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(54) A process for agglomerating mineral ore concentrate utilizing emulsions of polymer, binders or dry polymer binders.

(57) This invention is a method for agglomerating mineral ore concentrate comprising the commingling of mineral ore concentrate with a binding amount of a water soluble, high molecular weight polymer. The selected polymer is applied to the mineral ore concentrate either (1) dispersed in a water-in-oil emulsion or (2) as a dry powder. The most preferred polymers are water soluble poly(acrylamide) based polymers.

86401065.7

A PROCESS FOR AGGLOMERATING MINERAL ORE CONCENTRATE UTILIZING EMULSIONS OF POLYMER BINDERS OR DRY POLYMER BINDERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to methods for agglomerating or pelletizing mineral ore concentrate. More specifically, this invention relates to methods for agglomerating or pelletizing mineral ore concentrate using water soluble, high molecular weight polymer binder systems in either water-in-oil emulsions or as a dry powder.

2. Description of the Prior Art

It is customary in the mining industry to agglomerate or pelletize finely ground mineral ore concentrate so as to further facilitate the handling and shipping of the ore. Mineral ore concentrates can include iron oxides, copper oxides, barytes, lead and zinc sulfides, and nickel sulfides. Agglomerates of coal dust and nonmetalic minerals used to make bricks or ceramics are also formed. Agglomerate forms can include pellets, briquettes, and sinters.

Methods of pelletizing mineral ore concentrate are frequently used in mining operations where the ore is a low grade iron ore. Examples of low grade iron ores are taconite, hematite, and magnetite. Numerous other low grade ores exist wherein pelletizing of the ground particles is beneficial to the handling and shipment of the mineral ore. After the mineral ore has been mined, it is frequently ground and screened to remove large particles which are recycled for further grinding. Typically, an ore is passed through a 100 mesh (0.149mm) screen. The screened mineral ore is known as a "concentrate".

For example, taconite mineral ore concentrate after grinding and screening has an average moisture content of between about 6 to about 10 percent. The moisture content of the mineral ore concentrate can be selectively altered. The moisture content affects the strength of the pellets that are formed later in the process.

After screening, the mineral ore concentrate is transported on a first conveyor means to a balling drum or another means for pelletizing mineral ore concentrate. Prior to entering the balling drum, a binding agent is applied or mixed into the mineral ore concentrate. Commingling the binding agent with the mineral ore concentrate occurs both on the conveyor means and in the means for pelletizing. The binding agents hold the mineral ore concentrate together as pellets until after firing.

Balling drums are apparatuses comprising long cylindrical drums which are inclined and rotated. The mineral ore concentrate is simultaneously rotated about the balling drum's circumference and rolled in a downward direction through the drum. In this manner the mineral ore concentrate is rolled and tumbled together to form roughly spherical-shaped pellets. As the pellets grow in size and weight they travel down the incline of the drum and pass through the exit of the drum at which point they are dropped onto a second conveyor means which transports them to a kiln for firing. Inside the balling drum, different factors influence the mechanisms of union of the mineral ore concentrate. These factors include the moisture content of the ore, the shape and average size of the mineral ore particles, and the distribution of concentrate particles by size. Other properties of the mineral ore concentrate that influence the pelletizing operation include the mineral ore's wettability and chemical characteristics. The characteristics of the equipment used, such as its size and speed of rotation, can effect the efficiency of the pelletizing operation. The nature and quantity of the agglomerating or binding agent used in the concentrate is also a factor that determines part of the efficiency of the pelletizing operation.

The formation of agglomerates begins with the interfacial forces which have a cohesive effect between particles of mineral ore concentrate. These include capillary forces developed in liquid ridges between the particle surfaces. Numerous particles adhere to one another and form small pellets. The continued rolling of the small pellets within the balling drum causes more particles to come into contact with one another and adhere to each other by the capillary tension and compressive stress. These forces cause the union of particles in small pellets to grow in much the same manner as a snowball grows as it is rolled.

After the balling drum operation, the pellets are formed, but they are still wet. These pellets are commonly known as "green pellets" though taconite pellets, for example, are usually black in color. Green pellets usually have a density of about 2,083 kg/m^3 (130 lb/ft^3) in sizes between about 12.7 mm (1/2 inch) and about 9.5 mm (3/8 of an inch). The green pellets are transported to a kiln and heated in stages to an end temperature of approximately 1,538°C (2800°F). After heating, fired pellets are extremely hard and resist cracking upon being dropped and resist crushing when compressed.

Two standard tests are used to measure the strength of pellets whether the pellets are green pellets or fired pellets. These tests are the "drop" test and the "compression" test. The drop test requires dropping a random sampling of pellets a distance, usually about 457 mm (18 inches) or less, a number of times until the pellets crack. The number of drops to crack each pellet is recorded and averaged. Compression strength is measured by compressing or applying pressure to a random sampling of pellets until the pellets crumble. The pounds of force required to crush the pellets is recorded and averaged. These two tests are used to measure the strength of both wet and fired pellets. The drop and compressive test measurements are important because pellets, proceeding through the balling drum and subsequent conveyor belts, experience frequent drops as well as compressive forces from the weight of other pellets traveling on top of them.

Thermal shock resistance is a factor which must be taken into consideration in any process for agglomerating mineral ore concentrate. Increases in a pellet's thermal shock resistance improve that pellet's ability to resist internal pressures created by the sudden evaporation of water when the pellet is heated in a kiln. If the pellet has numerous pores through which the water vapor can escape thermal shock resistance is improved. If the surface of the pellet is smooth and continuous without pores the pellet has an increased tendency to shatter upon rapid heating. This causes a concurrent increase in the amount of "fines" or coarse particles in the pelletized mineral ore. A binder which increases the pores formed in a pellet improves that pellet's ability to resist thermal shock.

Bentonite is used as a binding agent in the pelletizing operations for taconite ore concentrate. Bentonite produces a high strength pellet having an acceptable drop strength, compressive strength, and thermal shock resistance. Bentonite has the disadvantage of increasing the silica content of the pellets that are formed. Silica decreases the efficiency of blast furnace operations used in smelting of the ore. For this reason bentonite requires a higher energy expenditure than do organic binders.

Other binding agents have proven to be better binders than bentonite. These agents include organic binders such as poly(acrylamide), polymethacrylamide, carboxymethylcellulose, hydroxyethylcellulose, carboxyhydroxyethylcellulose, poly(ethylene oxide), guar gum, and others. The use of organic binders in mineral ore pelletizing operations is desirable over the use of bentonite because organic binders do not increase the silica content of pellets and they improve the thermal shock resistance of the pellets. Organic binders burn during pellet firing operations and cause an increase in the porosity of the pellets. Firing conditions can be modified to improve fired pellets' mechanical properties for organic binder systems.

