(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 030 802**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 80304174.8

(22) Date of filing: 20.11.80

(51) Int. Cl.^{3}: **B 03 B 1/04**
B 07 C 5/342, B 07 C 5/344
B 07 C 5/346, B 03 B 13/02

(30) Priority: 05.12.79 US 100618
31.12.79 US 108611

(43) Date of publication of application:
24.06.81 Bulletin 81/25

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: **OCCIDENTAL RESEARCH CORPORATION**
2100 S.E. Main Street
Irvine, California 92714(US)

(72) Inventor: **DiGiacomo, Peter Michael**
27671 Estepona
Mission Viejo California 92691(US)

(72) Inventor: **White, William R.**
27502 Del Gado, 3
Capistrano Beach California 92624(US)

(72) Inventor: **McKinley, John Richard**
4 Calhoun
Irvine California 92714(US)

(72) Inventor: **Park, Won Choon**
4052 Old Mill Street
Irvine California 92714(US)

(74) Representative: **Jack, Bruce James et al,**
FORRESTER & BOEHMERT Widenmayerstrasse 5/IV
D-8000 Munchen 22(DE)

(54) Sorting particles.

(57) A process for separating one type of particle (e.g., ore particles) from a second type of particle (e.g., gangue particles) comprising the steps of (1) conditioning the particles to selectively mark one type of particle (i.e. either the ore particles or the gangue particles), to the substantial exclusion of the other; (2) detecting the marked particles; and (3) separating the detected marked particles from the substantially unmarked particles is characterised by the use, as a conditioning agent, of a compound having both a surface-selective functional group and a detectable moiety. In one embodiment, the detectable moiety is fluorescent and detecting is performed under ultraviolet radiation. The process is especially useful for separating higher grade limestone from lower grade limestone and/or gangue or for separating oil shale or coal of high heat value from lower heat content materials or for concentrating valuable minerals, such as silver or copper ores.

Croydon Printing Company Ltd

SORTING PARTICLES

THIS INVENTION relates to sorting particles in accordance with their respective properties and is particularly well suited for use with a mechanical apparatus for sorting ore particles. Thus the invention specifically relates to a process for separating a first type of particle from a second type of particle and comprising the steps of conditioning the particles with a conditioning agent selectively to mark either at least a portion of the first type of particle or at least a portion of the second type of particle to the substantial exclusion of the other; detecting the marked particles; and separating the detected, marked particles from the substantially unmarked particles.

U.S. Patent 3,356,211 (Mathews) describes a method for concentrating ore which involves preferentially coating the desired particles with a liquid fluorescent material, subjecting the ore to electromagnetic radiation so that at least the coated portion will fluoresce, and sensing the characteristic fluorescent wavelength emitted by the irradiated particles.

U.S. Patent 3,472,375 (Mathews) describes an apparatus which senses the emitted fluorescent radiation from gangue or ore particles, especially coated particles, and separates by selectively directing streams of a fluid to cause those fluorescent particles to be removed from the remaining quantity of undesired ore.

U.S. Patents 3,795,310 and 3,901,793 (Buchot et al.) disclose a process and apparatus similar to those in the said patents of Mathews. Successful operation of a mechanical sorting device such as that of Mathews or

Buchot is dependent upon the ability to selectively coat (or otherwise mark) either gangue or ore particles which contain a particular mineral component, while not coating (or marking) the other particles to a significant extent. The surface chemical properties of a specific ore or gangue particle depend upon the minerals which are present in that particle and, since the composition of individual particles can show a wide variation, the surface chemical properties of the particles will also vary.

To utilize a difference in surface chemical properties in the separation of ore particles, it is necessary to contact the mixture of particles with a surface-selective agent which will selectively react with certain mineral species present in the particles, due to the selectivity of the reagent in distinguishing between surface chemical properties. The reaction may be chemical, physical or a combination of those types. This process is referred to herein as "conditioning".

Methods of particle separation in which it is necessary to condition the particles include flotation separation and optical separation. In flotation separation, the particles to be separated are conditioned with a flotation agent, which coats the ore particles with which it is reactive and creates a hydrophobic mineral surface. When air bubbles are attached to this hydrophobic surface, the coated particles can be floated away from uncoated particles.

For an optical separation, the mixture of particles can be conditioned with a suitable surface-selective reagent and either a coloring agent or a fluorescent material, depending upon the nature of the separation process.

The procedure for applying a coating to ore particles for an optical separation usually involves application of the fluorescent or coloring agent in one of three forms: precipitated in an aqueous or non-aqueous slurry;

dissolved in an organic conditioning reagent (which may be then dispersed in an aqueous medium prior to application); or direct application of the agent (either alone, in solution, or dispersed in an aqueous medium) after a conditioning reagent has been applied to the particles.

U.S. Patent 3,346,111 (Thompson et al.) describes a method for rendering asbestos contained in a host rock differentially fluorescent in relation to the rock. A fluorescent dye is precipitated to form a gelatinous slurry, into which the asbestos-containing particles are dipped. Some quantity of the suspension is entrained in exposed asbestos fibers, giving those particles which contain more asbestos a higher fluorescense than the particles with less asbestos.

International Patent Application No. PCT/US79/00246 published as International Publication No.W079/00950 describes various methods for selectively coating limestone particles, or gangue particles which do not contain major amounts of limestone, with a fluorescent dye. For selectively coating limestone, a carboxylic acid such as oleic acid or caprylic acid is used as the coupling agent. If it is desirable to coat the siliceous gangue particles, an aliphatic amine is used as the coupling agent. The application contemplates either combining a fluorescent dye with the coupling agent prior to conditioning the ore particles or applying a fluorescent dye to the conditioned particles. However, the preferred method is to physically combine the coupling agent and fluorescent dye (e.g. by dissolving the dye in tall oil) prior to conditioning, both to realize a lower dye consumption and to simplify the process.

Examples of processes for the separation of oil shale particles may be found in U.S. Patent 4,169,045. An example of a process for the separation of coal particles is U.S. Patent 4,208,273.

The above-mentioned U.S. Patent 3,901,793 (Buchot et al.) describes a three-step process for applying a fluorescent coating to mineral particles, involving a preconditioning by washing with water plus a wetting and a scouring agent, treating with a collector ("second conditioning"), and finally applying the fluorescent reagent.

The selection of conditioning agents and coloring or fluorescing agents is of utmost importance in developing a sorting process for a particular ore, utilizing one of the previously described systems.

Excluding the disclosure of U.S. Patent 3,346,111, previously noted, which is a purely mechanical entrainment of fluorescent dye suspension by asbestos fibers, the foregoing references show the use of mixtures of coupling agents (which selectively bond to the desired ore particles) with fluorescent or coloring agents or the sequential application of a coupling agent and a mutually compatible fluorescent or coloring agent. When mixtures are contemplated, they comprise either solutions or dispersions (including emulsions) of coupling agent and fluorescent or coloring agent in an aqueous or organic carrier, depending upon the nature of the components.

