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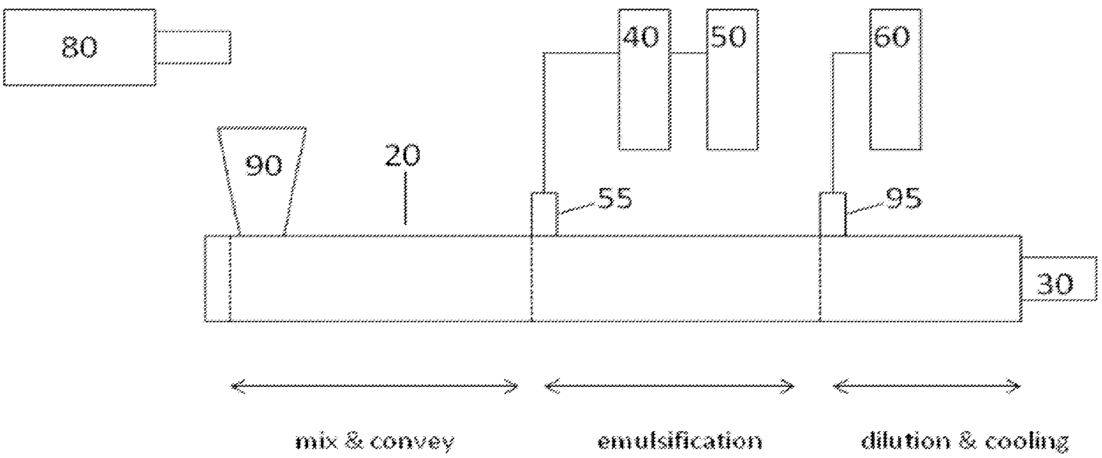
FIG. 1



(57) **Abstract:** Embodiments relate to methods for improving the effectiveness of froth flotation separation processes, especially for the mining industry. In particular, a method of improving the removal of a particular material from a comminuted mineral ore by a flotation separation process by the addition of a thermoplastic polymer dispersion.

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FLOTATION SEPARATION AID USEFUL FOR COLLECTION OF MINERAL ORE FINES

FIELD

Embodiments relate to methods for improving the effectiveness of froth flotation separation processes, especially for the mining industry. Embodiments may be suitable for improving the yield of recovering metal sulfide fines.

BACKGROUND

Flotation separation is a technique used in the mining industry for separating valuable mineral constituents from ore. The object of flotation separation is to separate and recover as much of a select mineral constituent(s) of the ore as possible in as high a concentration as possible, which may then be made available for further downstream processing steps such as thickening, filtration, and roasting. The flotation separation technique involves contacting gas bubble with a particle material to allow the particle to rupture the gas-slurry film and establish either attachment to or entrainment by gas bubbles. The total time required for this process may be the sum of contact time and induction time, whereas the contact time may be dependent on bubble and particle motion and on the hydrodynamics of the system and induction time is affected by the surface chemistry properties of the bubbles and particles. However, flotation separation has certain limitations that render flotation cells and flotation columns inefficient in many applications. Particularly, it has been recognized that conventional flotation is not very effective for the recovery of fine particles, which is a serious limitation. An explanation for this poor recovery is that particle momentum in traditional flotation devices is so slow that particle penetration of the gas-slurry film is inhibited, thus resulting in poor rates of attachment to the bubbles.

There exists a need for improved methods to provide improved recovery rates of the desired minerals in the selective flotation collection of mineral constitutes from ore.

SUMMARY

Embodiments may be realized by a flotation separation method that removes a mineral from comminuted ore that includes the stages of: (i) providing a suspension of the comminuted ore and a collector; (ii) adding an aqueous thermoplastic polymer dispersion that is different from the collector to the suspension of the comminuted ore and the collector to form a mixture, a polymer particle from the aqueous thermoplastic polymer dispersion and a mineral from the comminuted ore forming a particular material in the mixture; (iii) sparging the mixture to form a concentrate that includes the particular material and a slurry; and (iv) recovering the mineral from the concentrate..

BRIEF DESCRIPTION OF DRAWINGS

FIG.1 illustrates a schematic representation of an exemplary melt-extrusion apparatus used to prepare aqueous thermoplastic polymer dispersions.

DETAILED DESCRIPTION

Embodiments relate to the use of an aqueous thermoplastic polymer dispersion as flotation enhancing agent in a flotation separation process to remove select minerals from ore, such as one or more of a precious metal and/or one or more of a base metal. For example, the valuable metal recovered using flotation separation may be gold, silver, copper, lead, zinc, molybdenum, nickel, platinum, palladium, and any combination thereof. In exemplary embodiments, the ore may be sulfide mineral ore, copper ore, or a combination thereof.

Flotation Separation

The flotation separation may include forming a suspension of comminuted ore, which may be pre-treated with a collector, a frother, or both, and adding the aqueous thermoplastic polymer dispersion to the suspension of the comminuted ore. The aqueous thermoplastic polymer dispersion is separately added and different from the collector and the frother. The aqueous thermoplastic polymer dispersion is a pre-formed dispersion, i.e., it is not formed in-situ during the flotation separation (e.g., not formed in the flotation cell) and is different from a mere mixture of the components used to make the dispersion. For example, the aqueous thermoplastic polymer dispersion includes small polymer particles that are formed during the process of making the aqueous thermoplastic polymer dispersion, so as to be distinguished from a mere mixture of a thermoplastic polymer in water.

During the flotation separation process, a sufficient amount of residence time of the mixture of the aqueous thermoplastic polymer dispersion in the suspension of the comminuted ore may be used to enable the formation of a particular material in the mixture. In particular, a small polymer particle from the aqueous thermoplastic polymer dispersion and a mineral from the comminuted ore form the particular material, e.g., the particular material may include one or more small polymer particles and one or more minerals that are attached to each together. Then, a sparging stage with gas (such as air) is performed on the mixture to allow for floating of the particular material to form a concentrate and a slurry, which may be two separate identifiable layers.

Then, the particular material is recovered from the concentrate, which concentrate may be a top layer on the slurry, may be a bottom layer under the slurry, and/or may be embedded within the slurry within the flotation cell. For example, the concentrate may be within a froth layer that lies above the slurry in a flotation cell. The concentrate may include a higher concentration of the particular material than the slurry, e.g., at least 50 wt% of the total particular material in the flotation cell may be found within the concentrate. The concentrate may also include a higher concentration of the mineral to be recovered from the ore than the slurry. The concentrate may be removed from the slurry and then treated to recover at least the particular material. Then, the particular material may be treated, e.g., heat treated, to recover the mineral. The aqueous thermoplastic polymer dispersion flotation agent may be effective in improving the recovery yield of sulfide mineral ore fines as compared to the flotation agents of the prior art.

For the flotation separation technique, in preparation for flotation process, the ore is comminuted (ground up by such techniques as dry-grinding, wet-grinding, and like techniques) and then dispersed in water to form a suspension known as pulp.

