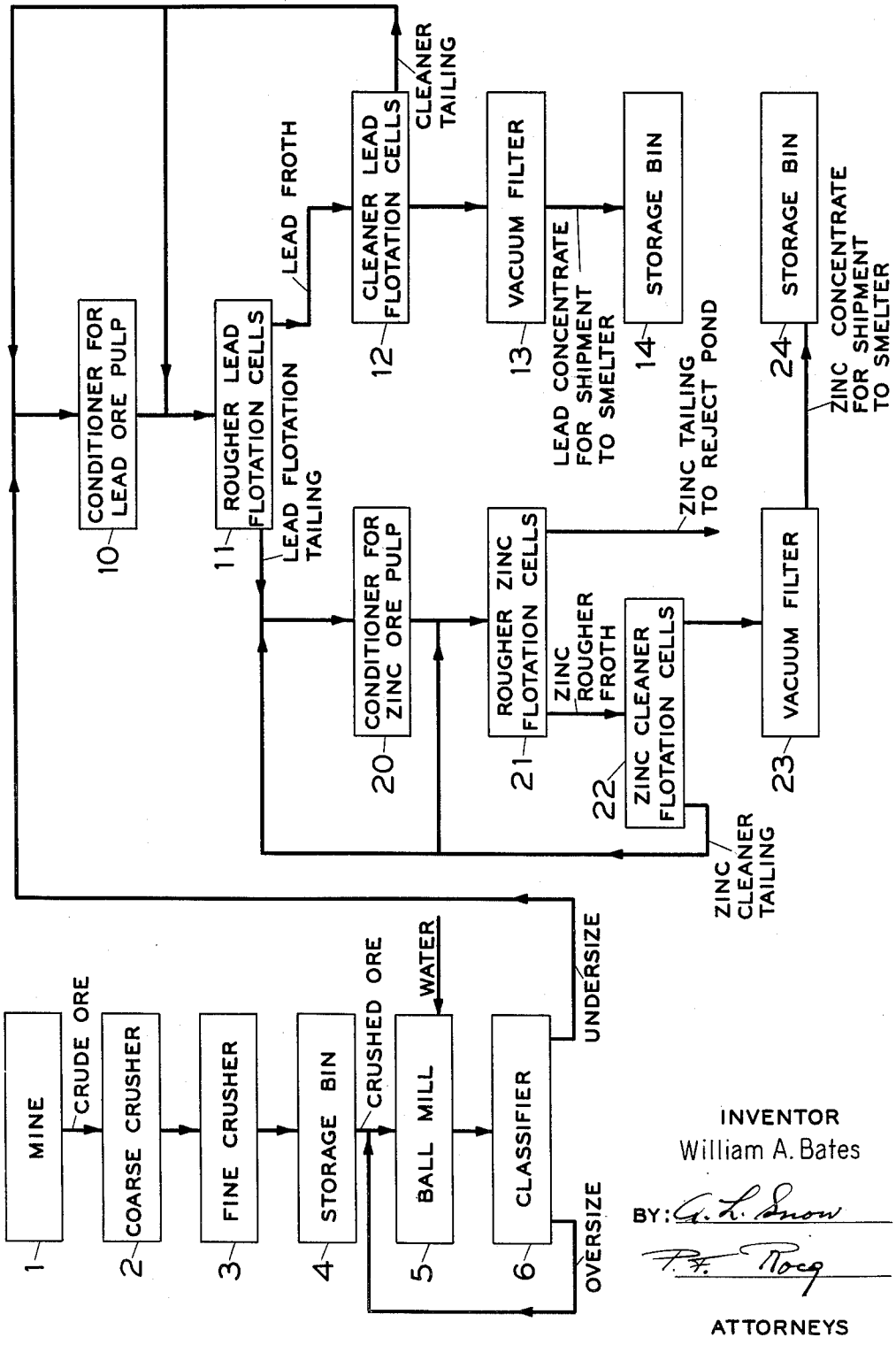
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RECOVERY OF ZINC VALUES BY SELECTIVE FLOTATION OF SULFIDE ORES

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RECOVERY OF ZINC VALUES BY SELECTIVE FLOTATION OF SULFIDE ORES

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This invention relates to the recovery of zinc sulfide from sulfide-type ores. More particularly, it relates to the recovery of zinc sulfide from polymetallic sulfide-type ores by a process of selective froth flotation. Still more particularly, this invention relates to the recovery of zinc sulfide from ores in which zinc sulfide is associated with lead sulfide and pyrites.

