition of organic sulfur compounds.

Salts of lead and/or thallium which have been employed effectively for this purpose are the chlorides, nitrates and acetates. The xanthates found effective are the ethyl, amyl, butyl and fenchyl. Various phosphocresylic acids and their corresponding salts are suited for this purpose. Thiocarbanilide is also effective. The foregoing compositions may be designated for convenience as "organic sulphur compounds of the collector type" and it should be noted that, in general, any such organic sulphur compound ordinarily employed in sulfide mineral flotation will be a satisfactory collector for this purpose, while the combination of such a soluble salt and an organic sulfur compound will give good frothing, collection and selectivity.

It will be noted that cresylic acid compositions have been described hereinbefore as suitable frothers and it will be understood that in the usual size ranges of the treatment phosphocresylic acids will give good frothing and collection in treating magnesium minerals when no soluble lead or thallium salts are added to the pulp.

In practicing the present invention, use is preferably made of the two-stage operation, previously described, to improve the separation and to more efficiently discard magnesium-containing constituents.

The cleaning step may be improved materially in the magnesium separation by introducing into the pulp a reagent, such as a phosphate, preferably tetra sodium pyrophosphate or sodium metaphosphate or equivalent salts of arsenic and antimony. Certain organic colloids, such as gums, like gum arabic, or tannates, such as tannic acid, or sodium carbonate and equivalent alkali salts may be used effectively for this purpose.

This group of reagents act as calcite inhibitors or depressors to cause materials containing lime, alumina, iron or silica minerals entrapped in the flotation froth to drop out and enrich the residue. While it is usually necessary to employ an inhibitor of this type only in the cleaner operation, under some conditions it may be desired to employ such an inhibitor in the rougher operation and the foregoing reagents may be used effectively in this way.

The final froth concentrate of the process, obtained by the selective action of the various reagent combinations hereinbefore described, usually is a product containing magnesium minerals which are the impurity of the material treated. These concentrates are reject products which are discarded from this process. The remainder of the minerals of the non-floated residue are purified compositions, suitable for the manufacture of Portland cement.

While the process is being described with particular reference to producing a product for cement manufacture, it will be understood that the process may be employed effectively whenever it is desired to remove the above-designated constituents from minerals of the character described.

For the purpose of cement production it is not necessary to remove all of the magnesia-containing material, but only to reduce the same to a safe limit for the class of work for which the cement is to be used. The main object is to obtain a maximum amount of usable tailing, and the efficiency of the operation may be high even where the recovery of magnesia is not particularly high.

Many magnesium minerals have shown significant selective flotation from calcite by the use of the aforementioned reagents, such as the following: brucite, talc, olivine, magnesite, dolomite, chlorite, enstatite, vermiculite, amphibole and pyroxene.

The foregoing minerals all belong in the general class of magnesium materials, and this term will be used to designate the group elsewhere in the description and claims. Other minerals possessing similar characteristics are also amenable to the treatment.

In the cement industry, clay is a common source of the acidic oxides in the mix. In testing the present process, it has been found that calcite and kaolin can be left behind in the residue in approximately the same proportion as they are present in the feed.

In preparing the pulp for the flotation operation, the material to be treated must be reduced to finely-divided condition. The effective size for a given material will vary to a considerable degree and workable results may be obtained in a relatively large range of sizes. Testing in the customary manner, well-known to those skilled in the art, will determine the best size for a given operation. In the operations hereinafter described, grinding to pass 65 mesh is employed, and this will provide a standard for testing particular compositions.

It will be noted that the process as described in the preceding remarks floats off the reject material from the constituents which comprise the final product of the treatment.

As the material floated comprises a relatively small percentage of the entire quantity of material treated, reagent costs and operating intervals are reduced to a minimum. If the procedure were reversed, for example, a much larger quantity of reagent would be required to float the final product of the same amount as produced by the present process, and the operating time required to effect such a separation would be increased proportionately.

Consequently, the present process effects important economies in reagent cost, operating cost, and plant capacity.

