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PROCESS FOR WASHING AND REMOVING ORGANIC HEAVY LIQUIDS FROM MINERAL PARTICLES

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This invention relates to separation of minerals or ores of different specific gravities in a heavy organic liquid medium and, more particularly, to recovery of the heavy organic liquid from the mineral grains after separation.

Heavy liquid separation of minerals with organic liquids has been used in the laboratory for many years. See, for example, Patent 2,193,957. However, the sink-float process using the heavy liquids has never been used commercially for any extended period of time. The use of a heavy liquid, such as an organic liquid, that has uniform chemical and physical properties offers the best method for gravity separation of fine particles of relatively close specific gravity. Furthermore, the sink and float products are not contaminated with entrapped heavy media particles as is often the case when using heavy media suspensions of ferrosilicon, magnetite, barite and the like. The primary reasons for not using heavy organic liquids commercially are that they are expensive and no simple, effective, rapid or cheap method for their recovery from mineral particles has yet been developed. The cost of recovering heavy liquid quite often is higher than the value of the material being separated. Thus, commercial adoption of the heavy liquid sink-float processes is dependent on development of methods that achieve an

Various methods have previously been employed for recovering heavy organic liquids from mineral particles, e.g., Patents 994,950 and 1,244,885 disclose the use of volatile solvents for removing the heavy liquid. However, these methods have not proved entirely satisfactory since the volatile solvents are expensive, difficult and often dangerous to use and separation of the heavy liquid from the voltatile solvent is difficult, usually requiring distillation.

It is therefore an object of the present invention to provide a simple and inexpensive method for the substantially complete removal and recovery of heavy organic liquid adhering to mineral or ore grains following separation of the minerals by gravity (sink-float) separation.

Another object of the invention is to provide a mineral product, from a gravity separation process, that is substantially free of heavy organic liquid.

A further object is to provide a method for separation of the heavy organic liquid from wash solutions to recover a substantially dry heavy liquid for reuse in gravity separations.

It has now been found that the above objects may be accomplished by means of a process in which the heavy liquid is separated from the mineral or ore grains by treatment with a water solution of a detergent or by treatment with steam, either alone or in combination with a detergent.

The heavy liquids most commonly used for gravity separation of minerals are halogenated hydrocarbons having a specific gravity range of about 1.2 to about 3.3. Acetylene tetrabromide (tetrabromethane), which has a specific gravity of nearly 3 and is readily available, is most often used and was employed in the specific examples below. This liquid also is easy to handle and may

be readily purified. However, the process of the invention is not limited to this specific heavy liquid but is also effective with other heavy liquids that are suitable for gravity separation, e.g., carbon tetrachloride, methylene iodide, etc.

The invention is applicable to a wide variety and type of minerals or mixtures of minerals regardless of their surface shape. The particle size of the minerals is also not critical, although they are usually ground to relatively fine particle size prior to separation. The actual gravity separation process is, however, conventional and is not the essence of the present invention.

According to one embodiment of the invention the mineral grains, following gravity separation, having heavy liquid entrapped by, adhering to or adsorbed on the surface are treated with or without agitation with water and a detergent such as sodium cetyl sulfate, magnesium lauryl sulfate, sodium lauryl sulfate or other alkyl or aryl sulfates, various simple and complex alkyl or aryl sulfonates or alkali soaps such as sodium, potassium or lithium oleates, etc. The mineral grains are then filtered on a filter or fine mesh screen, followed by washing by displacement using more water and detergent to remove substantially all the heavy liquid. Although hot water (65° C. or higher) is generally preferred and is used in the examples below, water of any temperature down to freezing is effective for removing the heavy liquid.

Filtration of the mineral grains yields a filtrate that ordinarily consists of three phases: (1) water containing detergent; (2) emulsion of heavy liquid, water and detergent and (3) heavy liquid. The relative amounts of these three phases may vary considerably depending on the type and amount of mineral or ore, the type of heavy liquid employed, amounts of water and detergent, etc. The heavy liquid phase is readily separated by conventional techniques and may be reused in a gravity separation process. The water-detergent phase may also be recirculated and used again in the separation process.

