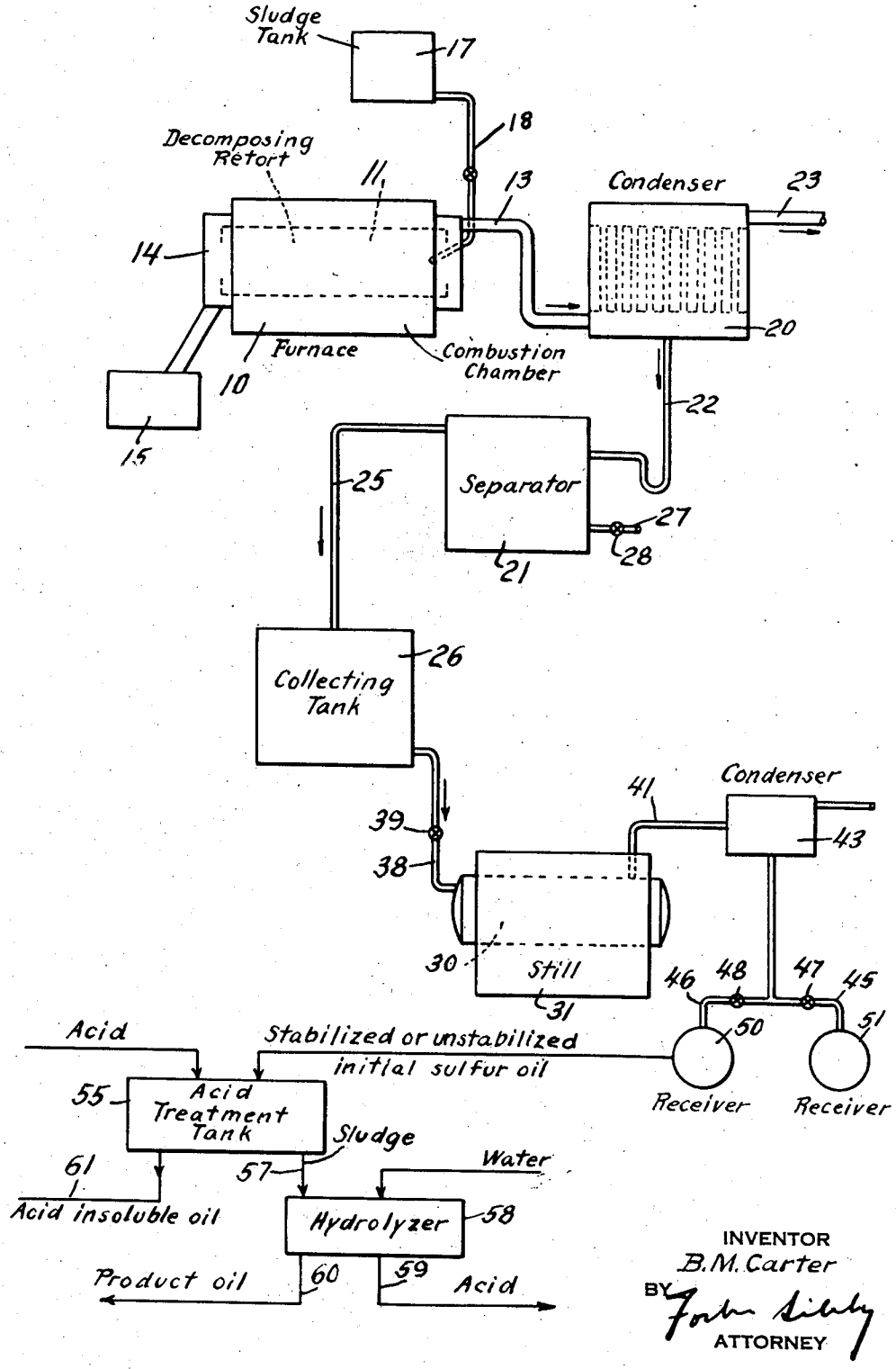
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ORE CONCENTRATION BY FLOTATION

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ORE CONCENTRATION BY FLOTATION

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This invention relates to flotation or mineral collecting agents and to separation of minerals and concentration of ores by flotation processes. The invention is more particularly directed to flotation or mineral collecting agents comprising sulfur bearing oils derived from sludges formed in oil refining processes in which sulfuric acid is employed, and is also particularly directed to processes for separation of minerals and concentration of ores carried out with utilization of such sulfur bearing oils as flotation or mineral collecting agents.

The principal objects of the invention are directed to improvements in separation of minerals and concentration of ores by flotation processes and to provision of markedly effective sulfur bearing oils for this purpose. It is a further aim of the invention to provide relatively concentrated and/or purified sulfur bearing flotation or mineral collecting oils having a high sulfur content substantially all of which sulfur is in chemical combination. It is a furthehr object of the invention to provide sulfur bearing flotation or mineral collecting oils which are stable, and do not deposit sulfur or become less effective on standing.