Illustrative Operations

To furnish a better understanding of the operation of the process, reference will be made hereinafter to specific treatments which illustrate the scope of the process in operating under various conditions.

A. General flotation using all reagents (General procedure—A)

By all reagents is meant all reagent types of demonstrated importance in the separation of brucite from calcite. The most commonly used reagents are listed below, but as discussed elsewhere the designated compositions are but specific examples of effective reagent types.

Cresylic acid or aerofloat or both.
A solution of calcium oleate in gas oil.
Lead salt.
Amyl xanthate.
Sodium pyrophosphate or gum arabic (depressors of calcite).

The following is an example illustrating the use of these reagents in the treatment of an interground mixture of raw materials for Portland cement manufacture. This mixture was composed of a limestone containing considerable brucite ($Mg(OH)_2$), with metamorphic and granitic rocks which supplied the more acidic oxides but also contained significant amounts of magnesia in other combinations. It was a wet grind made in short stages with intervening separation of material passing a 65 mesh screen, until practically all had passed this screen.

EXAMPLE NO. 1

Reagents	Roughing, lbs./ton	Cleaning, lbs./ton
Gas oil	3.3	
Calcium oleate	0.2	
Lead nitrate	0.5	
Amyl xanthate	0.5	
Cresylic acid	0.9	
Aerofloat #31	0.3	
Sodium pyrophosphate		0.8

Metallurgical Report

Assay No.	Product	Weight, grams	Per cent	Analyses, per centum				
				MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3
X	Cleaner conc	169	8.34	13.7	37.1	7.4	2.46	3.78
Y	Cleaner tail	644	31.8	3.69	44.5	10.6	3.02	1.68
Z	Rougher tail	1213	59.9	2.10	42.3	16.1	4.10	1.50
Calc	Heads	2026		3.56	42.4	13.6	3.61	1.74

Assay No.	Contents per 100 tons assay multiplied by percent					Per cent recovery based on actual weight of products				
	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3
X	1.14	3.09	.62	.20	.31	32.0	7.3	4.6	5.5	17.8
Y	1.16	13.99	3.33	.95	.53	32.6	33.0	24.5	26.3	30.5
Z	1.26	25.33	9.64	2.46	.90	35.4	59.7	70.9	68.2	51.7
Calc	3.56	42.41	13.59	3.61	1.74					

Remarks.—Rougher concentrate was thickened before cleaning.

In this test the first froth or rougher froth concentrate was cleaned producing a cleaner concentrate and cleaner tailing as shown. The volume of the froth was kept under control by the use of calcium oleate.

Magnesia minerals which have been mineralogically determined in the limestone used were: brucite, periclase, hydromagnesite, dolomite, chondrodite, spinel, xanthophyllite, monticellite.

Similarly, minerals found in the granodiorite were: hornblende, augite, chlorite, biotite, sericite.

The main minerals which remained in the unfloated pulp were calcite, quartz, feldspar, limonite and hematite.

Sulfide minerals like pyrite were incidental non-magnesium minerals which floated out of the pulp and concentrated with the magnesium minerals in the froth concentrate.

In milling practice, a cleaner tailing usually will be returned to the rougher treatment forming a closed circuit therewith. But in the treatment of some materials, the cleaner tailing may have a sufficiently low magnesia content to make a satisfactory clinker, in which case it may be used to make the clinker without further treatment.

The tailing produced in the test hereinbefore described would give the following cement clinker, assuming volatilization of all but the five oxides shown, and complete retention of these.

Calculated Clinker

Oxide	Percent
CaO	64.0
MgO	3.2
SiO_2	24.3
Al_2O_3	6.2
Fe_2O_3	2.3

Potential compound*

3 $CaO.SiO_2$	30.9	tri calcium silicate
2 $CaO.SiO_2$	46.4	di calcium silicate
3 $CaO.Al_2O_3$	12.5	tri calcium aluminate
4 $CaO.Al_2O_3.Fe_2O_3$	7.0	tetra calcium alumino ferrite
MgO	3.2	magnesia

*Equilibrium compounds, calculated according to the method of Bogue, Industrial and Engineering Chemistry, Anal. ed. 1, 192 (1929) (Standard reaction products).