The emulsion of heavy liquid, water and detergent is relatively stable but may be readily broken by batch centrifuging or passing through a small continuous centrifuge. The heavy liquid is thereby recovered substantially free of water and the water-detergent phase is substantially free of heavy liquid.

In a second embodiment of the invention the heavy liquid is separated from the mineral grains by steaming at atmospheric or elevated pressure. This procedure may also be modified by the use of detergents, as described above, in conjunction with the steam treatment. Subsequent separation of the heavy liquid is similar to that described above.

The quantities of water, steam and detergents and temperature used in the practice of the invention are subject to considerable variation and optimum quantities are best determined experimentally for any particular type or amount of ore or mineral treated. Purity and yield are reliable guides for reagent adjustment.

The exact procedure and apparatus used in the practice of the invention is also not critical as many variations will be obvious to those skilled in the art. For example, washing by multiple-stage repulping accompanied by several filtration steps, or in conjunction with countercurrent decantation may be used.

The invention will be further illustrated, but is not intended to be limited, by the following examples.

Example 1

Samples of various types of minerals were selected for experimentation in removing heavy organic liquid from mineral grains. These included nonporous (quartz), porous (limonite), bladed (kyanite), and platy (mica) minerals. The detergent employed in this example was

the commercial product "Tide," which is primarily a sodium salt of a sulfonated alkyl of 10 to 18 carbon atoms and a sodium salt of tetraphosphoric acid.

In carrying out the process for removing the heavy organic liquid according to this invention, the different minerals were first ground and screen sized. The size of mineral selected for the testwork was minus 48 plus 200 mesh. A 125-gram sample of the mineral was mixed with 200 grams of acetylene tetrabromide (specific gravity 2.95) and allowed to soak for periods of 1 to 24 hours to insure that the mineral particles were thoroughly saturated with the heavy liquid. The mixture of mineral and acetylene tetrabromide then was transferred to a small vacuum filter to remove most of the free heavy liquid from the solids. After filtration, approximately 12 to 16 percent of the total heavy liquid remained on the mineral surfaces. The mineral sample with the residual heavy liquid was then transferred to a small mechanical conditioner of standard design, and sufficient hot water (65° C.) added to give a pulp containing about 20 percent solids. The pulp was conditioned for 10 minutes with the equivalent of 40 pounds of detergent per ton of mineral, after which the pulp was screened on a 200-mesh screen to remove the water, detergent and acetylene tetrabromide from the mineral particles. The mineral sample then was repulped for 10 minutes in the mechanical conditioner at about 20 percent solids with hot water (65° C.) containing the equivalent of 40 pounds of detergent per ton of mineral. The pulp was screened a second time on the 200-mesh screen to remove separate phases of water containing detergent, acetylene tetrabromide, and an emulsion of acetylene tetrabromide, water and detergent. The water-detergent phase was low in acetylene tetrabromide, and the acetylene tetrabromide phase was substantially free of water and could be used for making additional sink and float separations. The emulsion of acetylene tetrabromide, water and detergent, however, required further treatment to separate and recover the acetylene tetrabromide. This was easily accomplished by passing the emulsion through a small continuous centrifuge. The acetylene tetrabromide recovered was substantially free of water, and the water-detergent phase was essentially free of acetylene tetrabromide.

A high recovery of the heavy liquid was obtained from the different mineral charges as shown in the following typical tests:

TABLE I

Type of mineral	Residual heavy liquid after filtration, lbs. per ton of mineral	Residual heavy liquid lost after application of detergent washing procedure, lbs. per ton of mineral	Residual heavy liquid recovered, percent
Nonporous (quartz)	240	0.2	99.9
Platy (mica)	250	0.2	99.9
Bladed (kyanite)	240	0.2	99.9
Porous (limonite)	320	10.0	96.9

Example 2

Samples of the various types of minerals (nonporous, porous, bladed and platy) were prepared by grinding, screening, mixing with heavy liquid and filtering using the procedure described in Example 1. The mineral samples with adhering and absorbed residual heavy liquid then were transferred to a small pressure filter in which steam under 10 pounds per square inch gauge pressure was passed through the mineral particle beds for 15 minutes. No detergent was used in these tests. Heavy liquid adhering to the washed mineral particles after steaming ranged from 1.2 pounds per ton on the bladed minerals to 9.6 pounds per ton on the porous minerals. The high recovery of heavy liquid demonstrated the ability to recover organic heavy liquids from mineral surfaces by steaming.