Some organic binders used in mineral ore pelletizing operations are dissolved in an aqueous solution which is sprayed onto the mineral ore concentrate prior to entering the balling drums. This application of an aqueous solution increases the moisture content above the natural or inherent moisture content of the mineral ore concentrate which requires a greater energy expenditure during the firing operation of the pellets. This increased moisture content also causes an increased likelihood of shattering due to inadequate thermal shock resistance during firing. Pellet formation is improved with the use of organic binders, but the drop strength and compression strength of the pellet are frequently below that desired or achieved with bentonite.

Other binders commonly used for agglomerating mineral ore concentrate include a mixture of bentonite, clay and a soap, Portland cement, sodium silicate, and a mixture of an alkali salt of carboxymethylcellulose and an alkali metal salt. The agglomerates made from these binding agents frequently encounter the problems described above of insufficient pellet strength or insufficient porosity for the rapid release of steam during induration with heat. Additionally, these binding agents are usually applied to a mineral ore concentrate in aqueous carrier solutions or as dry powders. Aqueous carrier solutions increase the amount of energy required to fire the pellets and increases the incidence of pellet shattering due to inadequate thermal shock resistance.

U.S. - A - 3,893,847 to Derrick discloses a binder and method for agglomerating mineral ore concentrate. The binder used is a high molecular weight, substantially straight chain water soluble polymer. This polymer is used in an aqueous solution. The polymers disclosed as useful with the Derrick invention include copolymers of acrylamide as well as other polymers. The Derrick invention claims the use of polymers in an "aqueous" solution. The use of water as a carrier solution for the binding agents increases the moisture of the agglomerates or pellets that are formed. The higher moisture content increases the energy required to fire the pellets and can increase the rate of destruction of the pellets during induration due to the rapid release of steam through the agglomerate.

The industry is lacking a method for agglomerating mineral ore concentrate utilizing low water content non-bentonite binder systems, such as water soluble, high molecular weight polymer binder systems in water-in-oil emulsions or dry powders. This invention provides pellets formed from the mineral ore concentrate of high mechanical strength properties.

SUMMARY OF THE INVENTION

This invention is a method for agglomerating a particulate material such as a mineral ore concentrate comprising the commingling of mineral ore concentrate with a binding amount of water soluble, high molecular weight polymers. The polymers are adapted to be selectively usable in at least one of either of two conditions of use. In a first condition of use the polymers are applied to the mineral ore concentrate as a dry powder. In a second condition of use the polymers are applied to the mineral ore concentrate in a water-in-oil emulsion.

This invention also includes a method comprising the commingling of dry poly(acrylamide) based polymer onto mineral ore concentrate wherein the inherent or added moisture content of the mineral ore concentrate is sufficient to activate the poly(acrylamide) based polymer to form pellets of the mineral ore.

This invention is particularly desirable when used with an iron ore concentrate and can also include the application of an inorganic salt such as sodium carbonate, calcium carbonate, sodium chloride, sodium metaphosphate and mixtures of these in conjunction with the polymer. The inorganic salt can be applied as a powder or an aqueous solution.

DETAILED DESCRIPTION OF THE INVENTION

This invention is a method for agglomerating particulate material such as a mineral ore concentrate using water soluble, high molecular weight polymers in an amount sufficient to bind the mineral ore concentrate. The polymers are applied to the particulate material in at least one of either a water-in-oil emulsion system or a dry powder system. The application of the polymers to a mineral ore concentrate can be in conjunction with an inorganic salt or mixtures of inorganic salts applied as powders or in aqueous solutions. The polymers and inorganic salts are commingled with the mineral ore concentrate. This composition then enters a standard means for pelletizing or a balling drum. The means for pelletizing further commingles the ingredients and forms wet or "green" pellets. The pellets are then transferred or conveyed to a furnace or kiln where they are indurated by heat at temperatures above about 982°C (1800°F) and more preferably at about 1,538°C (2800°F). After induration, the pellets are ready for shipping or further processing in a smelting operation such as a blast furnace.

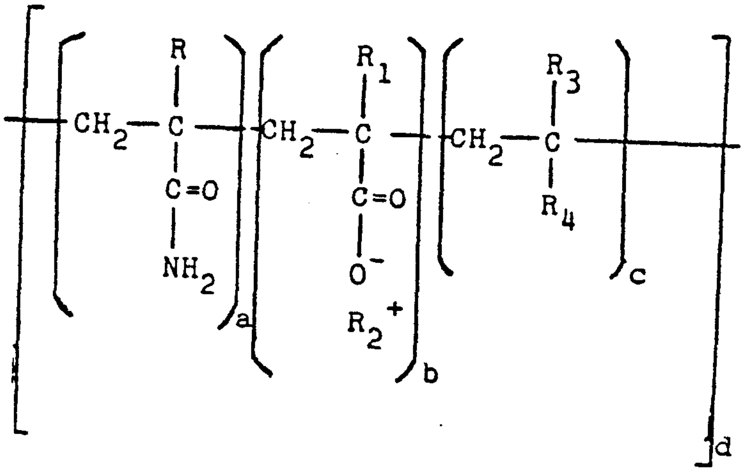
Suitable polymers useful in this invention include water soluble homopolymers, copolymers, terpolymers, and tetrapolymers. In a water-in-oil emulsion system the selected polymer is produced by polymerizing its monomeric water-in-oil emulsion precursor. Suitable polymers can be anionic, cationic, amphoteric, or nonionic. It is desirable in this invention to use polymers of high molecular weight as characterized by a high intrinsic viscosity. This invention is not limited to polymers of high intrinsic viscosity.

Polymers suitable for use with this invention, whether used in water-in-oil emulsion systems or in dry powder systems, are particularly desirable when they are of a high molecular weight. The particular molecular weight of a polymer is not limiting upon this invention. Suitable polymers include synthetic vinyl polymers and other polymers as distinguished from derivatives of natural cellulosic products such as carboxymethylcellulose, hydroxyethylcellulose, and other cellulose derivatives.

Useful measurements of a polymer's average molecular weight are determined by either the polymer's intrinsic viscosity or reduced viscosity. In general, polymers of high intrinsic viscosity or high reduced viscosity have a high molecular weight. An intrinsic viscosity is a more accurate determination of a polymer's average molecular weight than is a reduced viscosity measurement. A polymer's ability to form pellets of mineral ore concentrate is increased as the polymer's intrinsic viscosity or reduced viscosity is increased. The most desirable polymers used in the process of this invention have an intrinsic viscosity of from about 0.5 to about 40, preferably from about 2 to about 35 and most preferably from about 4 to about 30 dl/g as measured in a one normal (N) aqueous sodium chloride solution at 25°C.