In oil refining processes, involving treatment of petroleum distillate oils with sulfuric acid, large quantities of sludge are produced. When destructively decomposed by heating, these sludges form gas mixtures containing water vapor and condensable hydrocarbon vapors, and gases such as sulfur dioxide, carbon dioxide, nitrogen and uncondensable hydrocarbons.

When sludge material, resulting from treatment with sulfuric acid of relatively light hydrocarbon oil distillates containing substantial quantities of sulfur compounds, is dissociated preferably by destructive decomposition by heating to form a hot gas mixture containing hydrocarbon vapors and the gas mixture is cooled, for example to about normal temperature, an oily condensate is obtained which is a sulfur bearing oil. A sulfur oil of this type is of such nature that it may be treated, for example with sulfuric acid, in such a way as to effect a selective separation of a large portion of certain sulfur flotation or mineral collecting agent constituents from other sulfur and non-sulfur constituents. In accordance with the present invention it has been found that sulfur bearing oils containing said certain sulfur constituents and resulting from such sulfuric acid treatment possess properties rendering these oils especially suited for use as flotation or mineral collecting agents in the separation of minerals and the concentration of ores by flotation processes. The oils so produced are stable, as a general rule higher in sulfur than the initial oily condensate, and do not deposit free sulfur or become less effective on standing.

A further appreciation of the objects and advantages of the invention may be had from a consideration of the following description of the oils constituting the improved flotation or mineral collecting agents, of flotation processes involving utilization of the improved flotation or mineral collecting agents, and of methods for making the improved flotation or mineral collecting agents. The accompanying drawing illustrated diagrammatically apparatus by which the improved flotation or mineral collecting oils may be made.

Referring to the drawing, 10 indicates the combustion chamber of a furnace adapted to burn coal, coke, oil, natural gas or other fuel. Mounted in chamber 10 is a decomposing kiln or retort 11 of any desirable construction, for example a fixed shell provided with suitable mechanism such as a screw conveyor, not shown, to facilitate discharge of coke. A rotary retort may also be employed if desired. Preferably an externally heated kiln adapted to substantially exclude admission of air is used. One end of kiln 11 communicates with a gas outlet 13, and the opposite end projects into a header 14 into which the solid residue of the decomposition of the acid sludge is continuously discharged. Header 14 empties into air-lock 15 through which coke may be discharged without admitting air to the kiln. Acid sludges, constituting sources of the flotation or mineral collecting oils of the invention, are run into the kiln from supply tank 17 through a valve-controlled pipe 18. Gas outlet 13 is connected to the lower end of a cooler or condenser 20 of any suitable construction, either air or water cooled, and operated so as to reduce the temperature of the gas stream to substantially normal to condense the bulk of the water vapor and a major portion of condensable hydrocarbons contained in the gas. Condensate from the cooler drains into a separator or collecting tank 21 through a pipe 22 having a liquid seal.

The gases uncondensed in cooler 20, containing principally sulfur dioxide, are discharged through gas line 23, and may be used as desired, for example in the manufacture of sulfuric acid by the contact process.

Separator 21 may be a tank or vat large enough to permit continuous gravity separation of water and oil contained in the condensate discharged from condenser 20. The sulfur bearing hydrocarbon oils of the condensate rise to the top of the mass in the separator, and may be withdrawn continuously or intermittently through pipe 25 discharging into a collecting tank 26. Water settling to the bottom of the separator may be drawn off through pipe 27, controlled

by valve 28, and discharged to waste or otherwise disposed of.

The still 30, of any approved construction, may be externally heated by hot combustion gases generated in brickwork setting 31. Raw condensate from collecting tank 26 is run into the still through pipe 38, controlled by valve 39. Vapors generated in the still flow through line 41 to a condenser 43, the condensate of which drains through pipes 45 and 46, into receivers 50 and 51.

The improved flotation oils of the invention may be made in apparatus such as illustrated in the drawing and described above by operating substantially as follows.

In producing the improved flotation or mineral collecting agents, acid sludges which may be employed are those resulting from sulfuric acid treatment of light distillate oils obtained from petroleum crudes containing sulfur. The acid sludges employed in making the flotation or mineral collecting oils of the present invention are preferably sludges resulting from treatment with sulfuric acid of light hydrocarbon oil distillates such as gasolene and kerosene, containing not less than about 0.15% sulfur, although distillates containing less sulfur may be employed if desired. Illustrative examples of distillate oils from which sludges are produced of a character suitable for use in the present invention are straight-run gasolene distillates containing about 0.15% sulfur or more, and cracked distillate averaging 0.25 to 0.30% sulfur or more.

Sludge material of the type indicated and which may have for example a titratable acidity of 40% to 60% expressed as H_2SO_4 is continuously fed into kiln 11 from supply tank 17. The burners in furnace 10 are adjusted to maintain within the kiln temperatures desirably not in excess of about 750° F., as above this temperature the sulfur oils constituting the basis of the flotation or mineral collecting agents of the present invention tend to be decomposed. The preferred temperatures are about 250° F. at the sludge inlet end, and about 500° F. to 600° F. at the coke outlet end of the kiln.