Ordinarily, the coupling agent and the fluorescent or coloring agent are both insoluble in water so that subsequent steps, such as rinsing to remove the weakly adhering coating from undesired ore particles, will not greatly remove the coating from desired particles. The control of rinsing or washing conditions can significantly improve the selectivity of a separation. However, if it is desired to provide a dye to particles which are selectively non-coated with the coupling agent to the substantial exclusion of the coated particles, a water-insoluble coupling agent and a water-soluble dye, or a water-soluble coupling agent and a water-insoluble dye can be used.

Such contact between aqueous media and water-insoluble materials can result in the unwanted formation of emulsions. Emulsions which form can be particularly difficult to remove, since the fine ore particles which are produced during crushing to the desired size range cannot always be completely removed by pre-washing, and these particles are incorporated into the emulsions, thereby increasing the emulsion stability. This has the effect of causing difficulties in the handling of process streams and preventing the recycling of materials in the process.

U.S. Patent 2,560,425 (Fancher) describes the preparation of the choleretics having the formula Ar-CO-$(CH_2)_n$ COOH, in which Ar is either fluoranthyl or tetrahydrofluoranthyl, and n is 2 or 3. U.S. Patent 2,773,091 (Burtner) relates to similar derivatives of fluoranthene in which the $(CH_2)_n$ function is expanded to include bivalent, aliphatic hydrocarbon radicals containing up to 8 carbon atoms.

The patents of Fancher and Burtner are examples of fluorescent molecules (fluoranthene and tetrahydrofluoranthene) which have been provided with specific functional groups (carboxy and oxocarboxy). Such compounds, and the processes for their preparation, can be useful in the practice of the present invention.

The invention provides a process for separating a first type of particle (e.g. ore particles) from a second type of particle (e.g. gangue particles), comprising the steps of conditioning the particles with a conditioning agent selectively to mark (e.g. coat) either at least a portion of the first type of particle or at least a portion of the second type of particle to the substantial exclusion of the other; detecting the marked particles; and separating the detected, marked particles from the substantially unmarked particles, the process being characterised in that the conditioning agent comprises a compound having both a surface-selective functional group and a detectable moiety.

In preferred embodiments the detectable moiety of the conditioning agent is a fluorescent moiety.

The term "substantially non-fluorescing" as used herein means that at a particular wavelength or waveband there is a sufficiently lower degree of fluorescence (e.g. intensity of radiation or luminous flux) from a given particle to enable separation of said particle from particles having a higher degree of fluorescence at said wavelength or waveband.

When the process is applied to the separation of higher grade ore particles from lower grade ore particles, the fraction of particles which is selectively marked can be either the higher grade material or the lower grade material, as determined by the choice of conditioning agent.

Instead of fluorescence, other detectable properties may be imparted to the marked particles, including radioactivity, visible color, or the ability to exhibit characteristic properties upon stimulation by external electromagnetic radiation, subatomic particles or chemical reactions, by choice of a detectable moiety having the desired property.

As used herein the term "particle" includes any solid object of a size which can be separated by manpower or by machine from other similarly sized objects. This process includes separating relatively higher grade ore particles from relatively lower grade ore particles (wherein the relatively lower grade particles are considered as "gangue").

The term "substantial exclusion", as used herein, means a sufficient difference in the degree or nature of the marking (e.g. coating) on the relative types of particle (e.g. ore or gangue) to enable a difference in detection, either visually or by a detection device (e.g. photomultiplier, Geiger-counter etc.), of the detectable moiety sufficient to be useful in separating the types of marked particle.

The word "intensity", as used herein includes not only the scientific meaning of magnitude per unit (e.g. area) but also the broader concept of degree of strength of a property (such as photon emission) including detection of luminous flux.

The present invention includes separation of a mixture of particles (especially ore particles) containing differing surface concentrations of a selected component (e.g. a particular mineral or ion) into first, second and third fractions.

When each of two particles being compared have a face of similar total area, the term "surface content" refers to that portion of the surface area of each such face upon which the surface active agent has adhered. When the faces being compared have greatly differing surface area, the "relative surface content" of each is generally determined as the relative fraction of the surface area of the face upon which the surface active agent adhered.

In any event either a detectable difference in the marked surface area of at least one face of each of two particles can be used to effect separation or with particles of greatly differing surface area (and thus greatly differing mass) the proportion of marked area to unmarked area can be used to detect differing concentration of a desired substance.

The process of the present invention is based upon those differences which exist in the surface chemical properties of the various components present in ores. Due to these differences, there can be selected a surface-selective agent or a mixture of surface-selective agents which will effectively and selectively coat only certain components present in an ore. A separation based upon providing a distinctive marking based on surface chemical properties provides relatively more consistent separation results than do separation methods based upon other naturally-occurring properties, such as color, reflectance and conductivity. Such other properties in nature, generally tend to be substantially similar for the various components of an ore, such that a fine degree of resolution is required in order to distinguish between these properties for the various materials present in an ore. Such a fine degree of resolution may be difficult to obtain and, for this reason, the efficiency of separation based upon these naturally occurring properties suffers.

In the practice of the process of this invention with regard to a particular mineral ore, the ore is first subjected to a crushing step. In this crushing step, the ore is crushed to physically separate the components present within the ore. For example, some ores exist with stratifications and/or pockets of various components and crushing of the ore as mined is a means for physically separating these stratifications and/or pockets. Crushing also increases the surface area of the particles, thereby providing a greater reactive site with which the surface-selective functional group of the conditioning agent can react. The ore is crushed, typically to a particle size of from about 5mm to about 200mm. Particle sizes of less than 5mm can be used in the practice of this invention. However, particles of such small sizes require greater amounts of conditioning agent and are more difficult to separate, requiring greater amounts of time for separation for a given mass of ore. Particle sizes of greater than 200mm can be used in the practice of this invention but generally particles of such large sizes entrain such a substantial mixture of components that separation efficiency decreases. It is preferred to use ore particles of a size from about 10mm to about 100mm. Following crushing and sizing, the ore particles can be deslimed to remove soluble impurities and surface fines which can be present on the particulate ore.

The ore is conditioned following sizing with a conditioning agent or a mixture of conditioning agents (each) having a surface-selective functional group(s) that selectively adhere to one of the components present in the particulate mixture, to the substantial exclusion of adhering to the other components present, or that undergoes characteristic chemical reaction with a given component of the ore or gangue, as does 8-hydroxyquinoline with magnesium ores, such as talc. The conditioning agent is used in sufficient quantity to provide a thin film on the components towards which the surface-selective group is reactive. Due to the surface chemical property of the components the surface-selective group only adheres to and/or reacts with the selected components.

The ore is conditioned with the conditioning agent by mixing the latter in a surface reactive relationship with the particulate ore. Conditioning of the ore with the agent is accomplished by contacting the particulate mixture with the conditioning agent. Many techniques are available for contacting a particulate solid with a liquid reagent. Such techniques include dipping the solid particles into a liquid bath containing the conditioning agent, spraying the conditioning agent on to the solid particles, mixing the solid particles with the conditioning agent, and the like. It is preferred to spray the sized ore with the liquid reagent. Spraying techniques include, but are not limited to, spraying on to the ore on a vibrating screen or belt, or spraying the ore as it passes through a ring sprayer or a series of ring sprayers.