Additives such as a collector that includes one or more collectors may be added to the ore bearing suspension. The suspension may further include in a frother that includes one or more frothers and optionally other auxiliary agents such as regulators, depressors (deactivators) and/or activators, to enhance the selectivity of a flotation stage and facilitate the separation of the select mineral constituent(s) from the other constituents such as unwanted gangue constituents. The pulp, with the other additives such as collector, frother, and optional other auxiliary agents, may be conditioned for a period of time before the aqueous thermoplastic polymer dispersion is added and thereafter treated by a gas, such as air. The treatment with gas includes sparging gas into the mixture of the suspension and aqueous thermoplastic polymer dispersion to produce bubbles. The gas treatment may result in the formation of two separate identifiable layers of the concentrate and the slurry.

In a froth flotation separation technique minerals that adhere to the bubbles as they rise to the surface may be concentrated into a froth (e.g., a froth concentrate layer) that accumulates at the surface of the aerated pulp (e.g., the underlying slurry). The mineral-bearing froth may be skimmed or otherwise removed from the surface and processed further to obtain the desired minerals. The froth flotation processes in which the mineral ores are used, may be those which are well-known in the art. In most of these processes, use of one or more collector may be required.

The beneficiation of ores by flotation may utilize differences in hydrophobicity of various components of the suspension, and these differences in hydrobphobicity may be increased or decreased by judicious choice of chemical additives. In one form, the collector may be a hydrophobic agent, which is selectively engaged to the surface of a particular mineral constituent and increases the hydrophobicity of the mineral constituent. Gas bubbles admitted during the aeration step may preferentially adhere to the hydrophobically modified mineral constituent. Because the modified mineral components have been treated or modified with the collector, they may exhibit sufficiently increased hydrophobicity to be more readily removed from the aerated pulp by the bubbles than are other constituents that are less hydrophobic or hydrophilic. As such, the collector may efficiently pull particular mineral constituents out of the aqueous solution, whereas other constituents of the ore that have not are not modified by the collector may remain suspended in the aqueous phase. This process can also or instead utilize chemicals that increase the hydrophilic properties of materials selected to remain suspended within the aqueous phase.

The comminuted ore may have a wide particle size distribution and in floatation separation process the air bubbles may be tailored for the center of this distribution. Due to the nature of fluid flow around air bubbles, certain large and small particles containing valuable metal may not be collected. For example, large particles may be encased in gangue and/or too high in weight to be accessible for floatation and small particles (such as fines) may not encounter or adsorb to an air bubble. The use of aqueous thermoplastic polymer dispersion is proposed to increase the recovery of fines, whereas the dispersion includes small particles (also referred to as seed particles) of polymeric material well dispersed in an aqueous medium.

The polymeric particles of the aqueous thermoplastic polymer dispersion may be within a mean size range that is relatively close to that of the fines in the ore and may adsorb, attach, and/or adhere to the fines so as to create agglomerated particular material that may be sufficiently large for interaction with air bubbles during flotation separation, without being too large so as not to be accessible for flotation. The small size of the polymer particles may be due to the process used to make the dispersion, e.g., a process that includes use of an extrusion apparatus. Further, as the polymer particles are finely dispersed in an aqueous medium, the dispersion may be usable at a commercial scale flotation separation process. Also, the aqueous thermoplastic polymer dispersion may be stable at the wide temperature and pressure ranges typically found at a commercial scale flotation separation process, which stability typically is not found in a mere mixture of a thermoplastic polymer in an aqueous medium.

The flotation separation process with the addition of the aqueous thermoplastic polymer dispersion may be performed one or more times, e.g., in an initial flotation separation and one or more supplemental flotation separation. In an exemplary embodiment, an initial flotation separation may be performed without the aqueous thermoplastic polymer dispersion directed toward recovering a desired mineral from the medium/large ore particles. Then, one or more supplemental flotation separations may be performed with the aqueous thermoplastic polymer dispersion directed toward recovering the desired mineral from the fines (i.e., smaller ore particles). In other embodiment, at least the initial flotation may be directed toward the recovering the desired mineral from the smaller ore particles and at least one supplemental flotation may be directed toward recovering the desired mineral from the medium/larger ore particles. In other embodiments, the initial flotation separation includes the addition of the aqueous thermoplastic polymer dispersion and is directed toward recovering the desired mineral from both various sized ore particles.

The one or more aqueous thermoplastic polymer dispersions may be directly added to an aqueous suspension of a comminuted mineral ore, which suspension has been pre-treated with a collector and optionally a frother and/or other auxiliary agents. As such the one or more aqueous thermoplastic polymer dispersions may be added after a pre-treatment stage in which the mineral ore is comminated, dispersed in water, and mixed with at least a collector, e.g., such that the thermoplastic polymer dispersion is added to suspension of collector treated comminuted ore. The aqueous thermoplastic polymer dispersion may be added in an effective amount, e.g., in an amount of greater than 0.01, greater than 0.03, and/or greater than 0.04 grams of the aqueous thermoplastic polymer dispersion per kilogram of mineral ore. The aqueous thermoplastic polymer dispersion may be added in an effective amount, e.g., in an amount of less than 5.00, less than 1.00, and/or less than 0.60 grams of the aqueous thermoplastic polymer dispersion per kilogram of mineral ore. In an exemplary embodiment, for forming the particular material, the polymer particles have a mean particle size from 0.2 micron to 50 micron and the fines in the comminuted ore have a mean particle size that is less than 100 microns. The polymer particles in the aqueous thermoplastic polymer dispersion may adhere to specific fines in the comminuted mineral ore, e.g., the seed particles may adhere at least to metal sulphide rich particles to improve the recovery of metal sulphides during flotation separation.

The purification of the particular material recovered in the concentrate may involve removal of the residual polymer dispersion by oxidation in air at temperatures equal to or greater than 500°C. For example, the polymers in the dispersion may be burned in smeltering process, such that a complicated process is not required to remove the polymers from the recovered ore. The flotation separation process may include adding lead nitrate, copper sulfate, and any combination thereof to the suspension.

In exemplary embodiments, a method for the removal of a particular material from a comminuted mineral ore, such as a sulfide mineral ore or an arsenide mineral ore by a flotation separation process may include the stages of: (i) adding an effective amount of an aqueous thermoplastic polymer dispersion to a suspension of collector treated comminuted ore, the aqueous thermoplastic polymer dispersion may be made by extrusion melt blending resulting in thermoplastic polymer particles having a volume average particle size less than 50 micron, (ii) affording the aqueous thermoplastic polymer dispersion sufficient residence time in the suspension of collector treated comminuted ore to form a particular material, (iii) floating the particular material by sparging the suspension to form a concentrate and a slurry, and (iv) recovering the particular material from the appropriate concentrate or slurry.

In an exemplary embodiment, the flotation separation may be a froth flotation separation process that includes and/or consists essentially of the following stages: comminuting mineral ore, forming an aqueous suspension with comminuted ore, treating the aqueous suspension of the comminuted mineral ore with a collector and optionally a frother and/or other auxiliary agents, adding an effective amount of the thermoplastic polymer dispersion disclosed herein to the aqueous suspension, affording the thermoplastic polymer dispersion sufficient residence time in the suspension to form the particular material, selectively floating materials by sparging the suspension to form a concentrate and a slurry, and recovering the desired mineral from the appropriate suspension by removing a frothy concentrate layer above the slurry layer and further processing the frothy concentrate layer.