The sludge, gradually passed through the retort, is relatively gradually heated through the preferred temperature range and is decomposed by the action of heat, and the free and/or combined sulfuric acid of the sludge is reduced to sulfur dioxide by the hydrogen of the hydrocarbons and/or by the carbonaceous matter contained in the sludge. The sludge material is thus dissociated, as by the destructive distillation method indicated, with production of water vapor, and hydrocarbon vapors and sulfur compounds are formed. Residual coke is continuously discharged from the kiln through air-lock 15. The major part of the sulfur oils appear to have been evolved by the time the sludge has reached a temperature of 350–400° F.

The gas resulting from the decomposition of the sludge contains principally water vapor and sulfur dioxide, substantial amounts of condensable hydrocarbons and sulfur compounds and smaller quantities of uncondensable hydrocarbons and gases such as carbon dioxide, carbon monoxide, and nitrogen. For example, one representative sludge having a titratable acidity of about 50% expressed as H_2SO_4 yielded on decomposition by destructive distillation about 28% residual coke and a retort gas which, after cooling to about normal temperature, produced about 6% condensable oil, about 35% water, based on the weight of the sludge, the balance of the retort gas comprising sulfur dioxide, carbon dioxide, carbon monoxide, nitrogen and uncondensable hydrocarbons and water vapor. As previously noted, according to the preferred way for making the sulfur bearing oils, decomposition of sludges is effected in the kiln substantially in the absence of oxygen and in the absence of other extraneous gases. When so operating, the volume of gas formed of lessened and loss of sulfur oil by volatilization is decreased.

The hot gaseous and vaporous products of decomposition of the sludge are discharged from the kiln and passed through conduit 13 into condenser 20 in which the gases are cooled to substantially normal temperatures. Cooling may be accomplished by circulating through the condenser in indirect heat exchange relation with the retort gas mixture any suitable cooling liquid or gas. In place of the condenser illustrated in the drawing, a vertical tower having a spray head at the top for introduction of water may be employed. In such cases, the retort gas mixture is introduced into the bottom of the tower and flows upwardly, intimately contacting and mingling with the downwardly directed spray of water fed in at the top of the tower. The amount of cooling water introduced is so controlled as to cool the exit gases leaving the top of the tower to about normal atmospheric temperatures.

During cooling of the retort gas mixture in the condenser 20, substantially all of the water vapor and the major portion of the condensable hydrocarbon vapors and sulfur compounds are condensed out of the gas stream. The condensate of cooler 20, containing varying proportions of water and liquid hydrocarbons and sulfur compounds, is drained through pipe 22 into separator 21. In the latter, the oils rise to the top of the liquid mass in the tank, and may be intermittently or continuously withdrawn through pipe 25 into tank 26 for collecting what may be termed a raw condensate. The water settling to the bottom of the separator 21 may be discharged from the system through pipe 27.

The oil collecting in tank 26 is an oil containing generally from about 3 to about 22% sulfur, apparently in strong chemical combination. It will be understood the sulfur content of this condensate may vary considerably in accordance with the characteristics of the initial crude oils and of the acid sludges produced on treatment of the hydrocarbon oil distillates with sulfuric acid. For example, an acid sludge formed through sulfuric acid treatment of a straight-run gasolene yielded an oil condensate of 12% by volume of the sludge, the condensate analyzing 14.8% sulfur. A cracked distillate sludge yielded 10% by volume of oil condensate having a sulfur content of 7.5%. In another instance, a cracked distillate averaging about .25 to .30% sulfur produced on treatment with sulfuric acid a sludge which, on treatment in accordance with the present method, yielded 10.8% by volume of oil condensate analyzing 20.8% sulfur. For convenience in the following discussion, crude sulfur bearing oils of the kind just described are referred to herein as initial sulfur oils.

Initial sulfur oils of the type described apparently contain sulfur constituents and non-sulfur constituents and are of such nature that they may be treated, for example with sulfuric acid, in such a way as to bring about a selective separation of certain sulfur constituents from other sulfur and non-sulfur constituents. Such

separation treatment in most instances results in production of oils having substantially higher sulfur content than the initial sulfur oils and containing all or almost all of the said certain sulfur constituents of the initial sulfur oils. The high sulfur oils resulting from such treatment for convenience may be termed refined oils, or purified or concentrated or extracted oils. In accordance with the present invention, it has been found that these refined oils, or purified or concentrated or extracted high sulfur oils possess properties making such oils especially suited for use as flotation or mineral collecting agents for the separation of minerals and the concentration of ores by flotation processes.