The ores in which zinc values occur in the form of sulfide may be subdivided into three broad classes: (1) Straight zinc ores in which zinc sulfide is the only valuable metalliferous mineral, the remainder being quartz, limestone or other non-metalliferous gangue; (2) copper-zinc sulfide ores in which copper sulfide and zinc sulfide are the valuable metalliferous components; and (3) lead-zinc sulfide ore in which zinc sulfide and lead sulfide are the valuable metalliferous minerals. This latter type of ore—the lead-zinc sulfide ore—is by far the most important in the mineral dressing industry. Therefore, while my invention generally relates to the recovery of zinc sulfide from any sulfide-type ore, one of its particularly preferred ramifications is directed to the recovery of zinc sulfide from lead-zinc sulfide ores.

The aforementioned three types of sulfide ores generally contain considerable amounts of pyrites in addition to quartz or other non-sulfide gangue. This admixture of pyrites may range from a few per cent to almost one hundred per cent of the gangue in the ore. In addition, small but economically attractive amounts of gold and silver are frequently present in the ore, and in the case of marmatitic ores some of the zinc in the zinc blende is found replaced by iron and manganese in solid solution.

The separation of zinc sulfide from other components of sulfide-type ores by froth flotation techniques is not a simple operation, as almost invariably at least two distinct concentrates must be produced. In the case of lead-zinc sulfide ores, the lead concentrate must be substantially completely freed from zinc contamination, while a number of economical and metallurgical considerations rule out the presence of an excess of pyrites in the zinc concentrate. First of all, because of the low unit value content of zinc sulfide in the zinc concentrate, the low grade of this latter occasioned by the presence of large amounts of pyrites increases considerably the costs of transportation to the smelter and can render the recovery of zinc from such a concentrate unprofitable. In the second place, presence of iron in the form of pyrites is known to have

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an adverse effect on the operation of retorts in the thermal type of smelter, while in the electrolytic plants for the reduction of zinc the presence of pyrites in the zinc concentrate is apt to cause formation of insoluble zinc ferrites upon roasting, interfering with the recovery of zinc. In fact, difficulties are encountered in the treatment of practically all zinc-bearing sulfide-type ores, and are particularly annoying in the case of marmatitic ores which contain more than 10% pyrites.

Consequently, the discovery of new methods for beneficiating and recovering zinc sulfide from sulfide-type ores by froth flotation, which would yield zinc concentrates of a higher grade than has heretofore been obtained with sulfhydric-type collectors, e. g., with xanthates, is highly desirable.

I have found that zinc sulfide concentrates of improved grade can be recovered from sulfide-type ores by the application of a new and effective collecting agent of the cationic type. This collecting agent, referred to hereinafter in this specification as "petroleum nitrogen bases," represents a complex mixture of alkyl and polyalkyl nitrogen-bearing heterocyclic compounds produced in the thermal treatment (pyrolysis) of petroleum. Ordinarily crude petroleum, and especially the California crude mineral oil, contains a certain proportion of heterocyclic nitrogen-bearing compounds of an unknown and complex structure, which in the course of refining of the various petroleum fractions are pyrolyzed to mixtures of lower molecular weight heterocyclic nitrogen-bearing compounds known among the refiners as the petroleum nitrogen bases.

The exact composition of these mixtures is not known; however, they are believed to contain appreciable amounts of alkylated homologues of pyridine and quinoline. Among the various operations of petroleum refining, the cracking of naphthas represents one of the largest sources of formation of these petroleum nitrogen bases. Whether originating in cracked naphthas, or in gas oils, or in other fractions of petroleum, the usual procedure of recovering the nitrogen bases therefrom consists in agitating the petroleum fraction with dilute sulfuric acid of about 30–50% strength, or with other suitable acid of appropriate strength, separating an acid layer containing the nitrogen bases from an oil layer, and neutralizing the acid layer. The recovered nitrogen bases range in color from yellow (when freshly recovered) through red to black liquids (on settling and exposure to air). They are basic in char-

acter and possess the specific odor of heterocyclic nitrogen compounds of the pyridine and quinoline series. They consist essentially of a mixture of nitrogen-bearing alkylated heterocyclic compounds boiling between about 120° F. and about 630° F., approximately 75% coming over at about 510° F. Low-boiling petroleum fractions upon thermal treatment yield low-boiling mixtures of nitrogen bases of a correspondingly low average molecular weight, and conversely higher boiling petroleum fractions yield higher boiling mixtures of nitrogen bases of a higher average molecular weight. The individual components in these mixtures of petroleum nitrogen bases may range from mono- and dimethyl pyridines to compounds as complex as $C_{16}H_{25}N$; but, in any event, the molecular weights of these compounds are higher than the molecular weights of the corresponding mineral oil fractions or cracked naphthas from which they have been derived.