The frother may be to the suspension at any point within the process prior to recovering the desired material, e.g., the frother may be added prior to adding the aqueous thermoplastic polymer dispersion. Frothers that are suitable for beneficiation of mineral ores by froth flotation may be used. In at least one of the embodiments, the frother contains alcohol. Suitable frothers include some compounds that are useful as collectors such as fatty acids, soaps, and alkyl aryl sulfonates, but the best frothers may be those that have a minimum of collecting properties. Examples are polar-nonpolar molecules of the type C_5 $H_{11}OH$, amyl alcohol or $C_{10}H_{17}OH$, the active constituent of the well-known frother pine oil. The frother may be an alcohol, examples include aliphatic alcohols that have chain lengths of 5 to 8 carbon atoms, provided there is sufficient branching in the chain. Alcohols in the 10 to 12 carbon atom range may be good frothers. Other examples include polyalkylene glycols, polyoxyalkylene paraffins and cresylic acids. Blends of frothers may be used.

In at least one embodiment the flotation process is a direct flotation process and the desired material forms a concentrate at the top of the suspension. In at least one embodiment, the process further involves adding a frother to the suspension at any point within the process prior to recovering the desired material. In at least one of the embodiments, the frother contains alcohol.

In exemplary embodiments, a method for the removal of a particular material from a comminuted mineral ore, such as a sulfide mineral ore or an arsenide mineral ore by a flotation separation process may include the stages of: (i) adding an effective amount of an aqueous thermoplastic polymer dispersion to a suspension of collector treated comminuted ore, the aqueous thermoplastic polymer dispersion may be made by extrusion melt blending resulting in thermoplastic polymer particles having a volume average particle size less than 50 micron, (ii) affording the aqueous thermoplastic polymer dispersion sufficient residence time in the suspension of collector treated comminuted ore to form a particular material, (iii) floating the particular material by sparging the suspension to form a concentrate and a slurry, and (iv) recovering the particular material from the appropriate concentrate or slurry.

Collectors

Of particular interest for collectors for use in flotation separation in the mining industry are ones effective at selectively floating sulfide mineral ore constituents that comprise complexes with valuable metals such as gold, silver, copper, lead, zinc, molybdenum, nickel, platinum, palladium, and other metals. U.S. Patent No. 7,553,984 teaches that organic molecules containing sulfur are useful compounds for the froth flotation of sulfide minerals. Commonly used collectors for most sulfide minerals are sulfur-based chemicals such as xanthates, xanthogen formates, thionocarbamates, dithiophosphates, or mercaptans.

Numerous collectors are known in flotation practice or have been proposed in the technical and patent literature. Examples include xanthates, thiocarbamates, dithiophosphates, thiocarbanilide, xanthogen formates, alkylamines, quaternary ammonium compounds, sulfonates and the like. Specific examples include the sodium, potassium and ammonium forms of xanthates, dithiophosphates, dithiocarbamates and mercaptobenzothiozoles; esters of either thiocarbamate or dithiocarbamate; and dixanthogens. Any collector which is known in the art as suitable for the beneficiation by flotation of mineral ores can be used. Further blends of known collectors can also be used.

In at least one embodiment the collector is a xanthate, a thiocarbamate, a dithiophosphate, a thiocarbanilide, a xanthogen formate, an alkylamine, a quaternary ammonium compound, a sulfonates, or mixtures thereof. Specific examples include the sodium, potassium and ammonium forms of xanthates, dithiophosphates, dithiocarbamates, and mercaptobenzothiozoles; esters of either thiocarbamate or dithiocarbamate; and dixanthogens.

Aqueous Thermoplastic Polymer Dispersion

In embodiments, the aqueous thermoplastic polymer dispersion is pre-formed, i.e., formed prior to being added to an aqueous suspension of a comminuted mineral ore. The aqueous thermoplastic polymer dispersion may be derived from the melt blending of (a) a thermoplastic polymer that includes one or more different thermoplastic polymers in the presence of (b) a dispersing agent that includes one or more different dispersing agents, and (c) water. By dispersion it is meant a material having a continuous liquid phase component at ambient conditions of room temperature and atmospheric pressure and is derived from a liquid phase (such as water and/or dispersing agents) and a solid phase such as thermoplastic polymers and/or dispersing agents). The dispersion may be enabled by BLUEWAVE™ Technology, which is a proprietary and patented mechanical-dispersion technology that is a trademark of The Dow Chemical Company or an affiliated company of The Dow Chemical Company.

The thermoplastic polymer may comprise one or more of the following: an olefin block copolymer (for example see USP 8,455,576; 7,579,408; 7,355,089; 7,524,911; 7,514,517; 7,582,716; and 7,504,347), a linear ethylene polymer (USP 3,645,992;4,937,299; 4,701,432; 4,937,301; 4,935,397; and 5,055,438, EP 129368 and 260999; and WO 90/07526), a substantially linear ethylene polymer (USP 5,272,236 and 5,278,272), a random olefin copolymer, a polyethylene, a polypropylene, ethylene α-olefin copolymer, a non-conjugated dienes based copolymers, an ethylene-vinyl acetate, an ethylene-vinyl alcohol, a chlorinated polyethylene, an alcohol functionalized polyolefin, an amine functional polyolefin, a silane grafted polyolefin, a polyurethane (PU), an acrylic, an epoxy, an alkylds, a phenolic, a polyester, silicones, or nylons. For example, the thermoplastic polymer may be a polyolefin such as a polyethylene, a polypropylene, an olefin block copolymer, or a random olefin copolymer.

The thermoplastic polymer that is a polyolefin may be derived from one or more C_2 to C_8 olefins, so as to form a C_2 to C_8 olefin based polyolefin polymer dispersion. The thermoplastic polymer may be a high density polyethylene having a density that is at least 0.950 g/cm^3. The thermoplastic polymer may be a high density polyethylene having a density up to 0.960 g/cm^3. The thermoplastic polymer may have a melt flow rate (MFR) determined at 190°C under a load of 2.16Kg that is at least 8.0 g/10 min. The thermoplastic polymer may have a melt flow rate (MFR) determined at 190°C under a load of 2.16Kg that is up to 9.0 g/10 min. The thermoplastic polymer may have a Shore D hardness of at least 50.

The aqueous thermoplastic polymer dispersion is prepared in the presence of a dispersing agent (or stabilizing agent), e.g., to promote the formation of a stable dispersions. In selected embodiments, the stabilizing agent may be a surfactant, a polymer (different from the thermoplastic polymer detailed above), or mixtures thereof. In certain embodiments, the polymer may be a polar polymer, having a polar group as either a comonomer or grafted monomer. Examples of suitable polar polyolefin are ethylene-vinyl acetate, ethylene-vinyl alcohol, chlorinated polyethylene, alcohol or amine functional polyolefin, silane grafted polyolefin. In exemplary embodiments, the stabilizing agent comprises one or more polar polyolefins, having a polar group as either a comonomer or grafted monomer. For example, the dispersing agent may include an ethylene/alpha-beta unsaturated carboxylic acid copolymer. In some embodiments, the ethylene/alpha-beta unsaturated carboxylic acid copolymer may include an ethylene-acid copolymer, such as an ethylene-acrylic acid copolymer or an ethylene methacrylic acid copolymer.