The separation treatment of an initial sulfur oil to produce a refined oil (one such treatment being hereinafter described in detail) may be applied if desired directly to an initial sulfur oil as recovered in tank **26**. However, the initial oil in this state contains appreciable quantities of foreign matter, such as coke-dust and tars, which under most circumstances may be desirably removed. Separation of foreign matter from the initial oil may be effected by distilling the initial oil producing a coke or asphalt-like still residue and distillate or condensate which may be termed an unstabilized distillate oil. If desired, the separation treatment referred to may be applied to the sulfur bearing oil of tank **26** after removal of the foreign matter such as coke-dust and tars, (as by the distillation operation mentioned) that is, to the unstabilized distillate oil. Further, the initial sulfur oil in tank **26** and unstabilized distillate oil usually contain substances such as mercaptans and pyridines which impart to the oil an undesirable odor and may tend to render the refined product oil unstable. Hence, according to the more satisfactory procedure for making the refined flotation oils of the invention, it is preferred to (1) remove from the initial sulfur oil of tank **26** the foreign matter as coke and tars as by distillation; (2) simultaneously fractionate the initial oil during the distillation operation (since different fractions, e. g. a light fraction or a heavy fraction, may be suited for flotation of different types of ores); (3) stabilize the fractions (to remove mercaptans, pyridines, etc.); and then treat the stabilized oils or if desired the oils in unstabilized condition to produce the refined or purified or concentrated or extracted high sulfur flotation oils.

Removal of foreign matter from the raw condensate of tank **26** and splitting of the condensate into two or more fractions may be done by distillation. For this purpose, oils from tank **26** are run into still **30** through line **38**. The distillation operation may be carried out in any suitable still, preferably one provided with equipment for collecting separate fractions of distillate. It will be understood distillation of the raw condensate is principally for two purposes, first, to remove coke and tars from the oil, and second to produce preferably two fractions, one having a relatively low boiling point range, and another having a higher boiling point range. Distillation may be effected for example by externally heating still **30**. If desired, distillation of the crude condensate may also be accomplished at temperatures lower than those hereinafter mentioned by introducing live steam directly into the oil body while externally heating the same. If desired, distillation may also be effected, though possibly less desirably, by superheated live steam, using steam at slightly above atmospheric pressure and heated to say 225–250° F. before introduction into the oil. Vacuum distillation may be employed if desired.

Still **30** may be operated to produce a first cut including all the oils distilling over at temperatures up to about 350° F. at normal pressure. Vapors generated within this temperature range are liquefied in condenser **43**, and are run into receiver **50**. This relatively low boiling fraction may, for example, constitute approximately 20% by weight of the raw initial sulfur oil condensate fed into still **30**. When removal of these low boiling fractions from the oil in still **30** is substantially complete, the temperature is raised to distill over oils having boiling points ranging from about 350° F. up to about 650° F. Vapors formed are condensed in cooler **43**, and may be recovered in receiver **51**. This high boiling fraction may comprise for example 60–66% by weight of the raw condensate introduced into still **30**. Approximately 10% by weight of the original raw condensate withdrawn from tank **26** may remain as a coke or asphalt residue in the still, and around 5–10% by weight of the original raw condensate may be lost in the distillation operation as uncondensed vapors and gases. The low boiling cut recovered in receiver **50** contains a slightly higher percentage of sulfur than the higher boiling fraction collecting in receiver **51**. If desired, all of the vapors evolved in still **30** may be condensed and collected in a single receiver instead of in two receivers as **50** and **51**. In this situation, while there is some decomposition with liberation of H_2S, the condensate collected corresponds in a general way with the condensate collected in tank **26** except that foreign matter, such as coke-dust and tars, has been removed.

As indicated above, the hereinafter described sulfur constituent separation treatment may be applied directly to the raw condensate collecting in tank **26**, or the fractions collecting in receivers **50** and **51**, or to the condensate collecting in a single receiver used in place of receivers **50** and **51**. The oils, however, apparently contain substances such as pyridines and mercaptans which impart to the oils undesirable odors and which tend to render the oils somewhat unstable on standing. Accordingly, it is preferred to further treat the oils to stabilize the same and remove odors. This may be accomplished by treating the oils with a solution of caustic soda or sulfuric acid or both. When employing caustic alkali, as is preferred, the oil may be agitated with a 20% caustic soda solution at temperatures of about 190° F. until reaction appears complete. The reaction products are allowed to settle, and are withdrawn. The oil may then be washed with water to remove traces of alkali, and brightened as by blowing with air.

The oils may also be stabilized by treating with relatively low concentration sulfuric acid, say about equal volume, separating reaction products, and washing the oils with water and alkali to remove traces of acid. For this stabilization treatment, it is preferred to use acid of concentration not in excess of about 60% H_2SO_4, since acid of this or less concentration, while suitable for removing odor-imparting substances, does not appear to have appreciable effect on the desired sulfur compounds which should be left in the oils at this stage and recovered by the subsequent sulfur constituent separation treatment. If desired, the oils may be stabilized by using acid of greater concentration, say up to about 93.2% H_2SO_4 (66° Bé.) in which case the amount of

stronger acid should not desirably exceed 7% by volume of the oil treated.

Treatment of the oils with either caustic alkali or sulfuric acid notably improves the odor and increases the stability of the oils. In some instances, it is desirable to subject to the oils to treatment with both caustic alkali and sulfuric acid. In this case, after subjecting the oils to the caustic soda treatment noted above, and removing the alkali extract, the oils are washed with water to remove the alkali, and then treated with one or more washes of equal volume of dilute sulfuric acid, for example 30% H_2SO_4. The final oil products may be washed with water to remove traces of acid, and then brightened by blowing with air, or other methods.