A clinker of this composition will make a Portland cement of satisfactory quality for general use. Should it be desired to reduce the quantity of tricalcium aluminate, or to raise that of tricalcium silicate, or in any other way alter the

composition of the resultant clinker, there should be added to the product before clinkering such other commercial raw materials as produce the desired modification. For the specific purposes mentioned above, additions of iron oxide and limestone, respectively, would be suitable.

In this example, the flotation accomplished a reduction in the magnesia content of the product to such an extent that a suitable clinker was produced containing only 3.2% of this oxide in contrast to 5.5% which would result from the use of the untreated heads material. Tests indicate that most of the magnesia which was removed was present as brucite. However, experiments have shown that other magnesian minerals can be selectively floated from limestone by the use of the same reagents.

B. Use of special reagent combinations (special procedures—B)

It will be understood, however, that the above illustration of reagent use applies in general when there are several different magnesium minerals present. However, in secial cases where the magnesia is contained in certain specific minerals, it may not be necessary to employ all the reagents listed. For example, the depressor reagent was not found essential when the main magnesium minerals which were floated were talc, brucite and olivine.

Further, when cresylic acid or a phosphocresylic acid alone is used as a frothing and collector reagent satisfactory results are obtained when talc, serpentine and olivine are the main magnesium bearing minerals. Also, when the magnesia was mainly contained in serpentine, brucite and talc, a cresylic acid composition, lead salts and xanthates when used alone served to produce satisfactory results.

In addition, when brucite is the main magnesium mineral content, gas oil, calcium oleate and xanthate has been found to produce flotation of the brucite.

In general, it has been discovered that salts of thallium react like lead salts and can serve as substitutes for lead salts in foregoing illustrations. For example, a wet grind of limestone containing about 12% MgO, mainly as brucite, was made in stages with intervening screening until practically all passed a 65 mesh screen. A portion of this pulp containing 288 grams of solids was given a flotation test using the following reagent quantities:

EXAMPLE NO. 2

For 1st concentrate

	Grams
Gas oil (containing 5% calcium oleate)	0.83
Cresylic acid	0.16

For 2nd concentrate

	Grams
Thallic nitrate	0.033
Thallic chloride	0.054
Amyl xanthate	0.10
Cresylic acid	0.04

A mixture of thallic salts was used only because it was convenient to obtain the oxidized state by first preparing the thallous nitrate and then chlorinating it.

The results of the flotation tests were as follows:

Product	Weight, percent	MgO, percent
1st concentrate	6.95	21.2
2nd concentrate	18.05	24.8
Tailing	75.00	8.4

Further, in special cases where dolomite and magnesite are present, manganous, ferric, ferrous and cupric salts may also serve as substitutes for lead salts in the above reagent combinations, for the flotation of magnesium containing minerals.

EXAMPLE NO. 3

A magnesium containing limestone from Crestmore, California, was used in this example. The magnesia minerals associated with calcite in this example were mainly brucite, with smaller amounts of hydromagnesite, periclase, chondrodite, spinel, xanthophyllite, monticellite and dolomite.

In performing the demonstration the limestone was ground to 65 mesh, diluted with four parts by weight of water and subjected to a froth flotation treatment for five minutes in a laboratory flotation machine, using the following reagents in equivalent pounds per ton of limestone:

	Pounds
Cresylic acid	.60
Gas fuel oil containing 5% dissolved calcium oleate	16.00
Lead nitrate	1.70
Amyl xanthate	2.00
Tetra sodium pyrophosphate	.35

The products of this test were:

Product	Percent weight	Percent MgO	Parts MgO
Limestone as taken	100	17.8	
Froth concentrate	47.0	30.0	14.1
Flotation tailing	53.0	6.3	3.3
Total			17.4

The pH value of the flotation water was 9.5. The high alkalinity was due to the partial solubility of the brucite.