Typical dispersing agent polymers include ethylene-acrylic acid (EAA) and ethylene-methacrylic acid copolymers, such as those available under the trademarks PRIMACOR™ (trademark of SK Global Chemical), NUCREL™ (trademark of E.I. DuPont de Nemours), and ESCOR™ (trademark of ExxonMobil) and described in USP

4,599,392; 4,988,781; and 5,938,437, each of which is incorporated herein by reference in its entirety. Other polymers include ethylene-methacrylic acid (EMA), ethylene ethyl acrylate (EEA) copolymer, ethylene methyl methacrylate (EMMA), and ethylene butyl acrylate (EBA). Other ethylene-carboxylic acid copolymer may also be used. Those having ordinary skill in the art will recognize that a number of other useful polymers may also be used.

Other surfactants that may be used as the dispersing agent include long chain fatty acids or fatty acid salts having from 12 to 60 carbon atoms. In other embodiments, the long chain fatty acid or fatty acid salt may have from 12 to 40 carbon atoms.

If the polar group of the polymer is acidic or basic in nature, the stabilizing polymer may be partially or fully neutralized with a neutralizing agent to form the corresponding salt. In certain embodiments, neutralization of the stabilizing agent, such as a long chain fatty acid or EAA, may be from 25% to 200% on a molar basis; from 50% to 110% on a molar basis in other embodiments. For example, for EAA, the neutralizing agent is a base, such as ammonium hydroxide or potassium hydroxide, for example. Other neutralizing agents may include lithium hydroxide or sodium hydroxide, for example. Those having ordinary skill in the art will appreciate that the selection of an appropriate neutralizing agent depends on the specific composition formulated, and that such a choice is within the knowledge of those of ordinary skill in the art.

Additional surfactants that may be useful in the thermoplastic polymer dispersions include cationic surfactants, anionic surfactants, zwitterionic, or non-ionic surfactants. Examples of anionic surfactants include sulfonates, carboxylates, and phosphates. Examples of cationic surfactants include quaternary amines. Examples of non-ionic surfactants include block copolymers containing ethylene oxide and silicone surfactants. Surfactants useful in the practice of the present invention may be either external surfactants or internal surfactants. External surfactants are surfactants that do not become chemically reacted into the polymer during dispersion preparation. Examples of external surfactants useful herein include salts of dodecyl benzene sulfonic acid and lauryl sulfonic acid salt. Internal surfactants are surfactants that do become chemically reacted into the polymer during dispersion preparation. An example of an internal surfactant useful herein includes 2,2-dimethylol propionic acid and its salts.

In particular embodiments, the dispersing agent or stabilizing agent may be used in an amount ranging from greater than zero to about 60% by weight based on the amount of base polymer (or base polymer mixture) used. For example, long chain fatty acids or salts thereof may be used in an amount ranging from 0.5% to 10% by weight based on the amount of base polymer. In other embodiments, ethylene-acrylic acid or ethylene-methacrylic acid copolymers may be used in an amount from 0.5% to 60% by weight based on polymer. In yet other embodiments, sulfonic acid salts may be used in an amount from 0.5% to 10% by weight based on the amount of base polymer.

In yet another embodiment, acrylic polymers or ethylene oxide-propylene oxide polymers may be used in an amount from 0.5% to 15% by weight based on the amount of base polymer.

The dispersion may be prepared with a polymer composition that includes: from 20 wt% to 95 wt% (e.g., 30 wt% to 90 wt%, 40 wt% to 90 wt%, 50 wt% to 85 wt%, 60 wt% to 85 wt%, 70 wt% to 80 wt%, etc.) of polyolefin derived from one or more C_2 to C_8 olefins (such as polyethylene), from 2 wt% to 30 wt% (e.g., 5 wt% to 25 wt%, 10 wt% to 20 wt%, etc.) of an ethylene oxide-propylene copolymer, and from 2 wt% to 30 wt% (e.g., 5 wt% to 25 wt%, 5 wt% to 20 wt%, 5 wt% to 15 wt%, etc.) of a functionalized polyolefin derived from one or more C_2 to C_8 olefins (such as an anhydride grafted polyethylene).

The thermoplastic polymer of the aqueous thermoplastic polymer dispersion may have an advantageous particle size distribution. For example, the dispersed thermoplastic polymer has a volume average particle size equal to or greater than 0.1 μm, equal to or greater than 0.2 μm, equal to or greater than 0.5 μm, equal to or greater than 1 μm, and/or equal to or greater than 10 μm. The dispersed thermoplastic polymer may have a volume average particle size equal to or less than 100 μm, equal to or less than 50 μm, and/or equal to or less than 25 μm. The dispersed thermoplastic polymer may have a dispersity defined as (D90-D10)/D50 where the D# value is defined as the size at which #% of the volume of the particles are smaller than the D# value. In particular embodiments, the dispersed thermoplastic polymer has a dispersity less than 3, less than 2, and/or less than 1.5.

In exemplary embodiments, the polymer particles (i.e., seed particles) in the thermoplastic polymer dispersion may have a mean particle size ranging from 0.2 micron to 100 micron (e.g., 0.2 micron to 80 micron, 0.2 micron to 50 micron, 1 micron to 50 micron, 0.2 micron to 40 micron, 1 micron to 40 micron, 5 micron to 40 micron, 0.2 micron to 30 micron, 1 micron to 30 micron, 5 micron to 30 micron, 10 micron to 30 micron, 15 micron to 30 micron, 20 micron to 25 micron, etc.) Particle sizes less than 0.2 micron may cause health and safety concerns and may be too small to provide efficient adhesive between multiple ore particles (e.g. may not provide sufficient agglomeration with the desired fines in the ore). Particles sizes less than 100 microns may be too large to efficiently float in the flotation separation process. For particles that are not spherical the diameter of the particle is the average of the long and short axes of the particle. Particle sizes can be measured on a Coulter LS230 light-scattering particle size analyzer or other suitable device.

The dispersion may have a total solids concentration from 1 wt% to 80 wt% (e.g, 1 wt% to 70 wt%, 5 wt% to 70 wt%, 10 wt% to 70 wt%, 20 wt% to 70 wt%, 20 wt% to 60 wt%, 30 wt% to 60 wt%, 40 wt% to 55 wt%, 40 wt% to 50 wt%, 45 wt% to 50 wt%, etc.) based on a total weight of the aqueous thermoplastic polymer dispersion.

The dispersion may have a pH equal to or greater than 5, equal to or greater than 8, and/or equal to or greater than 9. The dispersions may have a pH equal to or less than 13.5, equal to or less than 13, equal to or less than 12, equal to or less than 11, and/or equal to or less than 10.