In the case where the foreign matter is removed from the condensate of tank **26**, as by distillation and collection of all the distillate in a single receiver, the resulting oil may be stabilized as described.

The oils stabilized, for example as mentioned above, are sulfur bearing mineral oils, light bodied, and have a relatively high sulfur content, substantially all of which is in strong chemical combination. It appears substantial amounts of the contained sulfur is present as alkyl sulfides and possibly also some disulfides and other sulfur bearing compounds. The sulfur content of the oils at this stage may vary from about 3 to about 22%, and on standing the oils do not become turbid or deposit sulfur. The oils are a light straw color. The specific gravity of a representative oil is about 0.98. The viscosity is low, about 32 to 34 Saybolt at 100° F.

The oils in unstabilized and stabilizer condition appear to comprise mixtures of sulfur constituents especially adapted for use as flotation or mineral collecting agents, and other less valuable sulfur and non-sulfur constituents. The ultimate refined oils, used in accordance with the invention as flotation or mineral collecting agents, are obtained by selectively separating the sought for sulfur constituents from other sulfur and non-sulfur constituents. This separation may be effected for example by treatment of unstabilized or stabilized oils with relatively strong sulfuric acid which does not appear to react to any great extent with the non-sulfur constituents but which does appear to have the property of dissolving or combining with the sought for sulfur constituents and forming an acid sludge containing such sulfur constituents. The sought for sulfur constituents may thus be separated from the other sulfur and non-sulfur constituents.

On treatment of raw condensate or any of the fractions mentioned, in stabilized or unstabilized condition, with acid as in tank or vat **55**, there is formed a sludge which contains at least the major portion and in most cases substantially all of the desired sulfur constituents of the oil. A preferred procedure for carrying out the sulfur constituent separation treatment is as follows: The particular oil being handled is treated with sulfuric acid of concentration preferably from about 80% to about 93.2% H_2SO_4 in two equal dumps, each dump of acid representing about 50% by volume of total acid used. The first dump of acid is added with agitation to the initial sulfur oil in tank or vat **55**. If heat of reaction is severe, the reaction mass may be cooled, since the temperature should preferably not exceed about 120° F. The acid is added to the oil gradually say over a period of about 15 minutes or more. The reaction mass is allowed to settle for say 30 minutes or more, after which time the acid sludge formed is withdrawn from tank **55** by gravity through line **57** and fed into hydrolyzer **58**. The acid insoluble oil from the first dump remaining in tank **55** is treated with a second dump of acid (about 50% by volume of the total acid used) in the same manner as with the first dump, allowed to settle, and the acid sludge withdrawn through line **57** and added to the sludge already in hydrolyzer **58** from the first dump. If desired, all of the acid used to treat the oil may be added thereto in one dump, although it is preferred to employ two or more dumps since this procedure brings about more complete extraction of sulfur constituents from the oil. The sludge in hydrolyzer **58** is treated with about twice the volume of water and is hydrolyzed, resulting in breaking up of the sludge and a separation of the sulfur oil constituents extracted out of the stabilized or unstabilized oil from the acid which was used to effect this extraction of sulfur constituents from the stabilized or unstabilized oil. During hydrolysis, the temperature is preferably not permitted to exceed about 130° F. The oil formed on hydrolysis of the sludge is generally lighter than the acid which settles and forms a layer of acid in the bottom of the hydrolyzer. After settling, the acid is drawn off through line **59**, and the oil discharged through pipe **60** is preferably given a light wash for example with caustic alkali, or several washes with water to neutralize traces of acid which may remain in the oil on account of imperfect separation of oil and acid in the hydroylzer. The oil may be brightened by filtering. Oils recovered in this way are the oils referred to herein as the refined oils, or purified or concentrated or extracted oils.

The sulfuric acid used to effect extraction of the sulfur inhibitor constituents should be of strength desirably not less than about 70% H_2SO_4, although it is preferred to use stronger acids. Satisfactory extraction may be obtained by utilizing 93.2% acid (66° Bé.) although indications are that acid of around 85% strength is more selective than the 93.2% acid. The amount of acid used to bring about separation of sought for sulfur constituents from other sulfur and non-sulfur constituents depends upon the amount of sulfur constituents contained in any given oil and the strength of the acid used. Acids of 75–85% strength have less solvent power than stronger acids of the order of 93%. As to the total amount of acid used in the separation operation, it is preferred to employ acid in amount corresponding to not less than about one volume of acid to one volume of refined sulfur oil, since experience indicates about such amount of acid is desired to dissolve or extract the sought for sulfur constituents from the initial stabilized or unstabilized oil. That is, for any given volume of the refined high sulfur oil recovered, preferably not less than about an equal volume of acid was used in one or more dumps to treat the stabilized or unstabilized oil to bring about separation of the sulfur constituents from the non-sulfur constituents. In practice, the amount of acid needed may be determined by taking a sample of the oil and adding thereto successive small amounts of acid until on further addition of sulfuric acid to the sample, further solution or dissolving of the oil ceases.