Water soluble polymers include, among others, poly(acrylamide) based polymers and those polymers which polymerize upon addition of vinyl or acrylic monomers in solution with a free radical. Typically, such polymers have ionic functional groups such as carboxyl, sulfamide, or quaternary ammonium groups. Suitable polymers can be derived from ethylenically unsaturated monomers including acrylamide, acrylic acid, and methylacrylamide. Alkali metal or ammonium salts of these polymers can also be useful.

Desirable polymers for use in this invention are preferably of the following general formula:

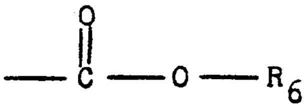


$$\left[\left(-\mathrm{CH_2}-\overset{\mathrm{R}}{\underset{\underset{\mathrm{NH_2}}{\mathrm{C{=}O}}}{\mathrm{C}}}- \right)_a \left(-\mathrm{CH_2}-\overset{\mathrm{R_1}}{\underset{\underset{\underset{\mathrm{R_2^+}}{\mathrm{O^-}}}{\mathrm{C{=}O}}}{\mathrm{C}}}- \right)_b \left(-\mathrm{CH_2}-\overset{\mathrm{R_3}}{\underset{\mathrm{R_4}}{\mathrm{C}}}- \right)_c \right]_d$$

wherein R, R_1 and R_3 are independently hydrogen or methyl, R_2+ is an alkali metal ion, such as Na+ or K+, R_4 is either

(1) $-OR_5$ wherein R_5 is an alkyl group having up to 5 carbon atoms;

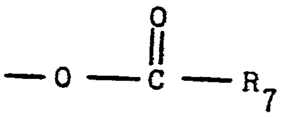
(2)



$$-\overset{O}{\overset{\|}{C}}-O-R_6$$

wherein R_6 is an alkyl group having up to 8 carbon atoms;

(3)



$$-O-\overset{O}{\overset{\|}{C}}-R_7$$

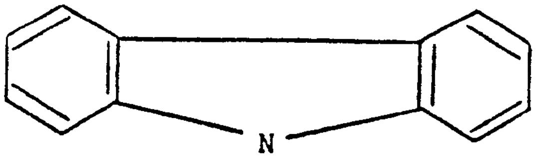
wherein R_7 is either methyl or ethyl;

(4) phenyl;

(5) substituted phenyl;

(6) -CN; or

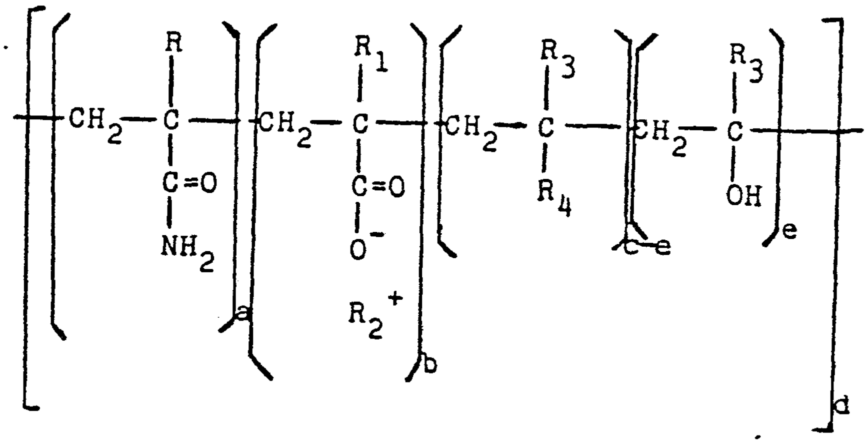
(7)



; and

wherein (a) is from 0 to about 90, preferably from about 30 to about 60 percent, (b) is from 0 to about 90, preferably from about 30 to about 60 percent, (c) is from about 0 to about 20 with the proviso that (a)+(b)+(c) equal 100 percent, and (d) is an integer of from about 1,000 to about 500,000.

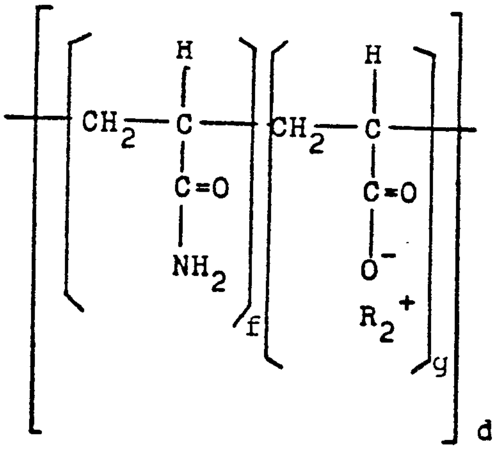
Under certain conditions, the alkoxy or acyloxy groups in the polymer can be partially hydrolyzed to the corresponding alcohol group and yield a tetrapolymer of the following general formula:



$$\left[\left(-CH_2-\underset{\underset{NH_2}{|}{\underset{C=O}{|}}}{\overset{R}{\overset{|}{C}}}- \right)_a \left(-CH_2-\underset{\underset{R_2^{+}}{}{\underset{O^-}{|}{\underset{C=O}{|}}}}{\overset{R_1}{\overset{|}{C}}}- \right)_b \left(-CH_2-\underset{\underset{R_4}{|}}{\overset{R_3}{\overset{|}{C}}}- \right)_{c-e} \left(-CH_2-\underset{\underset{OH}{|}}{\overset{R_3}{\overset{|}{C}}}- \right)_e \right]_d$$

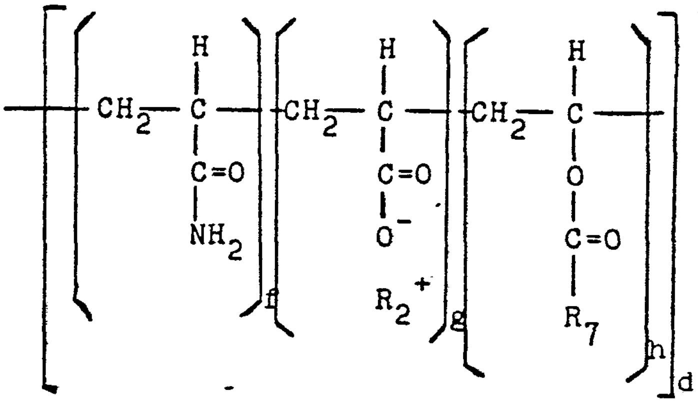
wherein R, R_1, R_2+, R_3, a, b, and d are as previously defined, R_4 is $-OR_5$ or $-O-\overset{\overset{O}{\|}}{C}-R_7$ wherein R_5 and R_7 are as defined previously, c is from about 0.2 to about 20 percent, and e is from about 0.1 to less than about 20 percent.