The complexity of the composition of nitrogen bases becomes clearly apparent upon considering the distillation data (ASTM) in Table I, obtained on a representative 500 cc. sample derived from cracked naphtha.

TABLE I

Cut No.	Temp. °F.	Per Cent Distilled	Gravity		Mol. Wt.	Per Cent C	Per Cent H	Per Cent N
			°A. P. I.	Sp. Gr.				
1	129–342	5	25.2	.9030				
2	342–370	10	22.5	.9188	130			
3	370–379	15	23.0	.9159				
4	379–396	20	23.1	.9153	141	78.26	9.88	9.91
5	396–401	25	22.8	.9170				
6	401–412	30	22.8	.9170	148.8	78.32	10.02	9.46
7	412–428	35	21.7	.9236				
8	428–444	40	20.1	.9334	154			
9	444–451	45	18.4	.9440				
10	451–456	50	16.9	.9535	171	79.88	9.91	9.04
11	456–469	55	16.1	.9587				
12	469–482	60	14.8	.9672	178	79.65	9.41	8.18
13	482–486	65	14.1	.9718	178.8			
14	486–510	70	13.0	.9792	179.5			
15	510–521	75	11.9	.9868				
16	521–531	80	11.2	.9916	183	80.14	8.83	7.79
17	531–542	85	10.1	.9993				
18	542–554	90	9.0	1.0071	186	81.11	8.71	7.73
19	554–562	95	9.0	1.0071				
20	562–635	100	8.2	1.0128	210			

The nitrogen bases suitable for the purposes of the present invention may contain from one to five per cent of water and up to ten per cent of neutral oil, depending on whether or not they have been subjected to distillation.

The following tabulation illustrates the various properties of two typical samples of petroleum nitrogen bases derived from cracked naphtha. The nitrogen bases of Example A have not been distilled; those of Example B have been distilled.

TABLE II

Example	A	B
Gravity °A. P. I. (ASTM/D-287)	11.6	14.2
Specific Gravity 60/60°F	0.9888	0.9712
Flash Point (Cleveland Open Cup °F.) ASTM/D-92	210	172
Water by distillation, per cent	5	1.5
Solubility in 30% H_2SO_4, per cent	92	99
Neutralization No., mgm. H_2SO_4/gm	270	320
Color, ASTM (ASTM D-155)	Black	Darker than 8.

I have discovered that petroleum nitrogen bases, when used as collectors in the froth flotation of sulfide-type zinc-bearing ores, are highly selective and display an unusual collecting power for zinc sulfide, but have practically no collecting effect with respect to pyrites and galena. This unexpected selectivity of petroleum nitrogen

bases employed as collectors in the froth flotation of sulfide-type ores permits of securing high-grade zinc concentrates low in lead and iron contents.

While all mixtures of petroleum nitrogen bases boiling between about 120° F. and about 630° F. are applicable in froth flotation of sulfide ores as selective collectors for zinc sulfide, those derived from cracked naphthas are found to be particularly effective. These preferred nitrogen base collectors for zinc sulfide are essentially mixtures of alkylated homologues of pyridine and quinoline with molecular weights ranging from about 130 to about 180 and even higher, as shown in Table I.

The application of petroleum nitrogen bases as collectors for froth flotation and recovery of zinc sulfide from sulfide-type ores in accordance with the present invention is rather straight-forward and does not call for a radical departure from the conventional technology of differential or selective froth flotation. Crude zinc sulfide ore, e. g., sphalerite, is ground in water and made into an aqueous ore pulp, the particle size of the ground ore ranging from 35 mesh at the maximum to as low as 200 mesh.

To permit the recovery of zinc values from a straight zinc sulfide ore pulp, or, in the case of a polymetallic sulfide-type ore, from the tailing from a previous lead sulfide or copper sulfide flotation step, this pulp or tailing is conditioned to establish alkalinity in the circuit, the pH being preferably of the order of from 7.0 to 11.0.

This desired alkalinity is secured by employing a pH regulator such as lime, sodium hydroxide, a suitable silicate or phosphate (e. g., sodium silicate or trisodium phosphate). However, soda ash is generally preferred for the purpose. If lime is used to impart alkalinity, it will be added in amounts not exceeding 1 pound per ton of ore. When soda ash is employed to regulate the pH of the circuit, as much as 3 pounds of soda ash per ton of ore, and even greater quantities if necessary, will be added. In all cases, flotation will be effected at a pH of from about 7.0 to about 11.0, the optimum value depending on the nature of the ore being treated. Thus, sphalerite is usually floated at a pH comprised between 7.0 and 8.5. On the other hand, marmatite is floated best at a pH ranging from 10.3 to 11.0.