The conditioning agent can be used in any suitable form such as in solution, suspension, dispersion, or by itself. It is preferred to use a solution or dispersion of the conditioning agent in water. Such a solution or dispersion can be readily applied to the particles and water is an economical and readily available carrier.

It is preferable, but not essential, that the conditioning agent be soluble in water to avoid the potential problems of emulsion formation within the system. In the case of normally water-insoluble longer-chain organic compounds, water-soluble salts thereof, especially alkali-metal salts thereof, can be employed as conditioning agents.

If the conditioning agent is not water-soluble (or only slightly water-soluble) it can be applied as an aqueous dispersion (or emulsion) or in a non-aqueous solvent. A further embodiment, which is considered to be within the scope of this invention, is the application of the conditioning agent to the particles in a dry state, e.g. "dusting" the particles with the agent. This can be accomplished either with or without an external driving force which facilitates the desired reaction between the agent and the surface of the particles, such as a technique analogous to electrostatic spray painting, in which an electrical charge would be imparted to the agent and an electrical charge of the opposite polarity given the particles, prior to the conditioning operation.

Following conditioning with an aqueous solution or dispersion, the particulate mixture is washed with an aqueous wash to remove excess conditioning agent, weakly adhering conditioning agent and any conditioning agent entrained within the particulate mixture. In some cases, it is possible to eliminate the washing step if the conditioning agent solution or dispersion is used in a sufficiently dilute form.

Some gradation in the amount of marking on the particles is normally observed, due to the inhomogeneity which is common to naturally occurring ore deposits. Typically, the crushing operation will not completely free the desired ore component from the gangue: particles will range in composition from nearly pure ore to nearly pure gangue material, including various mixtures of the components.

If the conditioning agent is chosen for marking the ore particles, the higher grade ore particles will be more heavily marked than the lower grade ore particles, and the more pure gangue particles will be substantially unmarked. Conversely, should the conditioning agent be chosen to mark the gangue, the gangue particles will be more heavily marked than the lower grade ore particles, and the higher grade ore particles will remain substantially unmarked.

The relative degree of particle marking is usually related to the surface area in a given particle attributable to that component which is reactive toward the chosen conditioning agent. A particle having a relatively higher percentage of the desired component will generally also have a relatively higher percentage of exposed surface area of that component, and will therefore accept a relatively larger amount of conditioning agent.

To distinguish between the marked particles and the unmarked particles, the conditioning agent chosen contains a detectable moiety such as a radioactive atom, a chromophore or a fluorescent moiety. The detectable moiety can be a moiety which can be detected after further chemical reaction, as by exposure to radiation such as heat or light, pH changes, or redox reaction. The ore can then be sorted by radiation detection, by visible optical means or by irradiation with electromagnetic radiation to induce fluorescence. In the latter case, the fluorescent conditioning agent that marks some of the particles fluoresces, while the unmarked material does not fluoresce to any substantial degree. The different materials can be separated, based upon this property. It is also possible to separate various grades of ore, based upon the knowledge that the more heavily marked particles will possess a more intense color or fluorescence than will the less heavily marked particles. Conversely, a conditioning agent can be used that will block ultraviolet radiation or that will absorb rather than reflect light. If a mechanical device is used to effect the separation, adjustment of the sensitivity of that device will alter the grade of ore product which is obtained.

The term "gangue" is used herein to include any mineral or assemblage of minerals other than that which is considered to be "ore" in a given separation procedure. In many instances, the gangue material contains minerals of economic interest, and therefore is not a discarded waste material, but may be subjected to a subsequent separation process which uses an agent having the ability to selectively mark an additional component. Should the recovery of other components be desired, further separations using different reagents may be used. From this, it can be seen that the terms "ore" and "gangue" have meaning only in terms of a specific separation to be performed: ore in a separation may be a component of the gangue from a previous separation.

Similarly, subsequent separation steps may be used to further separate the components of an "ore" fraction resulting from a procedure. This technique is useful in cases where a very pure ore mineral is desired and the additional expense of repeated processing to remove various impurities in a step-wise manner is not prohibitive, or in cases where a single conditioning agent does not provide the required selectivity for the desired separation to be conducted in one step. The term "ore" may be applied, therefore, to material which yields an ore fraction and a gangue fraction in a later separation.

Generally, "fluorescence" refers to the property of absorbing radiation at one particular wavelength and simultaneously re-emitting light of a different wavelength so long as the stimulus is active. Herein the term "fluorescence" is intended to indicate that property of absorbing at one particular wavelength and re-emitting it at a different wavelength, whether or not visible, during exposure to an active stimulus or after exposure or during both these time periods. Thus "fluorescence" is used generically herein to include fluorescence, phophorescence, and envisions the emission of electromagnetic waves whether or not within the visible spectrum.

Electromagnetic radiation generally refers to the emission of energy waves of all the various wavelengths encompassed by the entire electromagnetic spectrum. Herein the term "electromagnetic radiation" is intended to indicate any and all stimuli that will excite and induce fluorescence of a fluorescent material. Thus, "electromagnetic radiation" is used generically herein and envisions other stimuli that will excite and induce fluorescence of a fluorescent material. If a property other than fluorescence is to be detected, external influences such as heat, radioactivity, or chemical stimuli, including oxidation, reduction, pH changes or salt formation can be utilized in producing a detectable property in the conditioning agent.

The selection of the surface-selective functional group in a conditioning agent is directed by the properties of the mineral species which are to be selectively coated by the agent, and the properties of the other species which are present in the mixture of particles. Reaction of the surface-selective functional group with a mineral surface, resulting in a physical adsorption or the formation of a new surface compound by chemical bonding is a likely mechanism by which the detectable, e.g. fluorescent, moiety is attached to the surface of a particle.

The following table lists various types of compound having suitable surface-selective functional groups:

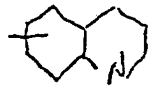
Type	Formula
phenol	R-ONa
xanthate	ROCSSNa
dithiophosphate	$(RO)_2PSSNa$
dithiocarbamate	$R_2NCSSNa$
thiol (mercaptan)	RSH
thiocarbanilide	$(RNH)_2CS$
carboxylic acid salt	RCOONa
arenesulfonate or alkylarenesulfonate	RSO_3Na
alkyl or aryl sulfate	$ROSO_3Na$
primary amine salt	$RNH_3^+X^-$
quaternary ammonium salt	$RN(CH_3)_3^+X^-$
alkylpyridinium salt	$RC_5H_4N.H^+X^-$
amine and amine salts	R_nNH_{3-n}, where n = 1, 2 or 3

In the above table, the free acid, or hydrogen, form can be used, but in most cases (especially with the dithiophosphates, phenols, xanthates and dithiocarbamates) the salt form is preferred and is so indicated in the table.