The preferred copolymers are of the following formula:



wherein R_2+ is an alkali metal ion, such as Na+ or K+, and f is from 5 to about 90, preferably from about 30 to about 60 percent, g is from 5 to about 90, preferably from about 30 to about 60 percent with the proviso that (f)+(g) equal 100 percent, and (d) is an integer of from about 1,000 to about 500,000.

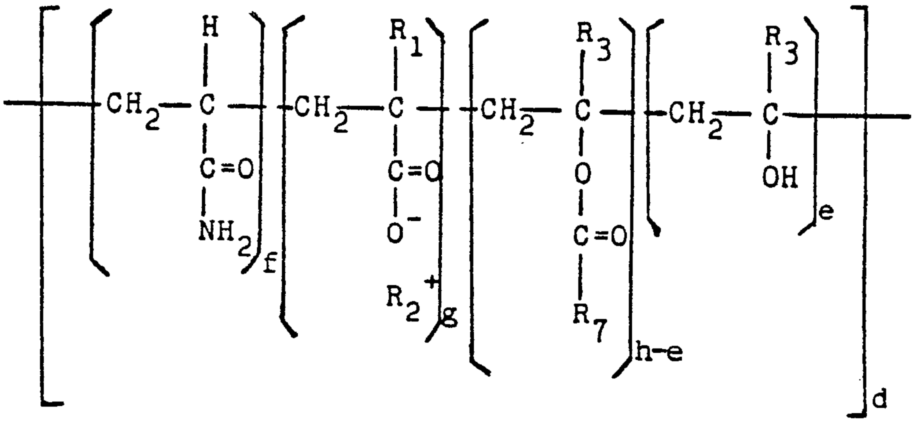
The preferred terpolymers are of the following formula:



$$\left[\left(-CH_2-\underset{\substack{|\\C=O\\|\\NH_2}}{\overset{\substack{H\\|}}{C}}-\right)_f\left(-CH_2-\underset{\substack{|\\C=O\\|\\O^-\\R_2^+}}{\overset{\substack{H\\|}}{C}}-\right)_g\left(-CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\R_7}}{\overset{\substack{H\\|}}{C}}-\right)_h\right]_d$$

wherein R_2+ is Na+ or K+, R_7 is methyl, ethyl, or butyl and f is from about 5 to about 90, preferably from about 30 to about 60 percent, g is from about 5 to 90, preferably from about 30 to 60 percent, h is from about 0.2 to about 20, with the proviso that (f)+(g)+(h) equal 100 percent and d is as previously defined.

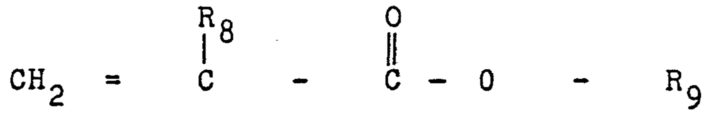
The preferred tetrapolymers are of the following formula:



$$\left[\left(CH_2-\overset{H}{\underset{\underset{NH_2}{C=O}}{C}} \right)_f \left(CH_2-\overset{R_1}{\underset{\underset{O^-\,R_2^+}{C=O}}{C}} \right)_g \left(CH_2-\overset{R_3}{\underset{\underset{\underset{R_7}{C=O}}{O}}{C}} \right)_{h-e} \left(CH_2-\overset{R_3}{\underset{OH}{C}} \right)_e \right]_d$$

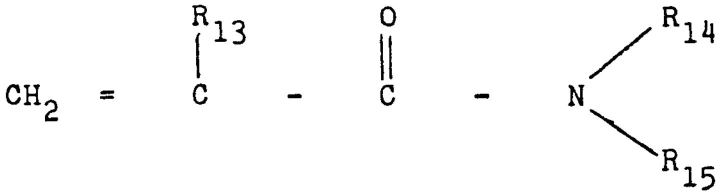
wherein R_1, R_2+, R_3, R_7, f, g, h, d, and e are as previously defined.

Other desirable water soluble polymers for use with this invention include those derived from homopolymerization and interpolymerization of one or more of the following water soluble monomers: acrylic and methacrylic acid; acrylic and methacrylic acid salts of the formula

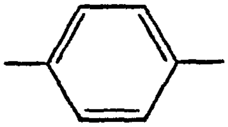


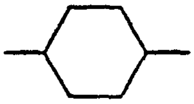
$$CH_2 = \overset{\overset{R_8}{|}}{C} - \overset{\overset{O}{\|}}{C} - O - R_9$$

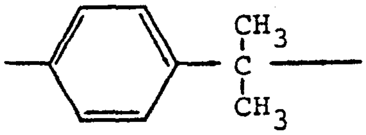
wherein R_8 is a hydrogen atom or a methyl group and R_9 is a hydrogen atom, an alkali metal atom (e.g., sodium, potassium), an ammonium group, an organoammonium group of the formula $(R_{10})(R_{11})(R_{12})$ NH+ (where R_{10}, R_{11} and R_{12} are independently selected from a hydrogen atom, and an alkyl group having from 1 to 18 carbon atoms (it may be necessary to control the number and length of long-chain alkyl groups to assure that the monomer is water soluble), such as 1 to 3 carbon atoms, an aryl group, such as a benzyl group, or a hydroxyalkyl group having from 1 to 3 carbon atoms, such as triethanolamine, or mixtures thereof); acrylamide and methacrylamide and derivatives including acrylamido- and methacrylamido monomers of the formula:



wherein R_{13} is a hydrogen atom or a methyl group; wherein R_{14} is a hydrogen atom, a methyl group or an ethyl group; wherein R_{15} is a hydrogen atom, a methyl group, an ethyl group or $-R_{16}-SO_3X$, wherein R_{16} is a divalent hydrocarbon group alkylene, phenylene, or cycloalkylene having from 1 to 13 carbon atoms, preferably an alkylene group having from 2 to 8 carbon atoms, a cycloalkylene group having from 6 to 8 carbon atoms, or phenylene, most preferably