In accordance with the usual practice of flotation of zinc sulfide, it should be adequately activated with copper sulfate pentahydrate

($CuSO_4.5H_2O$)

which is added to the pulp in amounts ranging from 0.5 to 1.5 pounds per ton of the ore. Conventional frothers may also be used, for instance, cresylic acid, pine oil and the like. Petroleum nitrogen bases will be employed as the selective collector for zinc sulfide in amounts which depend on the grade, i. e., the zinc content of the ore. Ordinarily, amounts from 0.01 to 0.5 pound per ton of ore are found to secure high grade zince sulfide concentrates. The addition of the various conditioning reagents is preferably effected in a special conditioning vessel or tank at a relatively high dilution of the pulp of the order of about 20 to 40% solids by weight of the pulp, though in some instances the pH regulator may be added to the grinding circuit and the collector may be introduced directly into the flotation cell. The conditioning treatment usually occupies from 5 to 30 minutes or more, the optimum duration being readily ascertainable by the operator.

When treating a zinc-bearing ore containing lead sulfide, this latter will be separated from zinc sulfide, pyrites and other gangue by a conventional froth flotation with a sulfhydric type collector, such as a xanthate, first deactivating and depressing zinc sulfide and pyrites with sodium cyanide, and then recovering by flotation with the sulfhydric collector a lead sulfide concentrate and a deleaded tailing. This tailing is conditioned with copper sulfate to reactivate zinc sulfide which is then floated away with the aid of petroleum nitrogen bases as the collector.

The original lead-zinc sulfide ore pulp is adjusted to the desired pH from about 7.0 to about 11.0. Sodium cyanide is added to depress pyrites and to deactivate zinc sulfide in amounts ranging from 0.1 to 0.5 pounds per ton of ore. If necessary, it may be replaced by calcium cyanide, or potassium cyanide. In many instances, zince sulfate in amounts from 0.1 to 2.0 pounds per ton of ore is added as an aid in deactivating zinc sulfide by virtue of a synergistic common-ion effect. Should the ore be exceptionally clean, particularly when it is free from copper, conditioning with sodium cyanide will become unnecessary. Conventional frothers, such as cresylic acid or pine oil, are also added, if necessary. All of these various reagents are added into a conditioning tank or "conditioner," except for the pH regulator, such as lime or soda ash mentioned hereinbefore, which, in some cases, may be added into the grinding circuit. A sulfhydric type collector, e. g., sodium secondary butyl xanthate or sodium dithiophosphate ("Aerofloat") in conventional amounts, from 0.01 to 0.5 pound per ton of ore is added to the conditioner after other reagents. Conditioning takes from 5 to 30 minutes or more, whereupon the pulp is subjected to flotation. Lead sulfide froth is skimmed off, and the deleaded tailing is treated in a second conditioner to readjust the pH, if necessary, and to reactivate zinc sulfide with copper sulfate as described hereinabove. The pH is adjusted by adding Na_2CO_3 or NaOH, depending on whether the pulp is too alkaline or not. Upon the addition of petroleum nitrogen-base selective collector, and after sufficient conditioning (5–30 minutes or more), zinc sulfide is floated away in the flotation cells, while pyrites and gangue are carried off as tailings.

When handling zinc-bearing ores containing copper sulfide, good recoveries will be obtained by following the general procedure outlined hereinabove for lead-zinc sulfide ores, namely: copper sulfide will be floated away in an alkaline circuit with the aid of well-known collectors of sulfhydric type, after having deactivated and depressed zinc sulfide and pyrites with sodium cyanide and zinc sulfate; thereupon copper sulfate will be added to the copper-free tailing to reactivate zinc sulfide which will then be floated away with the petroleum nitrogen-base collector in accordance with the invention.

However, the preferred procedure in treating a zinc-bearing ore containing copper sulfide is to form an alkaline pulp of a suitable pH (e. g., 7.0 to 11.0), to depress or deactivate zinc sulfide and pyrites with sodium cyanide, with or without an addition of zinc sulfate as may be required by the nature of the ore, and to float the copper sulfide with the aid of petroleum nitrogen bases, preferably in an amount from about 0.01 to about 0.5 pound per ton of the ore. The deactivated zinc sulfide in the copper sulfide tailing is then reactivated with copper sulfate and, upon flotation with petroleum nitrogen bases as indicated hereinbefore, a high grade zinc sulfide concentrate will be separated from the gangue.

Where the ore to be treated contains zinc sulfide, copper sulfide and lead sulfide in amounts which would justify the recovery of each of them, the preferred procedure will be to form an alkaline ore pulp, to condition this pulp by depressing zinc sulfide and pyrites with sodium cyanide and zinc sulfate, as described, and to float away a froth containing lead and copper with the aid of a conventional sulfhydric type collector. The lead-copper sulfide froth may then be treated in any known manner to separate lead from copper, whereas the lead-free and copper-free tailing is conditioned with copper sulfate to reactivate zinc sulfide and to float away the zinc with the aid of nitrogen bases as the selective collector for zinc sulfide in accordance with the invention.