Where Na appears in the listed formulae in the above table, it may be replaced by any of the alkali metals (e.g. K) if water solubility is desired, by an alkaline earth metal if oil solubility is needed, or by a transition metal such as aluminium or iron if a more insoluble compound is required for use in a dispersion. X^-, as used in the table above is an anionic group, such as halide (e.g. Cl), sulfate, sulfonate, carboxylate, etc

The R in the listed formulae is a group which contains a detectable moiety. The table provides a representative, though not exhaustive, list of compounds having useful surface-selective groups for the purposes of the present invention.

R can be selected from such types of groups as polynuclear aromatics (including fluoranthene), the groups in xanthene dyes (fluorescein, rhodamine, etc.) in dyes used for fabric whitening (coumarin derivatives), diaminostilbenedisulfonic acid-cyanuric chloride, distyrylbiphenyl, naphthotriazolystilbene, pyrazoline) and many other fluorescent groups.

An especially useful class of phenols is the hydroxyquinolines of general formula $Na^{+-}O$  where the oxygen can be on any carbon atom, but preferably is in the 8-position (e.g. 8-hydroxyquinoline, which is especially useful for marking magnesium compounds) and that may have additional substituents (e.g. halide, carboxylate, sulfate, sulfonate, alkyl, aryl, etc.), and similar condensed ring heterocyclic compounds (including 3, 4 or 5 condensed rings) containing at least one heteronitrogen atom and at least one hydroxyl group (e.g. the hydroxyquinazolines and hydroxyquinoxalines such as the sodium salt of

3-hydroxy-2-quinoxylinecarboxylic acid). The use of 8-hydroxyquinoline to mark magnesium-containing minerals on the surface of an ore is an example of the use of a chemically reactive, bifunctional marking agent, i.e., one containing a surface-selective group (e.g., the oxygen anion) and a detectable moiety which undergoes a chemical transformation which aids in detecting the marking agent when combined with a specific component of an ore (e.g., a magnesium compound). That is, the 8-hydroxyquinoline can be induced to fluoresce at a characteristic waveband or wavelength when it is combined with a magnesium mineral. In general, the hydroxyquinolines are useful in marking polyvalent metal ions in a mineral (especially divalent and trivalent ions).

In some cases, the detectable, e.g. fluorescent, moiety may be separated from the surface-selective group by a alkylene chain or other linking group. Since it is known that the structural features of such a linking group can influence the surface-selective properties of the surface-selective end groups, the linking group could be considered as part of the surface-selective group. Unsaturation in such a group could also contribute to fluorescent properties and thereby be considered part of a fluorescent moiety. Thus the alkali-metal salts (e.g., potassium salts) of fluorescent unsaturated carboxylic acids are contemplated as useful. A fluorescent moiety might also contain surface-selective groups, as in 7-diethyamino-4-methylcoumarin salts. The practice of the invention does not necessitate that the detectable and surface-selective moieties be separate and readily distinguishable, although that may be the case in a large number of fluorescent surfactants.

For the practice of this invention, the primary requirement is that the conditioning agent attaches to the surface of a particle. Such surfactant types as cationics, anionics, nonionics, amphoterics, chelates, etc. can be used to advantage.

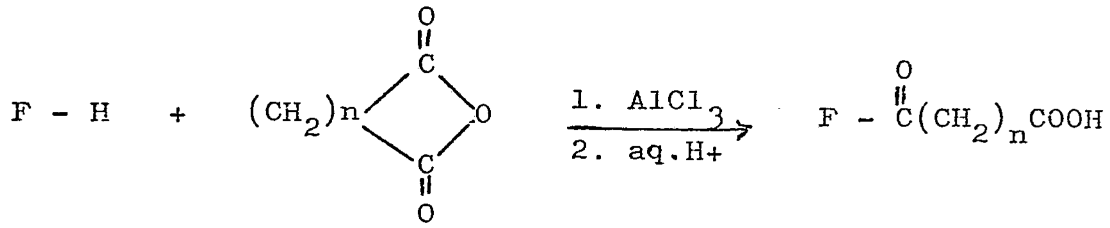
A variety of techniques are known in the practice of separations for increasing the selectivity of a collector. These techniques usually involve the use of modifying agents in combination with the collector, to influence the attachment of the collector on to the mineral surface. This invention relates to the selective attachment of surface-selective agents to mineral surfaces, and those techniques are included within the scope of this invention. The use of pH regulating agents, activators, depressants, dispersants, flocculants, and the like in combination with a suitable conditioning agent to achieve a desired selectivity is contemplated. Examples for the use of such modifying agents are contained in U.S. Patent 3,795,310 and within the literature of ore flotation, for example Taggart, Handbook of Mineral Dressing (1945), Section 12.

A further explanation of the invention is made by means of the following examples, which are not intended to be limiting, the scope of this invention being defined by the appended claims.

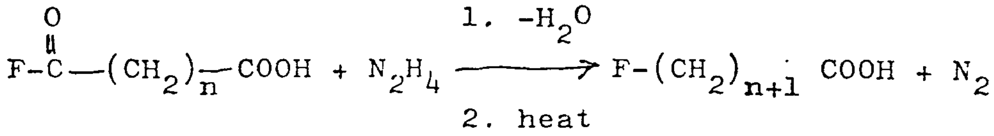
Example I

After being informed that coworkers had discovered that limestone in the presence of silicate minerals can be selectively coated with a mixture of a carboxylic acid and a fluorescent dye (e.g. as in the aforesaid International Publication No. WO 79/00950), carboxylic acid derivatives of fluoranthene were prepared using the following reaction I:

I



in which F - H is fluoranthene, $C_{16}H_{10}$, and n is 2, 4 or 8. Portions of each product were reduced with hydrazine according to the following reaction II:

II 

$$\mathrm{F\text{-}\overset{\overset{O}{\|}}{C}\text{—}(CH_2)_n\text{—}COOH + N_2H_4 \xrightarrow[2.\ heat]{1.\ -H_2O} F\text{-}(CH_2)_{n+1}\ COOH + N_2}$$

Since the free carboxylic acids as formed are insoluble in water, each product from reactions I and II was converted to its sodium salt by reaction with sodium hydroxide.

Each of the six salts thus obtained was dissolved in water and pieces of limestone ore were dipped into the solutions, then the pieces were irradiated with ultraviolet light. All of the compounds were found to coat the limestone in the particles, but the salts corresponding to the formulae where $n = 2$ were found to be the more selective in not coating silicate minerals. In each case, the reduced compound derived from reaction II exhibited a higher fluorescence intensity estimated visually, than its precursor from reaction I.

Based upon the above, and the superior solubility and rinsing characteristics exhibited, 4-(fluoranthyl)-butanoic acid, $\mathrm{F - (CH_2)_3\ COOH}$, was selected for further testing in the separation of limestone from siliceous gangue.

The foregoing example is typical of the procedure which is followed in selecting a fluorescent conditioning agent for use in selectively marking a given component of a mixture of ore particles.