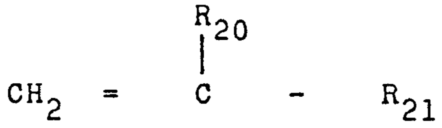
$-C(CH_3)_2-CH_2-$, $-CH_2CH_2-$, 

$-CH(CH_3)-CH_2-$,  and

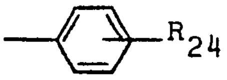


X is a monovalent cation such as a hydrogen atom, an alkali metal atom (e.g., sodium or potassium), an ammonium group, an organoammonium group of the formula $(R_{17})(R_{18})(R_{19})NH+$ wherein R_{17}, R_{18}, R_{19} are independently selected from a hydrogen atom, an alkyl group having from 1 to 18 carbon atoms (it may be necessary to control the number and length of long-chain alkyl groups to assure that the monomer is water soluble) such as 1 to 3 carbon atoms, an aryl group such as a phenyl or benzyl group, or a hydroxyalkyl group having from 1 to 3 carbon atoms such as triethanolamine, or mixtures thereof, and the like. Specific examples of water-soluble monomers which can be homopolymerized or interpolymerized and useful in the process of this invention are acrylamido- and methacrylamido- sulfonic acids and sulfonates such as 2-acrylamido-2-methylpropanesulfonic acid (available from the Lubrizol Corporation under its tradename, and hereinafter referred to as, AMPS), sodium AMPS, ammonium AMPS, organoammonium AMPS. These polymers can be effective binding agents for mineral ore concentrates in about the same concentrations or binding amounts used for the polyacrylamide based polymer binders.

These water soluble monomers can be interpolymerized with a minor amount (i.e., less than about 20 mole percent, preferably less than about 10 mole percent, based on the total monomers fed to the reaction) of one or more hydrophobic vinyl monomers. For example, vinyl monomers of the formula



$$CH_2 = \overset{\overset{R_{20}}{|}}{C} - R_{21}$$

wherein R_{20} is a hydrogen atom or a methyl group and R_{21} is $-O-\overset{\overset{O}{\|}}{C}-R_{22}$, a halogen atom (e.g., chlorine), $-O-R_{23}$,  $-R_{24}$ or $-\underset{\underset{O}{\|}}{C}-OR_{25}$, wherein R_{25} is an alkyl group, an aryl group or an aralkyl group having from 1 to 18 carbon atoms, wherein R_{22} is an alkyl group having from 1 to 8 carbon atoms, R_{23} is an alkyl group having from 1 to 6 carbon atoms, preferably 2-4 carbon atoms, R_{24} is a hydrogen atom, a methyl group, an ethyl group, or a halogen atom (e.g., chlorine), preferably a hydrogen atom or a methyl group, with the proviso that R_{20} is preferably a hydrogen atom when R_{22} is an alkyl group. Specific examples of suitable copolymerizable hydrophobic vinyl monomers are alkyl esters of acrylic and methacrylic acids such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, isobutyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, etc.; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, etc.; vinylbenzenes such as styrene, alpha-methyl styrene, vinyl toluene; vinyl ethers such as propyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, methyl vinyl ether, ethyl vinyl ether, etc.; vinyl halides such as vinyl chloride, vinylidene chloride, etc.; and the like.

The preferred water soluble monomers of these water soluble polymers are acrylamide, AMPS and sodium AMPS, sodium acrylate, and ammonium acrylate. The preferred hydrophobic monomers are vinyl acetate, ethyl acrylate, styrene and methyl methacrylate.

Examples of suitable polymers for use with this invention in water-in-oil emulsions are listed in Table I. This table provides a representative listing of suitable polymers for use in the water-in-oil emulsions, but does not encompass every suitable polymer or limit the polymers that can be used with this invention.

TABLE I

Poly(acrylamide) Emulsions[1]

Anionic Copolymers	Mole % PAM/Na Acrylate	Intrinsic Viscosity	% Solids
	85/15	16.2	30
	76/24	17.3	30
	59/41	20.0	30
Cationic Copolymers	PAM/Sipomer Q5-80[2]		
	94/16		
Nonionic Copolymers	PAM/N-decyl Acrylamide		
	99/1	5.8	
Anionic Terpolymers	PAM/NaA/Vinyl Acetate		
	47.5/47.6/4.9	10.8	30
		23.0	29.5
	71/24/5	20.0	30
	80/15/5	RV[3]=17.5	30
	PAM/NaAMPS/Vinyl Acetate		
	87/12/1	10.0	

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[1] abbreviations: PAM: poly(acrylamide); NaA: sodium acrylate; NaAMPS: sodium salt of 2-acrylamido-2-methylpropanesulfonic acid.

[2] Sipomer Q5-80 is a cationic compound of dimethylaminoethylmethacrylate/dimethyl sulfate quaternary salt.

[3] Reduced viscosity.

A second class of polymers includes those polymers used with this invention in dry powder form. These polymers must be water soluble, but do not necessarily lend themselves to the formation of water-in-oil emulsions. Typically, polymers which form water-in-oil emulsions are also useful with the invented method as dry powder. Table II represents a listing of polymers which are desirable for use with this invention as powders. The powders listed in Table II do not encompass all polymers which can be used as powders in this invention.

TABLE II

Poly(acrylamide) Powders

		Approximate mole % PAM/NaA
Nonionic	Rhone Poulenc AD-10[1] (intrinsic viscosity 15.4dl/g)	
Anionic		
	Percol® 725[2]	89/11
	Percol® 726	77/23

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[1] AD-10 is a poly(acrylamide) powder sold by Rhone Poulenc, 52 Vanderbilt Avenue, New York, NY.

[2] Percol® products have been analyzed to be copolymers containing the approximate mole % of PAM and NaA given in Table II and are sold by Allied Colloids of Fairfield, New Jersey.

Inorganic salts are optionally added to the mineral ore concentrate before balling drum operations to primarily increase the dry crush strength of the pellets. Inorganic salts can be added either before, after, or during the addition of the dry or emulsified polymer. Polymers alone improve the dry compression strength of pellets, but not to the same degree as an inorganic salt. For this reason, desirable embodiments of this invention include the addition of an inorganic salt, however, this addition is not considered limiting upon this invention. Similarly, the inorganic salt selected nor the method of addition is not limiting upon this invention. For purposes of this invention the term "polymer binder system" can include a water soluble, high molecular weight polymer in either a water-in-oil emulsion system or powder system used with or without inorganic salt powders or solutions.

Inorganic salts suitable for use in this invention include alkali and alkali metal salts of carbonates, halides, or phosphates. Specific examples of inorganic salts include sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$), sodium metaphosphate $(NaPO_3)_n$ where n is 2 or more, sodium chloride (NaCl), and mixtures of these. Other inorganic salts can be added to improve pellet compression strength. Additionally, inorganic salts can be added in mixtures with one another as powders or in solutions. As the concentration of inorganic salt increases in the mineral ore concentrate, the compression strength of the resulting pellets is increased.