Processes for Making Aqueous Thermoplastic Polymer Dispersion

While any method may be used, one convenient way to prepare the thermoplastic polymer dispersions described herein is by a mechanical process, e.g., by melt-kneading (such as any melt-kneading means known in the art). The melt-kneading may be conducted under the conditions which are typically used for melt-kneading the thermoplastic resin. They technology may utilize a high-shear mechanical process that may work by taking traditional thermoplastic resin and breaking the resin up into submicron particles. In some embodiments a kneader, a Banbury mixer, single-screw extruder, or a multi-screw extruder is used. A process for producing the dispersions in accordance with the present invention is not particularly limited.

One exemplary process, for example, is a process comprising melt-kneading the thermoplastic polymer and the dispersing agent, and any other additives according to USP 5,756,659; 7,763,676; and 7,935,755. For example, the process of producing the aqueous thermoplastic dispersion includes: (1) melt kneading (A) at least one thermoplastic resin and (B) at least one dispersing agent, to produce a melt-kneaded product and (2) diluting said melt-kneaded product.

A melt-kneading machine is, e.g., a multi screw extruder having two or more screws, to which a kneading block can be added at any position of the screws. If desired, the extruder may be provided with a first material-supplying inlet and a second material-supplying inlet, and further third and fourth material-supplying inlets in this order from the upper stream to the downstream along the flow direction of a material to be kneaded. Further, if desired, a vacuum vent may be added at an optional position of the extruder. In some embodiments, the thermoplastic polymer dispersion comprising the thermoplastic polymer, dispersing agent, and any other additives is first diluted to contain approximate 1 to approximately 3 percent by weight of water and then subsequently further diluted to comprise greater than 25 percent by weight of water. In some embodiments, the further dilution provides a dispersion with at least about 30 percent by weight of water. The aqueous dispersion obtained by the melt kneading may be further supplemented with a glycol, such as ethylene glycol. The aqueous thermoplastic depressant dispersions described hereinabove may be used as prepared or diluted further with additional water and/or glycol.

FIG. 1 schematically illustrates an exemplary extrusion apparatus that can be used in the preparation of the thermoplastic polymer dispersion. An extruder **20**, such as a twin screw extruder, is coupled to a back pressure regulator, melt pump, or gear pump, **30**. The apparatus may further comprise a base reservoir **40** and an initial water reservoir **50**, each of which includes a pump (not shown). Desired amounts of base and initial water are provided from the base reservoir **40** and the initial water reservoir **50**, respectively. Any suitable pump may be used, but in some embodiments a pump that provides a flow of approximately 150 cc/min at a pressure of 240 bar may be used to provide the base and the initial water to the extruder **20**. In other embodiments, a liquid injection pump provides a flow of 300 cc/min at 200 bar or 600 cc/min at 133 bar. In some embodiments the base and initial water are preheated in a preheater.

The thermoplastic polymer, in the form of pellets, powder, or flakes, is fed from the feeder **80** to an inlet **90** of the extruder **20** where the resin is melted or compounded. The dispersing agent and/or stabilizing agent is added to the resin through an opening along with the resin and in other embodiments, the dispersing agent and/or stabilizing agent is provided separately to the twin screw extruder **20**. The resin melt is then delivered from the mix and convey zone to an emulsification zone of the extruder where the initial amount of water and base from the reservoirs **40** and **50** is added through inlet **55**. In some embodiments, dispersing agent may be added additionally or exclusively to the water stream. In some embodiments, the emulsified mixture is further diluted with additional water and/or glycol and/or stabilizing agent via inlet **95** from reservoir **60** in a dilution and cooling zone of the extruder **20**. Typically, the dispersion is diluted to at least 30 weight percent water in the cooling zone. In addition, the diluted mixture may be diluted any number of times until the desired dilution level is achieved.

In one embodiment of the method to make the aqueous thermoplastic polymer dispersions, step a, all of the thermoplastic polymer, the dispersing agent, and water are combined to form an aqueous dispersion of thermoplastic polymer in one step.

In a another embodiment of the method to make the aqueous thermoplastic polymer dispersions, some or all of the water and/or stabilizing agent is not added into the twin screw extruder **20** but rather, step b, to a stream containing the dispersed polymer after it has exited from the extruder. In other words, step b does not occur in the extruder in which the aqueous dispersion of thermoplastic polymer is produced. In this manner, steam pressure build-up in the extruder **20** is minimized.

In exemplary embodiment, a basic substance or aqueous solution, dispersion or slurry thereof is added to the dispersion at any point of the process, such as to the extruder. Typically the basic substance is added as an aqueous solution. But in some embodiments, it is added in other convenient forms, such as pellets or granules. In some embodiments, the basic substance and water are added through separate inlets of the extruder. Examples of the basic substance which may be used for the neutralization or the saponification in the melt kneading process include alkaline metals and alkaline earth metals such as sodium, potassium, calcium, strontium, barium; inorganic amines such as hydroxylamine or hydrazine; organic amines such as methylamine, ethylamine, ethanolamine, cyclohexylamine, tetramethylammonium hydroxide; oxide, hydroxide, and hydride of alkaline metals and alkaline earth metals such as sodium oxide, sodium peroxide, potassium oxide, potassium peroxide, calcium oxide, strontium oxide, barium oxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, sodium hydride, potassium hydride, calcium hydride; and weak acid salts of alkaline metals and alkaline earth metals such as sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, calcium hydrogencarbonate, sodium acetate, potassium acetate, calcium acetate; or ammonium hydroxide. In particular embodiments, the basic substance is a hydroxide of an alkaline metal or a hydroxide of an alkali metal. In some embodiments, the basic substance is selected from potassium hydroxide, sodium hydroxide and combinations thereof.

In one embodiment of the method described herein above, the thermoplastic polymer dispersion comprises: (a) a thermoplastic polymer, (b) a dispersing agent, (c) water, and (d) a base. The thermoplastic polymer may be one or more of an olefin block copolymer, a random olefin copolymer, a polyethylene, a polypropylene, a propylene, ethylene, α-olefin, a non-conjugated dienes based copolymers, an ethylene-vinyl acetate, an ethylene-vinyl alcohol, a chlorinated polyethylene, an alcohol functionalized polyolefin, an amine functional polyolefin, or a silane grafted polyolefin. The dispersing agent may be a fatty acid/salt having the formula R_1COOR_2 wherein R_1 is a straight chain, saturated or unsaturated, hydrocarbon radical of 8 to 25 carbon atoms and R_2 is H or a base-forming radical; an alkyl, arene and/or alkylarene sulfonate; a salt of a polymer of alkyl acrylate and/or alkyl methacrylate and acrylic and/or methacrylic acid, or a salt of partial esters of maleic anhydride-styrene copolymers; a cationic surfactant; a zwitterionic surfactant; or a nonionic surfactant. For example, the dispersing agent may be ethylene acrylic acid (EAA), ethylene-methacrylic acid (EMA), ethylene ethyl acrylate (EEA) copolymer, ethylene methyl methacrylate (EMMA), or ethylene butyl acrylate (EBA).