Example II

A 2000 ml round bottom flask was charged with 100g of fluoranthene, 52g of succinic anhydride and 1 liter of 2-nitropropane. The mixture was stirred and 157g of aluminum chloride was added slowly, whereupon the temperarose to about 50° C, then cooled to room temperature and stirred over a weekend.

The reaction mixture was hydrolyzed by pouring slowly into about 1 liter of about 3N hydrochloric acid. Steam distillation was used to remove the solvent, and the solid residue was isolated by filtration with water washing. After transferring to a Soxhlet extractor, the solid was extracted into acetone.

The acetone extract was concentrated by distillation and 250 ml of deionized water was added, forming a slurry which dissolves after 800 ml of 2.5% sodium hydroxide was added. Upon acidification, the 4-(fluoranthyl)-4-oxobutanoic acid product precipitated and was collected by filtration. The product was partially dried under vacuum.

A 1000 ml flask was charged with 118g of the partially dried product, above, and 43.7g of potassium hydroxide, 39 ml of hydrazine hydrate, and 375 ml of diethylene glycol were added. The mixture was stirred and heated, during which excess water and hydrazine were collected and removed by means of a Dean-Stark trap, to a final temperature of about 195°C, and maintained at that temperature for about eight hours. After cooling and slurrying with 1500 ml of about 1.5N hydrochloric acid, the 4-(fluoranthyl)-butanoic acid product was isolated by filtration and dried in a desiccator.

Example III

A portion of the product from Example II was used, in a pilot plant based upon the apparatus of U.S. Patent 3,472,375, for the separation of limestone from siliceous gangue. The 4-(fluoranthyl)-butanoic acid was converted to its sodium salt, which was dissolved in water to form a 0.1% by weight solution, and applied to the mixed ore and gangue particles by spraying. Following a rinse to remove excess reagent, the particles were passed through an electro-optical sorter which ejected the selectively marked ore particles to separate them from the substantially unmarked gangue particles.

Six runs, totalling 752 kg. of a limestone feed, were made using the fluorescent conditioning agent. The feed material was obtained from a manufacturer of portland cement, and consisted of reject material from a hand sorting of limestone ore, having the average analysis

87.40% $CaCO_3$, 7.38% $MgCO_3$, 0.45% Fe_2O_3 and 5.17% SiO_2.

The following results were obtained from these six runs, showing the concentrating of limestone feed by impurity removal:

Run No.	Product of Stream	Distribution (% of total in feed)				Product %$CaCO_3$
		$CaCO_3$	$MgCO_3$	Fe_2O_3	SiO_2	
100	Lime Conc.	79.2	73.3	28.8	54.9	88.51
	Waste	20.8	26.7	71.2	45.1	77.42
101	Lime Conc.	62.9	41.9	10.8	34.8	89.58
	Waste	37.1	58.1	89.2	65.2	76.58
102	Lime Conc.	83.0	69.3	46.5	48.8	89.51
	Waste	17.0	30.7	53.5	51.2	75.53
103	Lime Conc.	88.2	79.8	33.6	60.8	89.43
	Waste	11.8	20.2	66.4	39.2	74.05
104	Lime Conc.	85.9	77.1	46.5	59.3	89.06
	Waste	14.1	22.9	53.5	40.7	75.83
106	Lime Conc.	71.1	57.3	14.9	32.6	90.90
	Waste	28.9	42.7	85.1	67.4	77.07

As shown above, the limestone concentrate in each run was upgraded to between 88.51 and 90.90% $CaCO_3$. Significant amounts of iron and silica remained in the waste stream particles. Considerable variability was noted in the results between runs, attributable to the inhomogeneous nature of the ore particles and the relatively small (84.5 to 163 kg.) quantities of material, which were processed in each run.

Example IV

To prepare a fluorescent conditioning agent for use in further separation testing, the procedure of Example II was repeated on a larger scale, as follows: a 12 liter reactor was placed in an ice bath, and 5 liters of 2-nitropropane, 700g of fluoranthene and 365g of succinic anhydride were added. After cooling the mixture to about 10°C, small portions of anhydrous aluminum chloride (totalling 1194g, over a one hour period) and an additional 2 liters of 2-nitropropane were added. The temperature rose to about 20°C during the ensuing reaction. After addition of the aluminum chloride, the bath was removed and the mixture stirred overnight. The mixture was hydrolyzed by the addition of one liter of 3N hydrochloric acid, and the solids recovered by filtration. Acetone was used to extract the solids in a Soxhlet extractor, and the acetone solution was removed. After the addition of 3.6 liters of deionized water, acetone was removed by distillation, and the remaining 4-(fluoranthyl)-4-oxobutanoic acid was removed by filtration, yielding a 1.8 Kg.wet cake.

A 905g portion of the wet cake was placed in a three-neck flask with 1.1 liter of diethylene glycol, 2.5. equivalents of potassium hydroxide and 2.8 equivalents of hydrazine hydrate. The mixture was heated to remove water and excess hydrazine, then the temperature was raised to 190°C. After cooling, the mixture was poured into 3 liters of cold, 1N hydrochloric acid, and the product, 4-(fluoranthyl)-butanoic acid dissolved in dilute sodium hydroxide solution, re-precipitated with aqueous hydrochloric acid, and collected by filtration.

Example V

Pilot plant testing of the product from Example IV yielded unsatisfactory results, apparently because the fluorescent compound did not properly adhere to the ore particles. This was considered to be a result of significantly greater than normal impurity levels in the compound.

A 200g portion of the product from Example IV was dissolved in 600ml of toluene at a temperature near the boiling point of the solution. After decanting the solution away from the dark, tar-like insolubles, it was cooled, and a small amount of a dark oil was removed. The solution was contacted with two liters of 2.5% by weight sodium hydroxide solution in a separatory funnel, and the organic layer was discarded. The aqueous layer was acidified and the purified product was collected as a wet cake by filtration.

The pilot plant test of Example III was repeated, using the purified 4-(fluoranthyl)-butanoic acid and feed material from the same lot as was previously used, yielding the following results for a total of 558 kg. of limestone feed:

Run No.	Product of Stream	Distribution (% of total in feed)				Product
		$CaCO_3$	$MgCO_3$	Fe_2O_3	SiO_2	$\%CaCO_3$
122	Lime Conc.	85.3	79.4	36.1	59.4	88.7
	Waste	14.7	20.6	63.9	40.6	71.1
123	Lime Conc.	92.7	89.8	57.1	72.3	89.3
	Waste	7.3	10.2	42.9	27.7	68.7
125	Lime Conc.	79.7	68.0	39.0	41.3	89.8
	Waste	20.3	32.0	61.0	58.7	69.7
126	Lime Conc.	65.8	54.5	9.3	41.8	90.0
	Waste	34.2	45.5	90.7	58.2	72.6
127	Lime Conc.	43.6	25.8	4.0	23.3	92.1
	Waste	56.4	74.2	96.0	76.7	79.9
128	Lime Conc.	57.5	37.2	8.9	30.4	91.0
	Waste	42.5	62.8	91.1	69.6	70.4

This demonstrates that impurities in a conditioning agent can influence its usefulness in selectively marking ore particles.