On hydrolysis of the acid sludges produced by

the sulfuric acid treatment of stabilized or unstabilized oils generally 85–90% as much oil is recovered as was removed from the stabilized or unstabilized oils on treatment with sulfuric acid, and the refined oils recovered on hydrolysis are as a rule considerably higher in sulfur content than the unextracted stabilized or unstabilized oils. For example, on treating a heavy fraction, stabilized by treatment with caustic alkali and weak sulfuric acid and boiling approximately within the range 350–650° F. and containing about 11.6% sulfur, with about twice the volume of 93.2% sulfuric acid (66° Bé.), the sulfur content of the unreacted oil after separation of the acid sludge formed was about 1.9%, and the sulfur content of the refined extracted oil obtained on hydrolysis of the acid sludge was about 19%. In another instance, on treating an unstabilized heavy fraction, boiling approximately within the range 350–650° F. and containing about 2.8% sulfur, with about one volume of 93.2% sulfuric acid, the sulfur content of the unreacted oil after separation of the acid sludge formed was about 0.6%, and the sulfur content of the refined extracted oil obtained on hydrolysis was about 8.9%. On treating an unstabilized light oil fraction, boiling at temperatures less than about 350° F. and containing about 18% sulfur, with about one volume of 93.2% sulfuric acid, the sulfur content of the unreacted oil after separation of the acid sludge formed was about 5.3% and the sulfur content of the refined extracted oil obtained on hydrolysis of the acid sludge was about 23%.

Instead of decomposing the acid sludge by heating as described in connection with the drawing, the original acid sludge may be subjected to hydrolysis as by steaming with live steam, for say an hour, until separation of weak acid (sludge acid) and an upper acid tar layer takes place. The weak acid may be drawn off and the resulting acid tar or sludge material decomposed by heating as in a retort 11. The oily distillate may be taken in two or more cuts if desired, although it is preferred to collect the oily distillate as in a tank 26. During steaming of the acid sludge a light colored distillate may be recovered in a suitable condenser. This distillate and the condensate collected in tank 26 may be separately treated as already described to produce high sulfur refined oils, or may be combined and then so treated.

In accordance with the invention, refined high sulfur oils obtained as described above may be used to marked advantage as flotation or mineral collecting agents for the separation of minerals or the concentration of ores by flotation processes carried out generally in accordance with the known practices.

While the agents of the present invention are effective as flotation or mineral collecting agents in ore concentration, in general they exhibit insufficient frothing qualities and therefore may be employed to best advantage in conjunction with any suitable or well-known frothing agent, e. g. pine oil, cresylic acid, other coal tar acids, terpineol, turpentine, etc.

The process of the present invention can be carried out in any suitable apparatus, for example, those of the pneumatic type such as the McIntosh cell, or those where the air is incorporated with the pulp by agitation such as the Fahrenwald or Denver apparatus, or the like. The flotation agents may be added to the ball or equivalent mill during grinding of the ore, to the conditioner, or to the flotation cell.

It is of advantage in some cases, as with certain copper or lead-zinc ores, to subject the ore pulp to the action of an amount of alkali sufficient to give it an alkaline reaction before subjecting it to flotation with the aid of the flotation agents of the present invention. The alkali may be caustic alkali such as caustic soda, or an alkaline salt such as soda ash, or it may be calcium oxide or hydrate.

In the differential separation of various minerals, such as lead and zinc of a lead-zinc ore, depressants and promoters known in the art such as alkali metal cyanide, zinc sulfate, copper sulfate or other salts may be used to advantage.

Different fractions of the refined high sulfur oils, such as the light and heavy fractions mentioned above may be used to advantage in treatment of different ores.

The amount of flotation or mineral collecting oils required to be used in any given flotation process will vary, depending partly on the character and composition of the ore, partly whether any of the water employed is reused in the process, partly on the character of the sludge material from which the oils are derived, and partly on other conditions encountered in practice.

This invention may be illustrated by the following specific examples:

Example 1

Flotation oil used: Oil A—light fraction, stabilized with 20% NaOH solution and 30% H_2SO_4, 66° Bé. H_2SO_4 treated, and hydrolyzed as described.

Ore used: lead-zinc-iron-sulfide ore containing Pb 1.52%, Zn 11.3%, Fe 4.8%.

Ore initially ground in ball mill with following reagents:

NaCN	0.30# per net ton of ore treated
$ZnSO_4.7H_2O$	1.0#
Na_2CO_3	0.2#
Cresylic acid	0.06#

Ore subjected to preferential flotation in mechanical machines to recover Pb and Zn. The water used in the entire operation, i. e. in grinding and in flotation, was new water, i. e. water that did not contain flotation agents previously used in the flotation process.

Reagents used to float Pb and Zn—

Lead float		*Zinc float*	
Cresylic acid	0.06#	Oil A	0.33#
Oil A	.07#	$CuSO_4.5H_2O$	2.0#
		Na_2CO_3	1.0#
		Pine oil	.04#
Temp	18° C.		18° C.