Sodium carbonate is an inorganic salt that achieves good results for improving the compression strength of pellets. Sodium carbonate is most effective, when used with either the dry or emulsified polymer, in an amount of at least 2 percent and preferably greater than 25 percent, calculated on the total weight of the added inorganic salt and active polymer. Preferably the concentration of sodium carbonate as a percent of the weight of the polymer binder system varies from about 25 percent to about 95 percent. More preferably, sodium carbonate is within the range of about 30 percent to about 90 percent with the most optimum range between about 50 percent to about 90 percent calculated on the total weight of the mixture of sodium carbonate and the polymer.

The invertible water-in-oil emulsion system used in this invention is a suspension of droplets comprised of both water soluble, high molecular weight polymers and water in a hydrophobic substance. Examples of suitable emulsion systems and methods to form suitable emulsions are found in U.S. Patent Number 4,485,209 to Fan et al. and U.S. Patent Number 4,452,940 to Rosen et al. each of which are herein incorporated by reference.

Desirable hydrophobic liquids used in these emulsion systems are isoparaffinic hydrocarbons. A suitable isoparaffinic hydrocarbon is that sold by the Exxon Corporation known as Isopar® M. Other suitable hydrophobic liquids for use as the external phase in an emulsion system include benzene, xylene, toluene, mineral oils, kerosenes, petroleum, paraffinic hydrocarbons, and mixtures of these.

In the most desirable embodiments of this invention, which include a polymer binding agent in a water-in-oil emulsion, two surfactants are used to form the emulsion. A first surfactant is used to form the water-in-oil emulsion system. After the water-in-oil emulsion system is formed, a second surfactant is added. The second surfactant is a water soluble inverting surfactant which, we believe, permits the inversion of the water-in-oil emulsion to an oil-in-water emulsion upon contact with the inherent or added moisture present in the mineral ore concentrate. Upon inversion of the water-in-oil emulsion the polymer is forced out of the internal aqueous phase and made available to the surface of the mineral ore concentrate. This release of the polymer onto the surface of the mineral ore concentrate allows for rapid commingling of the polymer with the mineral ore concentrate. Emulsions that do not contain inverting surfactants can be used with this invention.

The surfactants suitable for use in forming emulsions of this invention are usually oil-soluble having a Hydrophile-Lipophile Balance (HLB) value of from about 1 to about 10 and preferably from about 2 to about 6. These surfactants are normally referred to as water-in-oil type surfactants. Suitable surfactants include the acid esters such as sorbitan monolaurate, sorbitan monostearate, sorbitan monooleate, sorbitan trioleate, mono and diglycerides, such as mono and diglycerides obtained from the glycerolysis of edible fats, polyoxyethylenated fatty acid esters, such as polyoxyethylenated (4) sorbitan monosterate, polyoxyethylenated linear alcohol, such as Tergitol 15-S-3 and Tergitol-25-L-3 supplied by the Union Carbide Corporation, polyoxyethylene sorbitol esters, such as polyoxyethylene sorbital beeswax derivative, polyoxyethylenated alcohols such as polyoxyethylenated (2) cetyl ether, and the like.

Water-soluble inverting surfactants which can be used include polyoxyethylene alkyl phenol, polyoxyethylene (10 mole) cetyl ether, polyoxyethylene alkyl-aryl ether, quaternary ammonium derivatives, potassium oleate, N-cetyl N-ethyl morpholinium ethosulfate, sodium lauryl sulfate, condensation products of higher fatty alcohols with ethylene oxide, such as the reaction product of oleyl alcohol with 10 ethylene oxide units; condensation products of alkylphenols and ethylene oxide, such as the reaction products of isooctylphenol with 12 ethylene oxide units; condensation products of higher fatty acid amines with five, or more, ethylene oxide units; ethylene oxide condensation products of polyhydric alcohol partial higher fatty esters, and their inner anhydrides (mannitol-anhydride, called Mannitan, and sorbitol-anhydride, called Sorbitan). The preferred surfactants are ethoxylated nonyl phenols, ethoxylated nonyl phenol formaldehyde resins, and the like.

The inverting surfactant is used in amounts of from about 0.1 to about 20, preferably from about 1 to about 10 parts per one hundred parts of the polymer.

The mixture of both the aqueous phase and the oil phase of the emulsions used in this invention can contain about 20 to about 50 and preferably from about 22 to about 42 percent weight of the hydrophobic liquid and the hydrophobic monomers, based upon the total weight of the composition.

The aqueous solution used to form the emulsion systems of this invention can contain a mixture of water soluble monomers. These monomers have a water solubility of at least 5 weight percent and include acrylamide, methacrylamide, acrylic acid, methacrylic acid, and their alkali metal salts, aminoalkyl acrylate, aminoalkyl methacrylate, dialkylaminoalkyl acrylate, dialkylamino methacrylate and their quaternized salts with dimethyl sulfate or methyl chloride, vinyl benzyl dimethyl ammonium chloride, alkali metal and ammonium salts of 2-sulfoethylacrylate, alkali metal and ammonium salts of vinyl benzyl sulfonates, maleic anhydride, 2-acrylamide-2-methylpropanesulfonic acid, and the like. The preferred monomers are acrylamide, acrylic acid, and sodium salt of 2-acrylamido-2-methylpropanesulfonic acid.

If acrylic acid is used as a monomer it is reacted with a base, preferably with an equivalent amount of base, such as sodium hydroxide, so that the sodium acrylate solution has a pH of from about 5.0 to about 10.0, preferably from about 6.5 to about 8.5, depending on the type and amount of base employed. This solution is combined with another water soluble monomer, such as acrylamide, and then with water to form the aqueous phase.

Hydrophobic monomers which can be useful in forming the emulsion systems of this invention include one or more of vinyl esters such as vinyl acetate, alkyl acrylates such as ethylacrylate, alkyl methacrylates such as methacrylate, vinyl ethers such as butylvinyl ether, acrylonitrile, styrene and its derivatives such as alpha-methylstryrene, N-vinyl carbazole, and the like.

Appropriate reactors and catalysts are also used with this invention. These compounds can vary. Examples of suitable reactors and catalysts can be found in the Fan and Rosen patents identified above.

Emulsions used in this invention are made by any suitable method. A desirable method for making emulsions is disclosed in U.S. - A - 4,485,209 to Fan. This invention is not limited to a particular emulsion or method for producing an emulsion.