Example VI

Large-scale production of 4-(fluoranthyl)-butanoic acid was undertaken in a 3785 liter glass-lined jacketed reactor, equipped with an agitator, into which 250 kg. of fluoranthene, 2500 liters of 2-nitropropane and 125 kg. of succinic anhydride was placed. A temperature of about 10°C was obtained by circulating cooling brine through the jacket, and then 368 kg. of aluminum chloride was added in 23 to 45 kg. aliquots over a period of about 3.5 hours, such that the temperature did not exceed 20°C. A slight vacuum was used to remove oxides of nitrogen. The mixture was stirred overnight.

A quench solution was prepared in a 9500 liter agitated, resin-lined vessel by adding 757 liters of 10N hydrochloric acid to 757 liters of water and 907 kg. of ice. The reaction mixture, above, was added to the quench solution at a rate of about 38 to 57 liters per minute, and an additional 318 kg. of ice was also added, resulting in a final temperature of about 30°C. This mixture was stirred for about two hours, forming a three phase slurry of solids dispersed in organic and aqueous liquid phases.

About one-third of the solids were isolated by a slow filtration, yielding a very wet cake. Due to the highly unsatisfactory filtering rate, the solids and filtrate were returned to the quench vessel, and the organic solvent was removed by steam distillation. The remaining aqueous slurry filtered rapidly, yielding 435 kg. of wet solids.

The solids were stirred into a solution containing two parts acetone to one part water, and sufficient sodium hydroxide to provide about 10% in excess over that needed to dissolve the 4-(fluoranthyl)-4-oxobutanoic acid product. Insoluble tars were removed by filtration, and dilute hydrochloric acid was used to re-precipitate the acid product. After filtration, the solids were subjected to an additional dissolution in base and precipitation with acid, as described above, resulting in a purified material.

A 49.5kg. portion of the purified material was placed in the 3785 liter jacketed reactor with about 170 liters of diethylene glycol. The mixture was stirred and 21 kg. of potassium hydroxide and 19.5 kg. of hydrazine hydrate were added. Steam was passed through the jacket to obtain a temperature of about 120°C, and then the temperature was increased to 155°C. A nitrogen purge was used to maintain an oxygen content less than about 1%

and a distillation receiver was used to collect the water and excess hydrazine which was distilled from the reactor.

After cooling to about 25°C, the mixture was diluted with 416 liters of water and acidified with 45.5 liters of 10N hydrochloric acid in about 190 litres of water. The solid 4-(fluoranthyl)-butanoic acid which formed was collected on a filter

A sample of this product was tested in a pilot plant, as in Example III, using a different limestone ore feed material, and yielding the following results for a total of 184 kg. of feed:

Run No.	Product of Stream	Distribution (% of total in feed)				Product
		$CaCO_3$	$MgCO_3$	Fe_2O_3	SiO_2	%$CaCO_3$
243	Lime Conc.	36.6	20.8	6.3	22.0	90.0
	Waste	63.4	79.2	93.7	78.0	82.3
244	Lime Conc.	49.4	32.9	4.3	24.0	91.4
	Waste	50.6	67.1	95.7	76.0	81.8
247	Lime Conc.	55.5	34.2	2.6	20.2	91.5
	Waste	44.8	65.8	97.4	79.8	80.5

Example VII

Because of the rather low product yield obtained in the previous large-scale production run (Example VI), a further production of 4-(fluoranthyl)-butanoic acid was undertaken using a different solvent system. A 5680 liter jacketed reactor was charged with 2500 liters of chlorobenzene, 250 kg. of fluoranthene and 125 kg. of succinic anhydride. To this was added 365 kg. of aluminum chloride. The temperature was raised to about 60°C and maintained at 55±5°C for about 12 hours.

The reaction mixture was quenched by the slow addition of 757 liters of 10N hydrochloric acid in 1893 liters of cold water, and circulating cold water through the reactor jacket during the addition. By adjusting the addition rate, the reactor temperature was kept below about 80°C.

Steam distillation was used to remove the solvent. After cooling the mixture to about 35°C, the solid intermediate product was isolated by filtration, then transferred to a 3785 liter reactor.

To this product was added 1181 liters of diethylene glycol, 145 kg. of 91% potassium hydroxide, 138 kg. of 85% hydrazine hydrate and 142 liters of water. A nitrogen purge reduced the oxygen content of the reactor to less than 1%, and the mixture was heated to about 155°C. Excess hydrazine and water distilled from the reactor during the heating. The reaction mixture was maintained at about 155°C for eight hours, cooled to about 50°C and diluted with about 2839 liters of water.

A 38 liter portion of 10N hydrochloric acid was added and, after stirring for an hour, the mixture was filtered and washed with water, yielding 736 kg. of wet cake.

A sample of this product was tested in a pilot plant, as in Example III, using a different limestone ore feed material, and yielding the following results for a total of 820 kg. of feed:

Run No.	Product of Stream	Distribution (% of total in feed)				Product % $CaCO_3$
		$CaCO_3$	$MgCO_3$	Na_2O+K_2O	SiO_2	
355	Lime Conc.	72.9	62.1	22.3	46.6	82.5
	Waste	27.1	37.9	77.7	53.4	62.3
356	Lime Conc.	46.3	35.4	8.5	20.8	86.0
	Waste	53.7	64.6	91.5	79.2	70.4
358	Lime Conc.	15.1	7.5	4.8	7.9	87.2
	Waste	84.9	92.5	95.2	92.1	76.4
361	Lime Conc.	74.4	62.8	31.5	40.7	82.9
	Waste	25.6	37.2	68.5	59.3	59.3
362	Lime Conc.	93.5	87.0	84.4	85.6	77.9
	Waste	6.5	13.0	15.6	14.4	52.7
363	Lime Conc.	62.3	45.5	21.3	27.7	85.7
	Waste	37.7	54.5	78.7	72.3	62.5
367	Lime Conc.	79.2	70.0	13.6	30.0	86.4
	Waste	20.8	30.0	86.4	70.0	50.3

Example VIII

A fluorescent compound containing a cationic surfactant group, 7-diethylamino-4-methylcoumarin, acid sulfate was prepared by dissolving the commercially available amine in sulfuric acid and diluting to a 0.24% by weight solution. This solution was evaluated for its ability to selectively mark minerals by the immersion of a clean specimen in the solution for about 15 seconds, followed by rinsing of the specimen under running water and visual examination of the specimen under an ultraviolet light. The results were as follows:

Mineral	Fluorescence intensity
Quartzite, SiO_2	medium
Albite, $NaAlSi_3O_8$	medium
Wollastonite, $CaSiO_3$	strong
Quartz, SiO_2	medium
Calcite, $CaCO_3$	strong
Pyrite, (from coal), FeS_2	strong

Oil Shale (<4.2 liters/tonne)	medium
Oil Shale (>104.3 liters/tonne)	none
Coal	none
Chert, SiO_2	none
Slate	none

The results show that the following economically significant separations can be made using this compound as a conditioning agent with a technique as in Example III:

1. Coal can be separated from inorganic materials such as pyrite, calcite, dolomite or limestone; and coal of high heat content can be separated from lower heat content material.
2. Higher grade oil shale can be separated from lower grade oil shale and from calcite, dolomite or limestone.
3. Wollastonite can be separated from other silicates, such as albite and quartz.
4. Quartz can be separated from calcite, dolomite or limestone.
5. Calcite, dolomite, or limestone can be separated from fluorospar, or from phosphate minerals such as phosphate rock.