Rougher cells	Pb	Zn	Fe
	Per cent	*Per cent*	*Per cent*
Heads contained	1.52	11.3	4.8
Pb conc. contained	58.4	3.95	----------
Zn conc. contained	.35	53.0	----------
Tails contained	.1	.95	----------

Overall recovery of total Pb and Zn of initial ore—

Lead—

90.8% in Pb conc.
4.3% in Zn conc.
5.0% in tails

Zinc—

0.8% in Pb conc.
92.5% in Zn conc.
6.5% in tails

Example 2

Flotation oil used: Oil B—heavy fraction, stabilized with 20% NaOH solution and 30% H_2SO_4, 66° Bé. H_2SO_4 treated, and hydrolyzed as described.

Ore used: lead-zinc-iron-sulfide ore containing Pb 1.7%, Zn 11.3%, Fe 5.1%.

Ore initially ground in ball mill with following regents:

NaCN	0.30# per net ton of ore treated
$ZnSO_4.7H_2O$	1.0#
Na_2CO_3	2.0#
Cresylic acid	0.05#

Ore subjected to preferential flotation in mechanical machines to recover Pb and Zn. New water was used in the entire opertion.

Reagents used to float Pb and Zn—

Lead float		*Zinc float*	
Cresylic acid	0.06#	Oil B	0.44#
Oil B	.10#	$CuSO_4.5H_2O$	2.0#
		Na_2CO_3	1.0#
		Pine oil	.04#
Temp	17.5° C.		17.5° C.

Rougher cells	Pb	Zn	Fe
	Per cent	*Per cent*	*Per cen*
Heads contained	1.7	11.3	5.1
Pb conc. contained	52.1	5.35	----------
Zn conc. contained	0.2	51.5	----------
Tails contained	0.10	0.45	----------

Overall recovery of total Pb and Zn of initial ore—

Lead—
93.0% in Pb conc.
2.5% in Zn conc.
4.5% in tails

Zinc—
1.4% in Pb conc.
95.7% in Zn conc.
3.0% in tails

Example 3

Flotation oil used: Oil C—combined condensate collected in a single receiver used in place of receivers 50 and 51, 66° Bé. H_2SO_4 treated and hydrolyzed as described.

Ore used: lead-zinc-iron-sulfide ore containing Pb 3.9%, Zn 8.85%, Fe 3.98%.

Ore subjected to preferential flotation in mechanical machines to recover Pb and Zn. New water was used in the entire operation.

Reagents used (in pounds per net ton of ore treated) to float Pb and Zn—

Lead float		*Zinc float*	
NaCN	0.4#	Oil C	0.198#
Cresylic acid	0.10#	$CuSO_4.5H_2O$	3.0#
Na_2CO_3	1.00#	Na_2CO_3	3.0#
Oil C	0.11#		
$ZnSO_4.7H_2O$	1.5#	Pine oil	0.04#
pH	9.1	9.3	
Temp	19° C.	19° C.	

Rougher cells	Pb	Zn	Fe
	Per cent	*Per cent*	*Per cent*
Heads contained	3.9	8.85	3.98
Pb conc. contained	64.5	5.0	----------
Zn conc. contained	0.90	51.0	----------
Tails contained	0.03	0.40	----------

Recovery of 95.7% of total lead in lead concentrates.

Recovery of 93.4% of total zinc in zinc concentrates.

I claim:

1. The improvement in the concentration of minerals by flotation which comprises subjecting mineral in the form of a pulp to a froth flotation operation in the presence of a relatively light-bodied, light-colored, low viscosity sulfur oil boiling at temperatures less than about 650° F., stable with respect to sulfur deposition, substantially free of free sulfur, containing alkyl sulfides, having a sulfur content not less than about 3% and formed by dissociating sludge material, resulting from sulfuric acid treatment of hydrocarbon oils obtained from sulfur containing crudes, with aid of heat at temperatures not more than about 750° F. to break up the sludge under conditions to form a hot gas mixture containing water and sulfur bearing oil vapors, cooling the mixture to form a condensate comprising water and oil, separating water from oil, treating the oil with sulfuric acid of concentration not less than about 70% H_2SO_4 and in quantity sufficient to effect extraction of sulfur bearing oil constituents from said oil, separating the resulting sludge reaction product from said oil, subjecting said resulting sludge to hydrolysis to separate sulfur oil and acid, and recovering sulfur oil from the reaction product resulting from said hydrolysis.

2. The improvement in the concentration of minerals by flotation which comprises subjecting mineral in the form of a pulp to a froth flotation operation in the presence of a relatively light-bodied, light-colored, low viscosity sulfur oil boiling at temperatures less than about 650° F., stable with respect to sulfur deposition, substantially free of free sulfur, containing alkyl sulfides, having a sulfur content not less than about 3% and formed by dissociating sludge material, resulting from sulfuric acid treatment of hydrocarbon oils obtained from sulfur containing crudes, with aid of heat at temperatures not more than about 750° F. to break up the sludge under conditions to form a hot gas mixture containing water and sulfur bearing oil vapors, cooling the mixture to form a condensate comprising water and oil, separating water from oil, distilling the oil, recovering as condensate oil boiling at temperatures less than about 650° F., treating the oil with sulfuric acid of concentration not less than about 70% H_2SO_4 and in quantity sufficient to effect extraction of sulfur bearing oil constituents from said oil, separating the resulting sludge reaction product from said oil, subjecting said resulting sludge to hydrolysis to separate sulfur oil and acid, and recovering sulfur oil from the reaction product resulting from said hydrolysis.