An advantage to the use of water-in-oil emulsions in the formation of pellets is that the amount of water added to the mineral ore concentrate is greatly reduced from that required to deliver polymers in aqueous solutions, thus resulting in an energy savings upon firing of the pellets. Also, the hydrophobic liquid or oil in the inverted water-in-oil emulsion system is consumed during the firing operation. The burn out of the oil droplets from the interior of the pellets increases the porosity of the pellets in much the same manner as does the burning of the organic binder or polymer from the interior of the pellets. This increase in porosity is believed to improve the release of water vapor from the pellets and decrease the occurrence of thermal shock upon firing of the pellets.

An additional benefit realized by the use of a water-in-oil emulsion system to deliver a polymer binder to mineral ore concentrate in pelletizing operations is a decrease in the amount of contact time required for sufficient commingling of the polymer binder with the mineral ore concentrate. The contact time of a polymer after the emulsion is sprayed onto the mineral ore concentrate need only be sufficient to allow activation of the polymer on the surface of the mineral ore concentrate. The amount of time can vary depending upon the emulsion system used and the concentration of the polymer binder within the emulsion system as well as the total amount of polymer binder sprayed upon the mineral ore concentrate. In desirable embodiments of this invention, sufficient time for commingling of the polymer binder system into the mineral ore concentrate occur by spraying the water-in-oil emulsion onto the mineral ore concentrate just upstream of where the concentrate enters the balling drum.

Application of a water-in-oil emulsion at the mineral ore concentrate treatment site can be accomplished by applying the emulsion to the mineral ore concentrate through any conventional spraying apparatus. The inorganic salts are sprinkled from a vibrating hopper or other dispersing means onto the mineral ore concentrate and the composition is conveyed towards the balling drum. Alternatively salt can be delivered from aqueous solutions of 5 to 40 percent solid material depending on the solubility of the inorganic salt. The activation of the polymers onto the surface of the mineral ore concentrate is rapid, and because the polymers are evenly spread or commingled throughout the mineral ore concentrate, the time required for sufficient commingling to initiate pellet formation is about one minute or less.

This invention also includes the application of binding polymer systems to mineral ore concentrate that are dry powders. In these embodiments the dry powdered polymers are mixed together optionally with the dry inorganic salt. The resulting powder composition is sprinkled onto the mineral ore concentrate as the concentrate is conveyed towards the balling drum. The vibration of the conveyor means and the action of the balling drum commingles the powders into the mineral ore concentrate. Upon sufficient contact time with the moisture in the mineral ore concentrate, the polymers are adsorbed onto the surface of the concentrate. Suitable contact time can be essentially instantaneous, but often is between about 1 minute to 3 hours or more. Further commingling occurs in the mixing within the balling drum. The use of the dry powder polymer embodiments of this invention eliminates the need for emulsion spraying equipment. This invention also includes the application of powdered binders to a mineral ore concentrate in conjunction with an application of inorganic salt as an aqueous solution.

The useful range of the concentration of the polymer on an active basis is between about 0.001 percent to about 0.3 percent based on weight of bone dry concentrate. The preferred range is between about 0.001 percent and about 0.1 percent. These ranges are applicable for both dry and emulsified applications of polymer binders. The useful range of the concentration of the inorganic salt based upon the weight of bone dry concentrate is between about 0.001 percent and about 0.5 percent with the preferred range being between about 0.005 percent and about 0.3 percent.

The invention is further understood from the

Examples below, but is not to be limited to the Examples. The numbered Examples represent the present invention. The lettered Examples do not represent this invention and are for comparison purposes. Temperatures given are in °C unless otherwise stated. The following designations used in the Examples and elsewhere herein have the following meanings:

ABBREVIATION	DEFINITION
AM	acrylamide
Apx.	approximate
$CaCO_3$	calcium carbonate
cc	cubic centimeter
CMC	carboxymethylcellulose
CO_2	carbon dioxide
dl/g	deciliter per gram
°F	degrees fahrenheit
gm/cc	grams per cubic centimeter
gms	grams
HEC	hydroxyethylcellulose
IV	intrinsic viscosity
lb	pound or pounds
mm	millimeters
NaA	sodium acrylate
NaAMPS	sodium salt of 2-acrylamido

	-2-methylpropanesulfonic acid
NaCl	sodium chloride
$(NaPO_3)_n$	sodium metaphosphate where n is 2 or more
Na_2CO_3	sodium carbonate
Na_2O	sodium oxide
PAM	poly(acrylamide)
psi	pounds per square inch pressure
RPM	revolutions per minute
RV	reduced viscosity
tonne	metric ton
U.S.	United States
VA	vinyl acetate
wt	weight
wt %	weight percent
%	percent by weight unless otherwise specified

LABORATORY EXPERIMENTAL PROCEDURE

In these Examples taconite pelletizing consists of a two step procedure. Initially, seed balls are prepared from the taconite ore using bentonite clay as a binder. These seed balls are passed through screens to obtain seed balls of a size that pass through a 4 U.S. mesh screen having a 4.75 mm (0.187 inch) opening, but not through a 6 U.S. mesh screen having a 3.32 mm (0.132 inch) opening. The see balls are then used with additional concentrate and the binder of interest to prepare the larger green pellets. Finished green pellets are sieved to be in a size range between 13.2mm to 12.5mm. This can be accomplished by using USA Sieve Series ASTM-E-11-70. Following sieving, the green pellets are tested for wet crushing strength and wet dropping strength. Additional green pellets are dried (not fired) and tested for both dry crushing and dry dropping strength. For the examples cited, all testing was done with either wet or dry green pellets.

Seed ball formation in these examples is begun with a sample of 900 grams (bone dry weight) of taconite concentrate containing between 8 to 10% moisture. The concentrate is sieved through a 9, 10, or 12 mesh screen and spread evenly over an oil cloth. Next 7.0 grams of bentonite clay is spread evenly over the top of the concentrate and mixed until homogenous. The mixture is incrementally added to a revolving rubber drum having approximately a 406 mm (16 inch) diameter and a 152 mm (6 inch)cross section. The drum is rotated at 64 RPM. Humidity is not controlled in these Examples. Just prior to addition of concentrate, the inside of the drum is wet with water from a spray bottle. While rolling, several handfulls of the bentonite-concentrate mixture is added to the drum. Distilled water is added when the forming agglomerates begin to develop a dull appearance. As seed pellets are formed, they are screened to separate and obtain pellets which pass through a 4 mesh screen, but not through a 6 mesh screen. Captured fines are readded to the balling drum and oversized seeds are rejected. The procedure of readding captured fines is repeated several times until sufficient seed pellets of the desired size have been produced. The seed pellets are then rolled for one minute to finish the surface. Formed seed pellets can be placed in a sealed container containing a damp cloth so as to retard dehydration of the pellets.