In one embodiment of the method described herein above, the thermoplastic polymer dispersion is made by: A) adding the thermoplastic polymer (a) and dispersing agent (b) to an extruder having a mix and convey zone, an emulsification zone, and a dilution and cooling zone, B) forming a resin melt by melt kneading (a) and

(b) together in the mix and convey zone; C) delivering the resin melt to the emulsification zone; D) adding water (c) and the base (d) to the resin melt in the emulsification zone to form an aqueous dispersion of the thermoplastic composition, E) passing the aqueous dispersion of the thermoplastic composition through the dilution and cooling zone, and F) forming the aqueous thermoplastic polymer dispersion.

In one embodiment of the process of the present invention, the thermoplastic polymer dispersion comprises, consists essentially of, or consisting of: (a) a thermoplastic polymer, e.g., in an amount of from 12 to 50 weight percent; (b) a dispersing agent, e.g., in an amount of from 1 to 10 weight percent; said dispersing agent is a fatty acid/salt having the formula R_1COOR_2 wherein R_1 is a straight chain, saturated or unsaturated, hydrocarbon radical of 8 to 25 carbon atoms and R_2 is H or a base-forming radical; an alkyl, arene and/or alkylarene sulfonate; a salt of a polymer of alkyl acrylate and/or alkyl methacrylate and acrylic and/or methacrylic acid, or a salt of partial esters of maleic anhydride-styrene copolymers; a cationic surfactant; a zwitterionic surfactant; or a nonionic surfactant; (c) water; and (d) a base; and comprises the stages of: (A) adding the thermoplastic composition (i) and dispersing agent (ii) to an extruder having a mix and convey zone, an emulsification zone, and a dilution and cooling zone; (B) forming a resin melt by melt kneading (a) and (b) together in the mix and convey zone; (C) delivering the resin melt to the emulsification zone; (D) adding water (c) and the base (d) to the resin melt in the emulsification zone to form an aqueous dispersion of the thermoplastic composition; (E) passing the aqueous dispersion of the thermoplastic composition through the dilution and cooling zone; and (F) forming the aqueous thermoplastic polymer dispersion.

In one embodiment of the process described herein above, the extruder consists of the extruder coupled to a back pressure regulator, melt pump, or gear pump wherein the convey zone has an inlet fed by a feeder, the emulsification zone has an inlet fed by a base reservoir and a water reservoir, and the dilution and cooling zone has an inlet fed by a reservoir.

In one embodiment of the process described herein above, the aqueous thermoplastic polymer dispersion exits the cooling zone of the extruder at atmospheric pressure.

Evaluation

Any suitable method to determine the effectiveness of the aqueous thermoplastic polymer dispersion in a flotation separation process is acceptable. An exemplary lab scale test can include the following steps in sequence (i) preparation of a dispersion of the fines in water, (ii) addition of a collector molecule to this dispersion followed by mixing for a period of time to allow the collector molecule to bind to the ore-bearing fines, (iii) addition of the aqueous thermoplastic polymer dispersion to the dispersion generated in (ii) followed by mixing for a period of time to allow the ore-bearing fines to aggregate with the aqueous thermoplastic polymer dispersion, (iv) size-based filtration of the dispersion generated in (iii) to isolate the aggregated ore-bearing fines, (v) removing the aqueous thermoplastic polymer dispersion from the aggregated ore-bearing fines by heating them under air (oxidizing) in an oven at sufficiently high temperature, and (vi) measuring the concentration of the base metal or precious metal in the residual ore-bearing fines from (v) by X-ray Fluorescence (XRF),Inductively Coupled Plasma–Mass Spectroscopy (ICP-MS) or atomic absorption spectrometry (AAS) techniques, in a froth floatation cell such as Edemet MODEL CFLE-3.3 flotation cell or lab scale flotation cells produced by Brastorno or Metso/Denver. However, one skilled in the art would recognize other floatation cells would be appropriate as well. Characterization of samples from such flotation cells can be conducted using common XRF, AAS and/or ICP-MS techniques.

Without intending to be bound by this theory, it is believed that the thermoplastic polymer dispersion may enhance the flotation separation process by means of particles from the thermoplastic polymer dispersion adsorbing to the collectors attached to the fine particles that contain the desired base metal or precious metal. Each polymer particle that adsorbs one more mineral particles creates an agglomerate with a larger particle size than any of its constituents such that the agglomerate is in the appropriate size range to attach to an air bubble and be transported to the concentrate. Since aggregate formation is believed to be driven by adsorption of the ore particles on small polymer particles in the thermoplastic polymer dispersions, it is expected that the particle size distribution and the surface properties of both the ore particles and the dispersion would be important for this process. The surface properties can be quantified in terms of the surface energy, surface tension, zeta potential, Hamaker constant, or a combination thereof. They can be varied for the ore particles by changing the chemical composition of the collector molecule. They can be varied for the polyolefin dispersions by changing the chemical composition of particle, the chemical composition of the dispersing agent (including the use of blends of dispersing agents), and the concentration of the dispersing agent.

In at least one embodiment, the thermoplastic polymer dispersion increases the purity of the removed metal sulfide. Due to the range of mineral concentrations in naturally occurring ores along with the inherent rarity/value associated with the different types of metals in these ores, the thermoplastic polymer dispersion may be added to the flotation cells from between 0.5 ppm on polymer to ore weight ratio to at 1 to 1 weight ratio of polymer to ore.

Definitions

For purposes of this application the definition of these terms is as follows:

"Base metal" means a valuable metal that includes, but is not limited to, copper, lead, zinc, molybdenum, nickel, and any combination thereof.

"Collector" means a composition of matter that selectively adheres to a particular mineral constituent from ore and facilitates the adhesion of the particular mineral to the bubbles that result from the sparging of an ore bearing aqueous suspension.

"Comminuted" means powdered, pulverized, ground, or otherwise rendered into fine particles.

"Concentrate" means the portion of a comminuted ore which is separated by flotation and may be collected within the froth.

"Frother" means a composition of matter that enhances the formation of the bubbles and/or preserves the formed bubbles bearing the fine hydrophobic mineral fraction that results from the sparging of an ore bearing aqueous suspension.

"Precious metal" means a valuable metal which include, but is not limited to gold, silver, platinum, palladium, and any combination thereof.

"Supplemental Flotation" means at least one additional flotation separation process performed on an ore containing more than one desired material, which is performed after at least some of the gangue constituent has been removed from the ore material by a previous froth flotation separation process, and is performed to separate is at least one of the desired ore materials from another.

"Slurry" means the portion of a medium that contained comminuted ore that has undergone gas sparging that is below the concentrate.

"Sparging" means the introduction of gas into a liquid for the purpose of creating a plurality of bubbles that migrate up the liquid.

"Sulfide mineral ore" means an ore comprising at least one metal that forms a complex comprising a crystal structure between the metal and a chalcogen element (Group 16 in the periodic table of elements) including sulfur, tellurium, and selenium. Such minerals include but are not limited to, pyrite, arsenopyrite, pyrrhotite, stibnite, chalcopyrite, bornite, chalcocite, covellite, galena, sphalerite, molybdenite, pentlandite, cooperite, braggite, platarsite, moncheite the metal includes but is not limited to base metals and precious metals.

“Arsenide mineral ore” other minerals of interest can include arsenides with base or precious metals such as sperrylite, palladoarsenide, arsenopalladinite, stillwaterite, vincentite, palladodymite, and tornroosite.