The flotation tailing was suitable calcareous material when mixed with other low magnesia argellaceous and calcareous material for the manufacture of cement.

From the foregoing, it will be apparent that the process disclosed herein is of general application wherever it is desired to separate magnesium-containing materials from calcite or similar compositions, both of natural and artificial origin, which are designated herein as "calcareous materials".

The general description of the treatments together with the tests cited show the adaption of the process to different problems of treatment in which different factors are involved. By following the rules of procedure prescribed in the foregoing description, satisfactory results for any specific treatment can be obtained.

The term "reagent" as used in the claims is intended to designate one or more compositions productive of a reaction in which designated constituents of the material under treatment are selectively floated off from other constituents thereof.

While the invention has been described with particular reference to a froth flotation operation, it will be apparent that any type of separation, which utilizes in fundamentally the same way, the interfacial reactions between solids, liquids and gases, could be performed with the reagents herein described functioning to facilitate the separation.

In the description and claims, the expression "salt of the lead-thallium class" is intended to designate any salt possessing the properties of the salts of lead or thallium described herein as suitable for the purposes of the present invention.

In this connection, it appears that almost any metallic salt which can form relatively insoluble hydroxide or carbonate (probably colloidal) is capable of inducing the separation of dolomite or magnesite from calcite.

Where the term "gas oil" has been used in the description and claims, it is intended to designate a product of petroleum distillation, preferably a little heavier than gasoline.

Where the expression "a cresylic acid collector" has been used throughout the description and claims, it is intended to designate cresylic acid, the cresylic acid derivatives herein described as being satisfactory for the intended purpose, as well as other equivalents coming under the broad characterization of a cresylic acid composition.

Changes and modifications in the various steps and treatments may be availed of within the spirit and scope of the invention as defined in the hereunto appended claims.

What I claim and desire to secure by Letters Patent is:

1. In a process for the treatment of calcareous materials, wherein a plurality of constituents constituting impurities are to be removed, the steps of floating a plurality of impure constituents in a pulp containing calcareous material in finely-divided condition by the action of cresylic acid and a hydrocarbon in a froth flotation treatment, and controlling frothing by introducing an alkaline earth soap into the pulp.

2. In a process for the treatment of calcareous materials, wherein a plurality of constituents constituting impurities are to be removed, the steps of floating a plurality of impure constituents in a pulp containing calcareous materials in finely-divided condition by the action of cresylic acid and a hydrocarbon in a froth flotation treatment, and controlling frothing by introducing calcium oleate into the pulp.

3. In a process for the treatment of impure calcitic materials, wherein a plurality of constituents constituting impurities are to be removed, the steps of floating a plurality of impure constituents in a pulp containing impure calcitic material in finely-divided condition by the action of cresylic acid and a hydrocarbon in a froth flotation treatment, and controlling frothing by introducing magnesium oleate into the pulp.

4. In a process for the treatment of calcareous materials, wherein constituents constituting impurities are to be removed, the step of subjecting a pulp containing calcareous material in finely-divided condition to the action of a reagent composed of cresylic acid, a hydrocarbon, a soluble salt of the lead-thallium class, and a xanthate, in a froth flotation treatment.

5. The process of preparing materials for cement manufacture, which comprises forming a pulp of impure limestone in finely-divided condition in liquid suspension, subjecting the pulp to the action of a mixture of cresylic acid, gas oil, an alkaline earth soap, a soluble salt of the lead-thallium class, a xanthate and a phospho-cresylic acid composition, and collecting the non-floated residue of the separation as a product for calcining.

6. In a process for the treatment of calcareous materials containing brucite as an impurity, the step of floating brucite from a pulp of such a calcareous material in a froth flotation treatment by the action of a salt of the lead-thallium class and a xanthate, whereby a purified calcitic residue may be recovered separate from such froth product.

7. In a process for the treatment of calcareous materials containing brucite as an impurity, the step of floating brucite from a pulp of such a calcareous material in a froth flotation treatment by the action of a hydrocarbon, a cresylic acid composition, a salt of the lead-thallium class and a xanthate, whereby a purified calcitic residue may be recovered separate from such froth product.