Example IX

To more quantitatively test the separation technique for oil shale, the following experiment was conducted: a solution of 4.0 g of 7-diethylamino-4-methylcoumarin, acid sulfate was made in 2 liters of deionized water, giving a pH of about 1.5. Oil shale particles having a size in the range of about 25 to about 50 mm were immersed in the clear yellow solution, rinsed with deionized water and visually examined under an ultraviolet light. The more fluorescent particles were separated from the less fluorescent particles, and the two fractions were crushed for oil analysis by the Fischer assay.

"Barrel 27" is a high grade oil shale with an oil analysis which averages about 104 litres/tonne. "Barrel 187" is a low grade material which analyzes in the range of 33 to 46 liters/tonne.

The following results obtained from the experiment, showing the fraction weights, number of particles in the fraction, and oil content of each fraction:

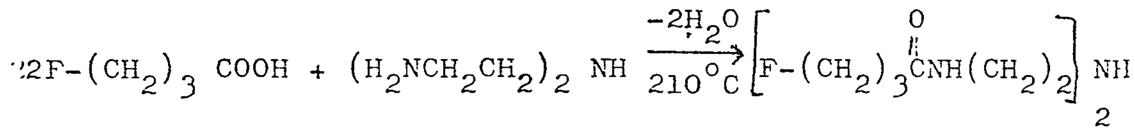
	Higher Fluorescence			Weak Fluorescence		
Barrel	Weight	Particles	liters/ tonne	Weight	Particles	liters/ tonne
27	1073g	15	3.75	258g	5	192
187	862g	20	30.4	513g	12	80.1

Another experiment was performed, using 644g (8 particles) from barrel 27 and 548g (10 particles) from barrel 187, which were mixed and treated as above. There were 12 particles (674g) with weak fluorescence, assaying 155 liters/tonne, and 6 particles (519g) with higher fluorescence which contained 36.7 liters/tonne of oil.

Each of these experiments shows that a substantial upgrading can be obtained by selectively labeling oil shale particles.

Example X

A cationic derivative of 4-(fluoranthyl)-butanoic acid was prepared by reaction with diethylenetriamine, using diethylene glycol as a solvent, according to the following reaction:



$$2F-(CH_2)_3\ COOH + (H_2NCH_2CH_2)_2\ NH \xrightarrow[210^\circ C]{-2H_2O} \left[F-(CH_2)_3\overset{O}{\overset{\|}{C}}NH(CH_2)_2\right]_2 NH$$

That portion of the reaction product which was insoluble in dilute sodium hydroxide was extracted with dilute acetic acid, and the resulting solution evaluated for coating minerals.

Mineral specimens were immersed in the solution for 20 to 30 seconds, rinsed with deionized water and visually examined under ultraviolet light, yielding the following results:

Mineral	Fluorescent intensity
Chert, SiO_2	moderate
Microcline, $KAlSi_3O_8$	moderate

Wollastonite, $CaSiO_3$	strong
Limestone, Ca, Mg, CO_3	weak

These results show utility of the compound as a conditioning agent for sorting mixtures of silicate minerals. This type of conditioning agent can be viewed as effective over the entire aqueous pH range, an important property due to the influence of pH on the adherence of collectors to ore surfaces, a phenomenon which has been observed in the ore flotation art. With cationic fluorescent compounds, a structure can be chosen for its usefulness in a given pH range, e.g. amine salts containing the $-NH^+$ group will be useful in the pH range dictated by the basicity of the amine, while quarternary amine salts will be useful over the entire pH range.

Example XI

In a manner similar to that of Example IX, the compound $F - (CH_2)_3\ CONH(CH_2)_2\ NH_2$ was prepared by the reaction of 4-(fluoranthyl)-butanoic acid and ethylene diamine in a diethylene glycol solvent, and precipitated by dilute sodium hydroxide. The product was extracted with a toluene-isopropanol mixture, and the extract was concentrated by distillation and, finally, evaporated of the solvents. After dispersal in water, the product was filtered and dried over phosphorus pentoxide, then dissolved in dilute acetic acid for marking experiments.

A specimen of microcline was marked by immersion in the acetic acid solution, but its visual fluorescence appeared to be too weak for a practical separation process. An activation step was conducted on a second speciment by immersion in a 0.4% solution of hydrofluoric acid for about 10 seconds, followed by a deionized water rinse. After this activation, the fluorescent conditioning agent marking yielded a more intense fluorescence, indicating that the activating step could be used to advantage.

Several mineral specimens were immersed in the acetic acid solution (at about pH 5) for 10 to 15 seconds, rinsed with deionized water, and visually examined under ultraviolet light, giving the following results:

Mineral	Fluorescent intensity
Quartzite, SiO_2	moderate
Albite, $NaALSi_3O_8$	moderate
Wollastonite, $CaSiO_3$	strong
Gneiss	moderate
Diopside, $CaMg(SiO_3)_2$	weak
Chert, SiO_2	weak

A separate test was conducted by simultaneously immersing samples of quartzite and limestone in the acetic acid solution (at about pH 3). The samples were removed, rinsed and evaluated under ultraviolet light. Selectivity of the marking was shown by the somewhat more intense fluorescence of quartzite relative to limestone.

Example XII

There are low grade refractory silver ores in which the dilute silver values are associated with a much larger amount of iron and/or manganese minerals in a siliceous (e.g., quartz, serpentine) matrix (e.g a limonitic ore). An example of such an ore can be found in the Candelaria Mining District of Nevada. A sample, consisting of both limonitic and non-limonitic 50-75 mm ore particles having cross-sections of about 50 mm to 75 mm, was treated with 0.1% (wt.) of the sodium salt of 4-(fluoranthyl)-butanoic acid (FBA), rinsed and examined for fluorescence intensity. The limonitic ore was more fluorescent than the non-limonitic ore. This indicates that concentration of the silver could be achieved even though the difference in fluorescence was small. Use of a more intense fluorescent moiety in the fluorescent conditioning agent and/or a more active surfactant moiety would increase the difference in the fluorescence. For example, a diaminostilbene cyanuric chloride-derived or a distyrylbiphenyl-derived fluorescent moiety would be more fluorescent than the fluoranthene derived moiety. The example also indicates that anionic fluorescent surfacts can be useful in sorting limonitic ores.

Example XIII

A Mexican silver (172g/tonne) ore containing silver associated with galena and sphalerite in a siliceous matrix contaminated by limestone was concentrated by conditioning and ejecting (with water jets in freefall) the selectively marked limestone. In this separation a 1% dispersion in water of a 0.5% 7-diethylamino-4-methyl-courmarin (DMC) in tall oil was sprayed on 12.9 kg. of ore and the ore sorted. The results are shown below.