“Fines” as used herein is any base or precious metal mineral containing ore that is below the particle size range that is removed by the flotation process, where the actual particle size will vary by target mineral, gangue minerals present in the ore, comminuting process, and flotation operation, but is generally, although not limited to, particles having an mean particle size that is less than 100 microns, less than 50 microns, less than 40 microns, less than 30 microns, less than 20 microns, and/or less than 10 microns.

In the event that the above definitions or a description stated elsewhere in this application is inconsistent with a meaning (explicit or implicit) which is commonly used, in a dictionary, or stated in a source incorporated by reference into this application, the application and the claim terms in particular are understood to be construed according to the definition or description in this application, and not according to the common definition, dictionary definition, or the definition that is incorporated by reference.

The foregoing may be better understood by the following Examples, which are presented for purposes of illustration and are not intended to limit the scope of this invention.

EXAMPLES

Approximate properties, characters, parameters, etc., are provided below with respect to the illustrative working examples, comparative examples, and the information used in the reported results for the working and comparative examples.

Preparation of Aqueous Thermoplastic Polymer Dispersion

The aqueous thermoplastic polymer dispersion is prepared with a polyolefin polymer, a dispersing agent, a compatibilizer agent, water, and the compatibilizer is neutralized with dimethylethanolamine (DMEA). The aqueous thermoplastic polymer dispersion is prepared using the method as described in USP 7,763,676. The specific composition, processing parameters, and characterizations for the aqueous thermoplastic polymer dispersion of Example 1 are given in Table 1.

The following components are used:

"EO-PO" is an ethylene oxide (EO) propylene oxide (PO) copolymer with 80% EO and 20% PO having a number average molecular weight of approximately 14,600, which is available as PLURONIC™ F-108 from BASF;

"HDPE" is a high density polyethylene having a density of 0.965 g/cm^3, an 8.3 g/10 min melt flow rate (MFR) determined at 190°C under a load of 2.16Kg, a melting temperature of 133°C, and a Shore D hardness of 61, which is available as DOW™ DMDA-8007 NT High Density Polyethylene Resin from The Dow Chemical Company; and

"Compatibilizer" is a maleic anhydride grafted polyethylene wax, which is available as LICOCENE™ 4351 from Clariant.

The extruder based mechanical dispersion process imparts high shear on a polymer melt/water mixture to facilitate a water continuous system with small polymer particles in the presence of surface active agents that reduce the surface tension between the polymer melt and water. A high solids content water continuous dispersion is formed in the emulsification zone of the extruder also known as high internal phase emulsion (HIPE) zone, which is then gradually diluted to the desired solids concentration, as the HIPE progresses from the emulsification zone to the first and second dilution zones.

The polyolefin polymer (HDPE) is fed into the feed throat of the extruder by means of a loss-in weight feeder. The dispersant (EO-PO) and compatibilizer (LICOCENE) are added with the polyolefin polymer. The extruder and its elements are made of Nitrided Carbon Steel. The extruder screw elements are chosen to perform different unit operations as the ingredients pass down the length of the screw. There is first a mixing and conveying zone, next an emulsification zone, and finally a dilution and cooling zone. Steam pressure at the feed end is contained by placing kneading blocks and blister elements between the melt mixing zone and is contained and controlled by using a Back-Pressure Regulator. ISCO dual-syringe pumps metered the Initial Water, Base, and Dilution flows to their respective injection ports. The polyolefin, dispersing agent, compatibilizer and water are melt kneaded in the twin screw extruder at a screw RPM of 450 and the compatibilizer is neutralized with dimethyethanolamine (DMEA).

Table 1

	Example 1
POLYMER COMPOSITION	
HDPE, wt %	75
EO-PO, wt %	15
Compatibilizer, wt %	10
ADJUSTMENT	
Base	DMEA
Degree of Neutralization, %	120
PROCESS PARAMETERS	
Total Polymer Composition Flow Rate (lbs/hr)	10
Initial Water Flow Rate (mL/min)	15

Dilution Water Flow Rate (mL/min)	98
Base Flow Rate (mL/min)	0.7
Extruder Pressure, psi	230
Dispersion Temperature, °C	170
DISPERSION CHARACTERISTICS	
Mean particle size, micron	22
pH	9.01
Solids Concentration, wt%	47
Dispersity (D90-D10)/D50	1.5

Referring to Table 1, the mean particle size of the dispersed polymer phase is measured by a Coulter LS230 particle analyzer consisted of an average volume diameter in microns. Solids are determined by moisture analyzer.

Evaluation of Flotation Separation

Referring to Table 2, samples of copper sulfide ore containing 0.86 wt% copper from the Coyancura mine in Chile with a mean volume average particle diameter less than 50 μm are evaluated in an exemplary flotation separation technique. For the flotation separation, added to the flotation cell are the following: copper sulfide ore, 50 ppm of a standard xanthate collector, 25 ppm of a standard methyl isobutyl carbinol frother, and the aqueous thermoplastic polymer dispersion from Example 1 are added. The result samples from the flotation separation are evaluated for the recovery of copper at different loadings of the thermoplastic polymer dispersion from Example 1. The copper content in this ore is measured by X-ray Fluorescence (XRF). Percent recovery of copper from a concentrate layer is determined using a Denver froth floatation cell. Characterization is conducted using atomic absorption spectrometry and the results are reported in grams recovered and wt% recovered in Table 2

Table 2

Seed Particle Loading (grams of Example 1/kilograms of ore)	Cu Recovery (grams)	Cu Recovery (wt%)
0	3.22	44.3
0.05	3.52	47.2
0.5	3.66	49.7

Referring to Table 2, it is seen that the recovery of copper from the ore during flotation separation is further improved by use of the aqueous thermoplastic polymer dispersion. Accordingly, it has been unexpectedly found that by adding finely dispersed polymers in the form of a dispersion to a suspension of comminuted ore, recovery of valuable particles can be further improved so as to improve the effectiveness of the flotation separation process. For example, use of the aqueous thermoplastic polymer dispersion may increase the weight percent recovery of cooper from a copper sulfide ore by at least 2 wt%, which on a commercial scale in the mining industry can be interpreted as a significant improvement.

What is claimed is:

1. A flotation separation method that removes a mineral from comminuted ore, the method comprising the stages of:

(i) providing a suspension of the comminuted ore and a collector;

(ii) adding an aqueous thermoplastic polymer dispersion that is different from the collector to the suspension of the comminuted ore and the collector to form a mixture, a polymer particle from the aqueous thermoplastic polymer dispersion and a mineral from the comminuted ore forming a particular material in the mixture;

(iii) sparging the mixture with a gas to form a concentrate that includes the particular material and a slurry; and

(iv) recovering the mineral from the concentrate.

2. The method as claimed in claim 1, wherein:

the aqueous thermoplastic polymer dispersion includes a plurality of polymer particles that have a mean particle size from 0.2 micron to 50 micron, the polymer particle from the aqueous thermoplastic polymer dispersion that forms the particular material being one of the plurality of polymer particles, and

the comminuted ore includes a plurality of minerals that have a mean particle size that is less than 100 microns, the mineral from the comminuted ore that forms the particular material being one of the plurality of minerals.