The operation of the process of this invention will be better understood from the following step-by-step description of the recovery of zinc sulfide from a typical lead-zinc marmatitic sulfide ore, as illustrated by the flow diagram of the process in the attached drawing.

In the drawing, the lead-zinc sulfide type ore is fed to the process from mine **1** and is subjected to crushing first in coarse crusher **2**, and then in fine crusher **3**, whence it is dumped into storage bin **4**. From this bin the ore is drawn out to be ground in the presence of water, for instance in a ball mill **5**; in this grinding operation, the ore is reduced to the desired particle size, and converted into an aqueous ore pulp which is sent to classifier **6**; the oversize particles of the ore in the pump are returned from this classifier to ball mill **5**, while the undersize particles proceed to conditioner **10** where they are conditioned prior to the flotation of lead sulfide. The ore pulp is brought to the desired pH, which may be, for instance, from about 7 to about 9.5, by the addition of lime or of soda ash to the circuit, either at conditioner **10** or at ball mill **5**. The pH-regulating reagent precipitates any extraneous iron ions likely to have formed by the oxidation of pyrites, as well as lead and copper ions which would otherwise activate zinc sulfide and cause its floatation simultaneously with galena. To depress pyrites and to deactivate zinc sulfide, sodium cyanide is admitted into the pulp undergoing the conditioning treatment in conditioner **10**. If necessary, zinc sulfate is added into conditioner **10** as an aid in deactivating zinc sulfide, as well as conventional frothers such as cresylic acid or pine oil. A collecting agent of the sulfhydric type, such as sodium or potassium ethyl;

isopropyl or butyl xanthates, or sodium diethyl dithiophosphate (sodium "Aerofloat"), is introduced into conditioner 10 in desired amounts. The action of sulfhydric collector may be augmented by the addition of a small amount of creosote oil. The conditioning treatment occupies from five to thirty minutes or more. After leaving conditioning vessel 10, the ore pulp passes to rougher lead flotation cells 11, where it is agitated and aerated, releasing a froth containing lead sulfide. This froth is then sent to cleaner lead flotation cells 12, while the final lead concentrate from cleaner lead flotation cells 12 is passed through a vacuum filter 13 into a storage bin 14 to await its shipment to the smelter. The presence of the vacuum filter is optional, and it may be omitted. The cleaner tailings from cleaner lead flotation cell 12 may be recirculated either to conditioner 10 or to rougher lead flotation cells 11.

The rougher lead tailings leaving cleaner lead flotation cells 11 enter conditioning vessel 20 where the deleaded ore pulp is conditioned prior to the flotation of zinc sulfide with the aid of petroleum nitrogen bases as the selective collector. The pulp is conditioned for about five to thirty minutes. If lime is present to an excess, soda ash may be added to precipitate lime and to maintain the desired pH. Should the alkalinity be too low as a result of the lead flotation treatment, sodium hydroxide may be used to raise the pH. Reactivation of zinc sulfide is secured by the addition of copper sulfate as herein before described. The conditioning agents, i. e., the pH regulator and the copper sulfate activator, are added together into conditioner 20, simultaneously with or immediately followed by the collecting agent for zinc sulfide.

This agent, in accordance with the invention, is constituted by petroleum nitrogen bases in amounts ranging from 0.01 to 0.5 pound per ton of ore, depending on the zinc content or grade of the ore. Usual frothing agents similar to those used in the lead circuit may also be employed. However, the amount of frother required will be considerably smaller than the amounts commonly used with sulfhydric collectors, since petroleum nitrogen bases are found to be frothing agents per se. From conditioner 20, the ore pulp is passed into rougher zinc flotation cells 21, whence the froth is passed into cleaner zinc flotation cells 22, yielding a final concentrate which, upon filtering through vacuum filter 23, is stored in storage bin 24 to await shipment to the smelter. Filter 23 is optional and may be omitted. The tailing from the rougher zinc flotation cell is withdrawn to the reject pond. The tailing from cleaner zinc flotation cell 22 may be recirculated, either to conditioning vessel 20 or to rougher zinc flotation cells 21.

In the application of selective froth flotation in accordance with the present invention, the employment of petroleum nitrogen bases as the collector for zinc sulfide is found to reduce the requirement for copper sulfate activator of zinc sulfide by as much as two-thirds as compared with the amounts of this activator required when employing sulfhydric collectors for the same purpose.