The results of typical tests made using the procedure are as follows:

TABLE II

Type of mineral	Residual heavy liquid after filtration, lbs. per ton of mineral	Residual heavy liquid lost after steaming procedure, lbs. per ton of mineral	Residual heavy liquid recovered, percent
Nonporous (quartz)	240	1.6	99.3
Platy (mica)	250	1.4	99.4
Bladed (kyanite)	240	1.2	99.5
Porous (limonite)	320	9.6	97.0

Example 3

Samples of the various types of minerals (nonporous, porous, bladed and platy) were prepared by grinding, screening, mixing with heavy liquid and filtering using the procedure outlined in Example 1. The mineral samples with the residual heavy liquid then were transferred to a small pressure filter where steam at 10 pounds per square inch gage pressure was passed through the bed of mineral particles for 15 minutes. During the time that the mineral samples were being steamed, detergent was fed into the pressure filter at the rate of 80 to 160 pounds per ton of mineral. The types of detergents used included magnesium lauryl sulfate, sodium lauryl sulfate, sodium cetyl sulfate, alkyl benzene sulfonate and other similar types of alkyl sulfates and sulfonates, and well-known commercial detergents with trade names such as "Tide" and "Dreft." Three liquid phases were obtained as in Example 1, and the emulsion phase was passed through a small centrifuge to recover dry, high specific gravity acetylene tetrabromide and water containing the detergent. The water-detergent solution and dry acetylene tetrabromide were reused in other testwork. The heavy liquid losses ranged from 0.5 pound per ton on the nonporous and platy minerals to 6.2 pounds per ton on the porous minerals. The use of detergent in conjunction with steaming yielded a higher recovery of the heavy liquid than when using steam alone.

The results of typical tests were as follows:

TABLE III

Type of mineral	Residual heavy liquid after filtration, lbs. per ton of mineral	Residual heavy liquid lost after application of steam-detergent washing procedure, lbs. per ton of mineral	Residual heavy liquid recovered, percent
Nonporous (quartz)	240	0.5	99.8
Platy (mica)	250	0.5	99.8
Bladed (kyanite)	240	0.6	99.7
Porous (limonite)	320	6.2	98.1

Example 4

Recovery of the heavy organic liquid by hot water, steam and/or detergent washing results in the formation of an emulsion consisting of acetylene tetrabromide and detergent dispersed in water. The emulsion is stable and will not break even on prolonged standing. The emulsion can be readily separated by passing through a small centrifuge, for example, a Sharples Laboratory Supercentrifuge, to recover a dry acetylene tetrabromide fraction of specific gravity 2.94 to 2.95, and a solution or colloidal suspension of detergent in water substantially free of acetylene tetrabromide. The acetylene tetrabromide is of suitable specific gravity and dryness for reuse without further treatment, and the water-detergent solution or colloidal suspension may be reused for washing more acetylene tetrabromide from minerals. A description of a laboratory centrifuge of the type used may be found in

Catalog 1269, published by the Sharples Corporation, Philadelphia, Pa. The results of a typical centrifugation test of an acetylene tetrabromide emulsion is given below.

TABLE IV

Product	Weight, percent	Solution analysis, percent acetylene tetrabromide	Distribution, percent acetylene tetrabromide
Emulsion before centrifugation	100.0	6.409	----------
Water and detergent phase after centrifugation	93.6	0.010	0.1
Acetylene tetrabromide phase after centrifugation	6.4	100.000	99.9

What is claimed is:

1. In a process for gravity separation of minerals by means of a heavy organic liquid, the improvement which

comprises removal of the heavy liquid from the separated mineral particles by treatment of the mineral particles with steam alone.

2. Process of claim 1 in which the heavy liquid is acetylene tetrabromide.

3. Process of claim 1 in which the mineral is selected from the group consisting of quartz, mica, kyanite and limonite.

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