Waste	37.5 g/tonne	9.5% silver	43.4% wt.
Concentrate	275 g/tonne	90.5% silver	56.6% wt.

These results demonstrate the concentration of more than 90% of the silver in 56% of the ore. It is also possible to label and eject the siliceous minerals (e.g. quartz) as in a second conditioning and separation procedure, thereby further concentrating the silver values (or, the siliceous separation could be made instead of separating the limestone). In general siliceous materials can be selectively marked with compounds containing an amino-group.

Although, in this example, the tall oil is probably the major influence on the surface-selectivity, if the DMC is dissolved in dilute, aqueous mineral acid to produce an acidic solution (e.g. below about pH 5, typically about pH 2 to about pH 3), the DMC can function as both the surface-selective group and the detectable moiety (e.g by induced fluorescence). Alternatively a water soluble salt of fluorescent unsaturated carboxylic acid, such as the Na or K salt of FBA, can be used in aqueous solution in the concentration of silver ores which contain limestone as a diluent or impurity.

Although the above Examples XII and XIII are of silver ores where the silver mineral is associated with a gross mineral such as the limonitic quartz ore of Example XII or the quartz of Example XIII and/or where there is also present a third mineral which can be considered a contaminant such as the quartz in Example XII and the limestone in Example XIII and many other desirable minerals, such as those of gold, tungsten, uranium, boron, chromium, nickel, lead, zinc, and antimony, can be concentrated in these examples and the other description in this application.

Of course, in an ore where the desirable mineral is concentrated in a limestone fraction, a limestone marking agent can be used to aid in concentrating the desired mineral value by separating the limestone from other minerals in the ore.

Example XIV

A synthetic sample of magnesite, calcite and siliceous rock was formulated containing 26.8% magnesite, 30.4% calcite and 42.8% siliceous rock in particles of about 25 mm to about 75 mm screen size. After washing, the material was conditioned with a 0.1% solution of 8-hydroxyquinoline in water, as the sodium salt. After conditioning, the material was rinsed and passed through an irradiation device to induce fluorescence.

Hand sorting of the conditioned, fluorescing particles produced the fractions shown below:

FRACTION	% Separation	% Magnesite	% Dist.
Eject	25.1	88.0	82.3
Reject	74.9	12.0	17.7
Head	100.0	26.8	100.0

By "eject" is meant that in a Mathews-type separator, the particle would be deflected (or ejected) from its free-fall path.

Visible fluorescence is a desirable property for the rapid evaluation of a conditioning agent, and is also convenient for plant operators to use in empirical quality control checks of a separation process. However, an agent having no visible-region fluorescence or only a weak visible fluorescence can be quite useful in those processes which detect fluorescence by means of an electro-optical instrument, since the wavelength to which such an instrument responds can be altered as required.

CLAIMS

1. A process for separating a first type of particle from second type of particle, comprising the steps of conditioning the particles with a conditioning agent selectively to mark either at least a portion of the first type of particle or at least a portion of the second type of particle to the substantial exclusion of the other; detecting the marked particles; and separating the detected, marked particles from the substantially unmarked particles, characterised in that said conditioning agent comprises a compound having both a surface-selective functional group and a detectable moiety.

2. A process according to claim 1, further characterised in that said conditioning agent comprises a compound having both a surface-selective functional group and a fluorescent moiety, which renders the compound fluorescent when exposed to external radiation, and in that the conditioned particles are irradiated to excite and induce fluorescence of the agent to a degree sufficient for distinguishing the marked particles from the substantially unmarked particles.

3. A process according to claim 2, further characterised in that the fluorescent moiety comprises a polynuclear aromatic group.

4. A process according to claim 3, further characterised in that the conditioning agent comprises 4-(fluoranthyl)-butanoic acid.

5. A process according to claim 4, further characterised in that the conditioning agent comprises a cationic derivative of 4-(fluoranthyl)-butanoic acid.

6. A process according to claim 5, further characterised in that said derivative is prepared by reaction of the acid with a polyamine.

7. A process according to claim 3, further characterised in that the conditioning agent comprises a salt of 7-diethylamino-4-methylcoumarin.

8. A process according to claim 7, further characterised in that said salt is a hydrochloride, a sulfate, a sulfonate, a bisulfate, a nitrate or an alpha-haloacetate.

9. A process according to any preceding claim, further characterised in that the surface-selective functional group comprises a cationic surfactant.

10. A process according to any one of claims 1 to 8, further characterised in that the surface-selective functional group comprises an anionic surfactant.

11. A process according to any one of claims 1 to 8, further characterised in that the surface-selective functional group comprises a nonionic surfactant.

12. A process according to any one of claims 1 to 8, further characterised in that the surface-selective functional group comprises an amphoteric surfactant.

13. A process according to any one of claims 1 to 8, further characterised in that said surface-selective functional group comprises a chelating functional group.

14. A process according to claim 13, further characterised in that said chelating functional group is a metal-ion chelating group.

15. A process according to claim 14, further character-

ised in that said surface-selective group is 8-hydroxyquinoline or a derivative thereof.

16. A process according to any preceding claim, further characterised in that the conditioning agent is soluble in water.

17. A process according to claim 16, further characterised in that the conditioning step comprises immersion of the particles in an aqueous solution of the conditioning agent.

18. A process according to claim 16, further characterised in that the conditioning comprises spraying the particles with an aqueous solution of the conditioning agent.

19. A process according to any preceding claim, further characterised in that the particles have a mesh or screen size ranging from about 5 mm to about 200 mm.

20. A process according to claim 19, further characterised in that the particles have a size ranging from 10mm to 100 mm.

21. A process according to any preceding claim for separating higher grade ore particles from lower grade ore particles and gangue particles.

22. A process according to claim 21, further characterised in that said ore particles comprise limestone.

23. A process according to any one of claims 1 to 20 for separating higher BTU coal particles from particulate coal comprising higher BTU coal particles and lower BTU particles.

24. A process according to any one of claims 1 to 20 for separating higher surface kerogen content oil shale particles from lower surface kerogen content particles.

25. A process according to any one of claims 1 to 20, for separating particles of a first gangue mineral from particles of a second mineral in which there is distributed a desired third mineral, thereby concentrating the desired third mineral.

26. A process according to claim 1, further characterised in that said conditioning agent undergoes a chemical reaction with a component of the surface of one of said particle types whereby the detectable moiety has a different detectable characteristic than said moiety had before said reaction; said difference in said detectable characteristic is detected; and the particles having said detectable characteristic are separated from the other particles.

27. A process according to claim 26, further characterised in that said component of the surface comprises a mineral of magnesium, said conditioning agent comprises 8-hydroxyquinoline, and said detectable characteristic is induced fluorescence at a characteristic wavelength or group of wavelengths.

28. A process according to claim 27, further characterised in that said mineral of magnesium comprises talc.