A particularly important consequence of the application of petroleum nitrogen bases as the collector for the selective froth flotation of zinc sulfide is the superior grade of zinc concentrates obtained thereby, as will be seen from the following examples:

Example I.—This example is a typical case of the selective froth flotation of a marmatitic ore, employing petroleum nitrogen bases as the collector for zinc sulfide in the zinc circuit. The ore pulp fed to the lead circuit contained 7.5 per cent of zinc and 18 per cent of iron as pyrites. After the recovery of lead by flotation with a sulfhydric collector, e. g., a xanthate, the deleaded pulp contained about 22 per cent by weight of solids, and the pH thereof was less than 9.0. Two parallel flotation runs were made with this deleaded pulp—one (B) using petroleum nitrogen bases as the collector for zinc, and the other (A) using sodium secondary butyl xanthate to collect zinc. Other reagents employed in these two runs in addition to the collectors for zinc sulfide were the following:

	Lbs. per ton
Lime, added at the ball mill, to secure alkalinity	1.0
Sodium cyanide, added at the ball mill, to depress zinc sulfide and pyrites in the lead circuit	0.5
Zinc sulfate, added at the ball mill, to depress zinc sulfide	0.5
Copper sulfate to activate zinc sulfide in the deleaded pulp, added into the conditioner in the zinc circuit	1.5
Frother, such as cresylic acid or pine oil, added into the flotation cell, as needed	1.5
Sodium secondary butyl xanthate as the collector for zinc sulfide in Run A	0.12
Petroleum nitrogen bases as the collector for zinc sulfide in Run B (average molecular weight of about 160–165)	0.11

The results of the two runs are presented in Table III.

TABLE III

	Cleaner Concentrate		Rougher Concentrate		Per Cent Recovery Zn	Per Cent Rejection Fe
	Per Cent Zn	Per Cent Fe	Per Cent Zn	Per Cent Fe		
Run A	41.6	17.0	17.5	31.2	84.6	44.9
Run B	52.2	11.7	40.5	14.4	84.0	89.0

These results definitely indicate that the employment of petroleum nitrogen bases as the collector in the flotation of zinc sulfide yields a concentrate of a greatly superior grade as compared with the concentrate obtained with a xanthate-type collector, while the recovery of the zinc mineral is practically the same in both runs.

Example II.—In this series of tests, a marmatitic ore containing lead sulfide, zinc sulfide and pyrites was ground substantially entirely through 65 mesh and diluted with water to 35% solids. The ore pulp was then conditioned with the following reagents added into the conditioner in the order of their tabulation:

	Lbs./ton of ore
Lime	2.0
Sodium cyanide	0.15
Sodium secondary butyl xanthate	0.08
Pine oil	0.5

The conditioning treatment lasted five minutes, and the pH of the ore pulp was brought to 11.0. After recovering the lead concentrate by froth flotation with a xanthate collector, as described hereinbefore in this specification, the lead concentrate was found to be equal to 8.4% of the weight of the original ore feed. It contained 4.45% of

zinc. Two runs, C and D, were then made to recover zinc sulfide from the lead tailing. In run C, soda ash was used to maintain alkalinity, in the amount of 3 pounds per ton of ore. In run D, the same amount of soda ash was used with an addition of lime in the amount of 1 pound per ton of ore. In both runs C and D, 0.8 pounds per ton of copper sulfate was employed to reactivate zinc sulfide. The pH of run C was 10.3, that of run D was 11.3. In run C, 0.2 pounds of petroleum nitrogen bases per ton of ore was used to collect zinc sulfide, while 0.08 pounds of petroleum nitrogen bases per ton of ore was used to collect zinc sulfide in run D. These nitrogen bases had an average molecular weight of about 160–165. The conditioning treatment occupied approximately five minutes. In a comparison mill run E, the following reagents were used: Sodium secondary butyl xanthate as the collector for zinc sulfide in an amount of 0.59 pounds per ton of ore, lime in the amount of 3.7 pounds per ton of ore to secure a pH of 12.0, and copper sulfate in an amount of 1.87 pounds per ton of ore to activate zinc sulfide.

The results of runs C, D and E are given in Table IV, as follows:

TABLE IV

	Run C	Run D	Run E
Weight of Zn in cleaner Zn concentrate in per cent of original feed	24.4	23.4	22.1
Per cent Zn in cleaner Zn concentrate	52.0	53.0	(1)
Per cent Zn in cleaner Zn tailing	4.85	9.4	------
Per cent Zn in rougher Zn tailing	0.77	0.96	0.79
Per cent Zn in original feed	13.7	13.8	12.0
Recovery of Zn in per cent of original feed	93.0	89.7	92.6

[1] About 50.0.