3. The method as claimed in claim 1 or claim 2, wherein the aqueous thermoplastic polymer dispersion has a total solids concentration from 20 wt% to 70 wt%, based on a total weight of the aqueous thermoplastic polymer dispersion.

4. The method as claimed in any one of claims 1 to 3, further comprising preparing the aqueous thermoplastic polymer dispersion by adding at least a thermoplastic polymer, a dispersing agent, and water to an extrusion apparatus, the aqueous thermoplastic polymer dispersion being pre-formed so as to be prepared prior to forming the mixture.

5. The method as claimed in claim 4, wherein the thermoplastic polymer is a polyolefin.

6. The method as claimed in claim 4 or claim 5, wherein the thermoplastic polymer is melted or compounded in the extrusion apparatus to form the aqueous thermoplastic polymer dispersion.

7. The method as claimed in claim 4 or claim 5, wherein the aqueous thermoplastic polymer dispersion is prepared by

a) adding the thermoplastic polymer and the dispersing agent to an extruder in the extrusion apparatus, the extruder having a mix and convey zone, an emulsification zone, and a dilution and cooling zone,

b) forming a resin melt by melt kneading at least the thermoplastic polymer and the dispersing agent in the mix and convey zone,

c) delivering the resin melt to the emulsification zone,

d) adding at least water to the resin melt in the emulsification zone to form an aqueous dispersion of a thermoplastic composition,

e) passing the aqueous dispersion of the thermoplastic composition through the dilution and cooling zone, and

f) forming the aqueous thermoplastic polymer dispersion.

8. The method as claimed in any one of claims 1 to 7, further comprising:

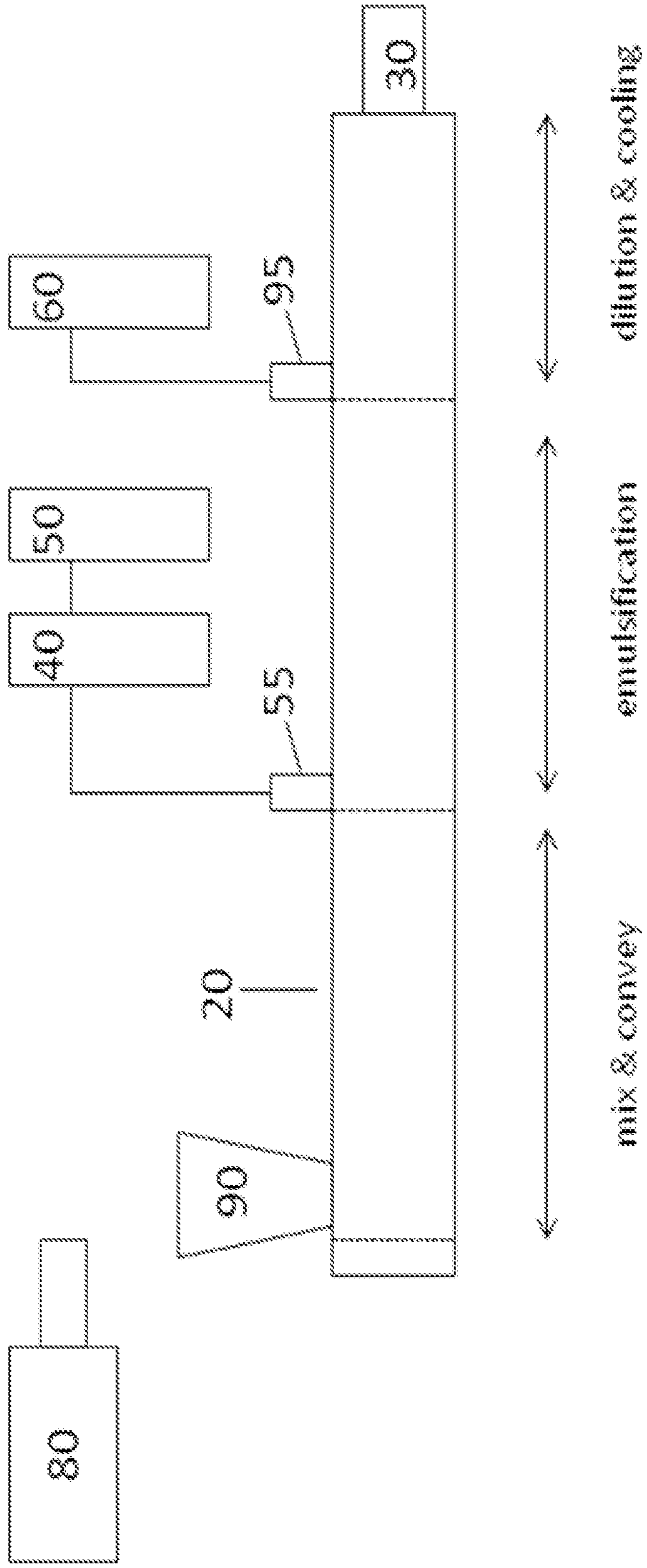
preparing the suspension of the comminuted ore by comminuting ore and forming an aqueous suspension with the comminuted ore, and

adding the collector to the suspension of the comminuted ore.

9. The method as claimed any one of claims 1 to 8, further comprising adding a frother to the suspension of the comminuted ore prior to adding the aqueous thermoplastic polymer dispersion to the suspension of the comminuted ore and the collector.

10. The method as claimed any one of claims 1 to 9, wherein recovering the mineral from the concentrate includes heating the particular material to separate the polymer particle from the mineral.

FIG. 1


80
90
20
40
50
55
60
95
30
mix & convey
emulsification
dilution & cooling

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/063961

A. CLASSIFICATION OF SUBJECT MATTER
INV. B03D1/02
ADD. B03D103/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B03D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 339 337 A (ENGELHARD MIN & CHEM) 5 December 1973 (1973-12-05) examples V,VI	1-4,6-10
X	RU 2 099 146 C1 (TOM POLITEKHN UNI [SU]) 20 December 1997 (1997-12-20) claim 1	1-10
X	XIANGFENG ZHANG ET AL: "The Effect of Polystyrene on the Carrier Flotation of Fine Smithsonite", MINERALS, vol. 7, no. 4, 29 March 2017 (2017-03-29), page 52, XP055565922, DOI: 10.3390/min7040052 page 1 - page 2	1,3,4, 6-10

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
8 March 2019

Date of mailing of the international search report
20/03/2019

Name and mailing address of the ISA/
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Form PCT/ISA/210 (second sheet) (April 2005)

International application No
PCT/US2018/063961

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JORGE RUBIO ET AL: "The process of separation of fine mineral particles by flotation with hydrophobic polymeric carrier", INTERNATIONAL JOURNAL OF MINERAL PROCESSING, vol. 37, no. 1-2, 1 January 1993 (1993-01-01), pages 109-122, XP055049003, ISSN: 0301-7516, DOI: 10.1016/0301-7516(93)90008-X page 11 - page 113 -----	1,3-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2018/063961

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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RU 2099146 C1	20-12-1997	NONE	