3. The improvement in the concentration of minerals by flotation which comprises subjecting mineral in the form of a pulp to a froth flotation operation in the presence of a relatively light-bodied, light-colored, low viscosity sulfur oil boiling at temperatures less than about 650° F., stable with respect to sulfur deposition, substantially free of free sulfur, containing alkyl sulfides, having a sulfur content not less than about 3% and formed by dissociating sludge material, resulting from sulfuric acid treatment of hydrocarbon oils obtained from sulfur containing crudes, with aid of heat at temperatures not more than about 750° F. to break up the sludge under conditions to form a hot gas mixture containing water and sulfur bearing oil vapors, cooling the mixture to form a condensate comprising water and oil, separating water from oil, distilling the oil, re-

covering as condensate oil boiling at temperatures less than about 650° F., stabilizing the oil, treating the oil with sulfuric acid of concentration not less than about 70% H_2SO_4 and in quantity sufficient to effect extraction of sulfur bearing oil constituents from said oil, separating the resulting sludge reaction product from said oil, subjecting said resulting sludge to hydrolysis to separate sulfur oil and acid, and recovering sulfur oil from the reaction product resulting from said hydrolysis.

4. The improvement in the concentration of minerals by flotation which comprises subjecting mineral in the form of a pulp to a froth flotation operation in the presence of a relatively light-bodied, light-colored, low viscosity sulfur oil boiling at temperatures less than about 650° F., stable with respect to sulfur deposition, substantially free of free sulfur, containing alkyl sulfides, having a sulfur content not less than about 3% and formed by dissociating sludge material, resulting from sulfuric acid treatment of hydrocarbon distillate oils containing not less than about 0.15% sulfur, with aid of heat at temperatures not more than about 750° F. to break up the sludge under conditions to form a hot gas mixture containing water and sulfur bearing oil vapors, cooling the mixture to form a condensate comprising water and oil, separating water from oil, treating the oil with sulfuric acid of concentration not less than about 70% H_2SO_4 and in quantity sufficient to effect extraction of sulfur bearing oil constituents from said oil, separating the resulting sludge reaction product from said oil, subjecting said resulting sludge to hydrolysis to separate sulfur oil and acid, and recovering sulfur oil from the reaction product resulting from said hydrolysis.

5. The improvement in the concentration of minerals by flotation which comprises subjecting mineral in the form of a pulp to a froth flotation operation in the presence of a relatively light-bodied, light-colored, low viscosity sulfur oil boiling at temperatures not more than about 350° F., stable with respect to sulfur deposition, substantially free of free sulfur, containing alkyl sulfides, having a sulfur content not less than about 3% and formed by dissociating sludge material, resulting from sulfuric acid treatment of hydrocarbon distillate oils obtained from sulfur containing crudes, with aid of heat at temperatures not more than about 750° F. to break up the sludge under conditions to form a hot gas mixture containing water and sulfur bearing oil vapors, cooling the mixture to form a condensate comprising water and oil, separating water from oil, distilling the oil, and recovering as condensate a fraction boiling at temperatures not more than about 350° F., treating the fraction with sulfuric acid of concentration not less than about 70% H_2SO_4 and in quantity sufficient to effect extraction of sulfur bearing oil constituents from said fraction, separating the resulting sludge reaction product from said fraction, subjecting said resulting sludge to hydrolysis to separate sulfur oil and acid, and recovering sulfur oil from the reaction product resulting from said hydrolysis.

6. The improvement in the concentration of minerals by flotation which comprises subjecting mineral in the form of a pulp to a froth flotation operation in the presence of a relatively light-bodied, light-colored, low viscosity sulfur oil boiling substantially within the range 350° F. to 650° F., stable with respect to sulfur deposition, substantially free of free sulfur, containing alkyl sulfides, having a sulfur content not less than about 3% and formed by dissociating sludge material, resulting from sulfuric acid treatment of hydrocarbon distillate oils obtained from sulfur containing crudes, with aid of heat at temperatures not more than about 750° F. to break up the sludge under conditions to form a hot gas mixture containing water and sulfur bearing oil vapors, cooling the mixture to form a condensate comprising water and oil, separating water from oil, distilling the oil, recovering as condensate a fraction boiling substantially within the range 350° F. to 650° F., treating the fraction with sulfuric acid of concentration not less than about 70% H_2SO_4 and in quantity sufficient to effect extraction of sulfur bearing oil constituents from said fraction, separating the resulting sludge reaction product from said fraction, subjecting said resulting sludge to hydrolysis to separate sulfur oil and acid, and recovering sulfur oil from the reaction product resulting from said hydrolysis.

BERNARD M. CARTER.