The above data clearly indicate the superiority of petroleum nitrogen bases as the collector for the selective froth flotation of zinc sulfide. The grade of zinc concentrate is noted to reach the values of 52 and 53%, as compared with the grade of about 50% obtained with the xanthate-type collector, while the recovery of zinc is practically the same with either type of collector. Thus, the application of nitrogen bases achieves a substantial improvement of the grade of zinc sulfide concentrates.

Example III.—The high selectivity of petroleum nitrogen bases as the collector for zinc sulfide at a pH of the pulp of less than 8.0 can be seen from the following data obtained from the runs F and G on a rather difficult lead-zinc sulfide ore constituted by a fine-grained intergrowth of galena and marmatite and a pyrrhotite gangue. In this instance, the ore is first ground to a moderately fine grind (about 50% passing through a 200-mesh screen), and as much of the fine lead and zinc-free gangue as possible is eliminated in the first flotation stage. Two 500 g. samples of 10-mesh ore are ground for 10 minutes in a ball mill in the presence of 300 cc. of water, and the resulting pulp conditioned first with 1.0 pounds of $Ca(OH)_2$ and 0.2 pound of NaCN per ton of the ore. It is transferred to a flotation cell where it is further conditioned for 5 minutes with sodium isopropyl xanthate (0.04 pound per ton of ore) and a mixture of 85% coal-tar creosote and 15% cresylic acid (0.09 pound per ton of ore). Upon flotation of the lead froth, in both runs, the pulp is conditioned in the cell with copper sulfate pentahydrate (1.0 pounds per ton of ore) for about 5 minutes. In run F, 0.06 pounds of sodium diethyl dithiophosphate per ton of the ore is used as the collector, supplemented by 0.2 pounds per ton of ore of cresylic acid frother. After conditioning for 3 minutes, the pulp having a pH of 7.4 is passed to the flotation cell and a zinc froth skimmed off. In Run G, in lieu of dithiophosphate, 0.09 pounds of petroleum nitrogen bases per ton of the ore is added as the selective collector (average molecular weight of about 160–165), the cresylic acid frother being unnecessary since petroleum nitrogen bases furnished sufficient froth. The pH of the conditioned pulp is 7.5. The recovery of Zn with the dithiophosphate collector in Run F is equal to 54.0%, the figure obtained with petroleum nitrogen bases in Run G is 55.7%. The zinc concentrate grade obtained with petroleum nitrogen bases is equal to 32% and is strikingly superior to that secured with the dithiophosphate (24.6%), proving the high selectivity of petroleum nitrogen bases. Only 7.4% of the iron is present in the zinc concentrate secured with petroleum nitrogen bases as compared with 12.7% Fe obtained with dithiophosphate.

I have found petroleum nitrogen bases just as selective and more powerful than sodium or potassium ethyl and butyl xanthates when employed as collectors for the froth flotation of zinc sulfide. They are likewise more effective and just as selective as the sodium diethyl dithiophosphate collector employed in the past to separate zinc sulfide from pyrites. Lower-boiling fractions of petroleum nitrogen bases are more selective toward zinc sulfide (and copper sulfide) than the higher boiling fractions but are less powerful collectors than these latter. In actual practice, it is preferred to employ mixtures containing both low and high boiling fractions, i. e., mixtures distilling between about 120° to about 630° F., with 75% coming over at about 510° F., to secure effective collection of zinc values from the ore pulp.

It is to be understood that the invention described hereinabove with reference to petroleum nitrogen bases derived from cracked naphthas is operative with all equivalent petroleum nitrogen bases derived from other fractions of petroleum in the course of refining, e. g., from the so-called SO_2 pearl extract, various gas oil fractions, etc.

In fact, the invention may be successfully practiced by employing other equivalent nitrogen bases of heterocyclic structure as may be obtained, for instance, by shale-oil or coal-tar distillation, by synthesis, and as by-products of various industrial processes.

My new process based on the application of petroleum nitrogen bases as the selective collector for the flotation of zinc sulfide is not limited to the examples or to the flow diagram presented hereinabove. The remarkable results secured by the employment of this collecting agent extend generally to other types of sulfide ores in which zinc sulfide is present. Thus, one practicing the invention may vary the quantities of the various reagents to suit the requirements of each particular case and the nature of each particular ore. The rougher zinc concentrate may be cleaned and recleaned as many times as one may wish. In addition, other collectors, pH regulators, depressors, deactivators, activators, and frothers which will not interfere with the selective action of petroleum nitrogen bases as the selective collector for zinc sulfide may be used in the aforedescribed process without departing from the scope of the present invention, which includes all the modifications and variations of

said process except as limited in the appended claims.