8. In a process for the treatment of calcareous materials containing a magnesium-bearing carbonate as an impurity, the step of floating said carbonate from a pulp of such a calcareous material in a froth flotation treatment by the action of a collector reagent formed by the interaction of a salt of the lead-thallium class and a xanthate, whereby a purified calcitic residue may be recovered separate from such froth product.

9. In a process for the treatment of calcareous materials containing a magnesium-bearing carbonate as an impurity, the step of floating said carbonate from a pulp of such a calcareous material in a froth flotation treatment by the action of a hydrocarbon, a cresylic acid composition, a salt of the lead-thallium class and a xanthate, whereby a purified calcitic residue may be recovered separate from such froth product.

10. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a cresylic acid collector and an alkaline earth soap and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

11. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of a salt of the lead-thallium class and an organic sulphur compound of the sulfide collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

12. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing

silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of a salt of the lead-thallium class and a xanthate, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

13. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of cresylic acid, a hydrocarbon and an organic sulphur compound of the sulfide collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

14. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of a salt of the lead-thallium class, cresylic acid and an organic sulphur compound of the sulfide collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

15. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of a salt of the lead-thallium class, a hydrocarbon, and an organic sulphur compound of the sulfide collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

16. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of cresylic acid, a hydrocarbon and an alkaline earth soap, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

17. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of a hydrocarbon, an alkaline earth soap and a xanthate, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

18. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a hydrocarbon, a cresylic acid composition, a salt of the lead-thallium class, and an organic sulphur compound of the sulfide collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcite residue of the pulp.

19. The process of purifying calcarous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of an alkaline earth soap, a cresylic acid collector, a salt of the lead-thallium class and an organic sulphur compound of the sulfide collector type selected from the group consisting of xanthates, thiocarbonalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

20. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a hydrocarbon, a cresylic acid collector, an alkaline earth soap, a salt of the lead thallium class, a xanthate, and a phosphocresylic acid composition, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

21. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a hydrocarbon, a cresylic acid collector, an alkaline earth soap, a salt of the lead-thallium class, and an organic sulphur compound of the sulfide collector type

selected from the group consisting of xanthate, thiocarbanalide and phosphocresylic acids, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

22. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent of the collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp and depressing the calcitic constituents during the flotation reaction by the action of a calcitic inhibitor of the class consisting of alkali phosphates.

23. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent of the collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp and subjecting the floated concentrate of such separation to a secondary floation treatment in the presence of a calcitic inhibitor reagent of the class consisting of organic colloids.

24. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent of the collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp and subjecting the calcitic constituents during the flotation reaction to the action of an alkali phosphate.

25. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent of the collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp and subjecting the calcitic constituents during the flotation reaction to the action of an organic colloid.

26. In a process of treating calcareous materials, wherein brucite constituting an impurity is to be removed, the steps of floating brucite constituents in a pulp containing calcareous material in finely-divided condition by the action of cresylic acid and a hydrocarbon in a froth flotation treatment, and controlling frothing by introducing an alkaline earth soap into the pulp.

27. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely-divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent formed by the interaction of cresylic acid and a hydrocarbon, depressing calcitic constituents by the presence of a phosphatic inhibitor, and collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp.

28. The process of purifying calcareous materials having one or more magnesium constituents of the class of brucite, magnesium-bearing carbonates, and anhydrous magnesium-bearing silicates constituting impurities therein, which comprises the treatment of such a calcareous material in finely divided condition in a pulp in which such impurities are present, selectively filming such impurities by the action of a reagent of the collector type selected from the group consisting of xanthates, thiocarbanalide and phosphocresylic acids, collectively floating such impure constituents so filmed on the surface separate from the calcitic residue of the pulp and subjecting the floated concentrate of such separation to a secondary floation treatment in the presence of a calcitic inhibitor reagent of the class consisting of gum arabic.

ARTHUR J. WEINIG.