I claim:

1. A process for the recovery of zinc sulfide from a sulfide ore containing zinc sulfide in admixture with pyrites and non-sulfide gangue, which comprises effecting froth flotation of a pulp of said ore in an alkaline circuit having a pH from about 7.0 to about 11.0 in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. to about 630° F. as the selective collector for zinc sulfide, and separating a froth of beneficiated zinc sulfide from a tailing containing pyrites and non-sulfide gangue.

2. A process for the recovery of zinc sulfide from lead-zinc sulfide ore which comprises the steps of forming a pulp of said ore having a pH from about 10.3 to about 11.0; conditioning said pulp to deactivate and to depress zinc sulfide and pyrites therefrom; effecting froth flotation of said pulp in the presence of a sulfhydric collector; collecting a lead sulfide froth and a deleaded tailing; reactivating zinc sulfide in said deleaded tailing with copper sulfate; subjecting said deleaded tailing containing said reactivated zinc sulfide to froth flotation in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° to about 630° F. and being present in an amount from about 0.01 to about 0.5 pound per ton of ore; and recovering a froth containing beneficiated zinc sulfide.

3. A process for the recovery of zinc sulfide from a zinc-copper sulfide ore which comprises the steps of forming an alkaline pulp of said ore; deactivating and depressing zinc sulfide and pyrites therefrom; effecting froth flotation of copper sulfide in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. and about 630° F. as the collector for copper sulfide; reactivating zinc sulfide in the copper-free tailing from said flotation with copper sulfate; effecting froth flotation of said tailing in the presence of a mixture of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. to about 630° F. as the selective collector for zinc sulfide; and recovering a froth containing beneficiated zinc sulfide.

4. A process for the recovery of zinc sulfide from a zinc-copper sulfide ore which comprises the steps of forming an alkaline pulp of said ore; deactivating and depressing zinc sulfide and pyrites therefrom; effecting froth flotation of copper sulfide in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. to about 630° F. as the selective collector for copper sulfide, said nitrogen bases being present in an amount from about 0.01 to about 0.5 lb. per ton of the ore; reactivating zinc sulfide in the copper-free tailing from said flotation with copper sulfate; effecting froth flotation of said tailing in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. to about 630° F., said nitrogen bases being present in an amount from about 0.01 to about 0.5 pounds per ton of the ore; and recovering a froth containing beneficiated zinc sulfide.

5. A process for the recovery of zinc sulfide from a sulfide ore containing zinc sulfide in admixture with iron sulfides and non-sulfide gangue, which comprises effecting froth flotation of a pulp of said ore in an alkaline circuit having a pH from about 7.0 to about 11.0 in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. and about 630° F. as the selective collector for zinc sulfide, and separating a froth of beneficiated zinc sulfide from a tailing containing iron sulfides and non-sulfide gangue.

6. A process for the recovery of zinc sulfide from a sulfide ore containing sphalerite in admixture with iron sulfides and non-sulfide gangue, which comprises effecting froth flotation of a pulp of said ore in an alkaline circuit having a pH from about 7.0 to about 11.0 in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. and about 630° F. as the selective collector for zinc sulfide, and separating a froth of beneficiated sphalerite from a tailing containing iron sulfides and non-sulfide gangue.

7. A process for the recovery of zinc sulfide from a sulfide ore containing sphalerite in admixture with pyrites and non-sulfide gangue, which comprises effecting froth flotation of a pulp of said ore in an alkaline circuit having a pH from about 7.0 to about 11.0 in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. and about 630° F. as the selective collector for zinc sulfide, and separating a froth of beneficiated zinc sulfide from a tailing containing pyrites and non-sulfide gangue.

8. A process for the recovery of zinc sulfide from a marmatitic ore containing zinc sulfide, iron sulfides and non-sulfide gangue, which comprises effecting froth flotation of a pulp of said ore in an alkaline circuit having a pH from about 7.0 to about 11.0 in the presence of petroleum nitrogen bases consisting essentially of a mixture of alkylated heterocyclic nitrogen-bearing compounds boiling between about 120° F. and about 630° F. as the selective collector for zinc sulfide, and recovering a froth of beneficiated zinc sulfide from a tailing containing iron sulfides and non-sulfide gangue.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,302,966	Perkins	May 6, 1919
1,438,436	Frederick	Dec. 12, 1922
1,490,736	Frederick	Apr. 15, 1924
1,590,196	Klees	June 29, 1926
1,610,298	Lewis	Dec. 14, 1926
2,287,274	Ralston et al.	June 23, 1942

OTHER REFERENCES

Mining and Metallurgy, August 1936, pp. 386–389, article by R. A. Pallanch, entitled "Factors Governing the Separation of Lead and Zinc in Ore by Flotation."