Green pellet formation in these Examples is begun with a sample of 1800 grams (bone dry weight) of mineral ore containing between 8 to 10% moisture. The concentrate is added into a 305 mm (12 inch) diameter Cincinnati

Muller and mixed for 1.0 minute. Thereafter, an amount of binder to be used in the Example is uniformly distributed over the surface of the concentrate. In Examples using emulsion polymers, the emulsified polymers are uniformly delivered dropwise from a syringe. When an inorganic salt, such as Na_2CO_3, is used in an Example, it is sprinkled over the surface of the concentrate. For those examples which employ a Na_2CO_3 solution, a 30 percent salt solution is used. For those examples which employ powdered polymers, the powder is dry blended with the inorganic salt and the resulting mixture is then uniformly sprinkled over the concentrate in the muller. The muller is then turned on for three minutes to mix the binder with the concentrate. The uniform mixture is then screened through an 8 mesh screen.

After moistening the inside of the rotating balling drum of tire, about 40 grams of seed pellets are added to the tire. Then the concentrate and binder mixture is incrementally fed into the tire over a period of six minutes with intermittent use of distilled water spray. During the initial portion of this process, small amounts of the concentrate and binder mixture are added each time the surface of the pellets appear shiny. Typically, the latter portion of the six minute rotating period requires an increased amount of the concentrate and binder mixture when compared to the initial part of the rotating period. Water spray is applied each time the surface of the pellets takes on a dull appearance. After the six minute rotating period is complete, the balling drum is rotated one additional minute to "finish off" the pellet surface. No water spray is used during the final one minute period. Following completion of this procedure, the green pellets are screened for testing purposes to a size between 13.2mm and 12.5 mm.

Compression testing in these Examples is performed by using a Chatillon Spring Tester of 11,3 kg (25 pound) range (Model LTCM - Serial No. 567). Twenty green pellets are crushed in the tester within 30 minutes of pellet completion at a loading rate of 2.54 mm (0.1 inches) per second. The pounds of force required to crush each pellet is averaged for the twenty pellets and is herein called the wet crush strength. An additional twenty pellets are dried for one hour at 177°C (350°F). While these pellets are still warm to the touch, the crushing procedure is repeated to obtain the dry crush strength average measured in pounds per square inch (psi).

Drop testing in these Examples is performed with twenty green pellets which are tested whithin 30 minutes of their formation. These pellets are dropped one at a time from a height of 457 mm (18 inches) onto a steel plate. The number of drops to obtain pellet failure is recorded. Pellet failure is determined when a crack in a pellet of approximately a 0.7 or greater occurs. The average for twenty wet pellet drops is reported. Twenty additional green pellets are dried by the procedure set out for the compression test and then each is dropped from a 3 inch height. The average number of drops to obtain pellet failure for twenty pellets is determined and recorded.

Definition of acceptable or target pellet mechanical properties is defined in these Examples, within limits of experimental error, by a comparison to the performance of Peridur, a commercial binder. Peridur was analyzed to be 68 percent carboxymethylcellulose with about 16 percent NaCl and about 16 percent Na_2CO_3. Peridur is known to produce acceptable results in some plant scale pelletizing operations at a dose of 1.55 lb product/tonne of concentrate. Since the product is about 68% sodium carboxymethylcellulose, Peridur is used at an active polymer dose of about 1.05 lb/tonne. Peridur is sold by Dreeland Colloids, 1670 Broadway, Denver, Colorado.

Wet drop numbers above about 2.5 and wet crush numbers above about 3.0 are useful. Dry drop numbers greater than about 2.0 and dry crush numbers above about 4 are acceptable. Comparisons of pellet mechanical properties for different binders need to be made at approximately equal pellet moisture contents. Wet pellet properties are important because wet pellets are transported by conveyors and are dropped from one conveyor to another during their movement. Dry properties are important because in kiln operations pellets can be stacked 152 to 178 mm (6 to 7 inches) high or more. The pellets at the bottom of such a pile must be strong enough so as not to be crushed by the weight of the pellets on top of them. Dry pellets are also conveyed and must resist breakage upon dropping.

Unless otherwise stated in the following examples, the term, water-in-oil emulsion, refers to a water-in-oil emulsion containing an inverting surfactant. In these emulsions the oil phase is Isopar® M.

EXAMPLE A

The experimental procedure described above was used to prepare and test two samples of green pellets of taconate concentrate formed with a commercial CMC/NaCl/Na_2CO_3 binding agent system. The amount of binding agent used and the results are presented in Table III.

TABLE III

kg Peridur per tonne	kg active polymer/ tonne	wet crush	wet drop	dry crush	wet drop	% H_2O
0.53	0.36+	4.6	2.7	4.2	2.1	---
		4.6	2.5	4.8	2.1	9.2

\+ carboxymethylcellulose

EXAMPLE I

The experimental procedure described above was used to prepare and test two samples of green pellets of taconite concentrate formed with a PAM/NaA/VA binding agent in a water-in-oil emulsion. The mole percent of PAM/NaA/VA is 47.5/47.6/4.9. The oil used in the external phase was Isopar® M. The intrinsic viscosity of the polymer was 23 dl/g. The amount of binding agent used and the results are presented in Table IV.

TABLE IV

kg emulsion per tonne	kg active polymer/ tonne	wet crush	wet drop	dry crush	dry drop	% H_2O
0.62*	0.18	4.0	4.5	4.9	2.7	9.1
0.41	0.12	3.5	3.0	3.6	2.4	9.1

---

* also contains 0.35 kg Na_2CO_3/tonne

This example shows that the dual addition of an emulsion containing the polymer derived from acrylamide, sodium acrylate, and vinyl acetate in a 47.5/47.6/4.9 mole ratio along with Na_2CO_3 produce a taconite binder which is superior to the binder system used in Example A which employs a CMC/NaCl/Na_2CO_3 binding agent. At one half the active polymer dose the PAM/NaA/VA-Na_2CO_3 system gave a higher wet drop number than the control binder of Example A.

EXAMPLE B

The experimental procedures described in Examples A and I were used to prepare and test the green pellets of taconite concentrate in this Example. The pellets of this Example are formed with either a commerical CMC/NaCl/Na_2CO_3 or HEC/Na_2CO_3 binder system. The concentration and test results are in Table V below.

TABLE V

binder	kg active polymer/ tonne	wet crush	wet drop	dry crush	dry drop	% H_2O
HEC/Na_2CO_3+	0.35	3.3	3.0	4.0	2.5	---
CMC/NaCl/ Na_2CO_3++	0.48	4.0	2.9	5.4	2.8	8.0

\+ 50/50 mixture.
++ 68/16/16 wt% (average of 3 runs)

EXAMPLE II

The experimental procedures described in Examples A and I were used to prepare and test green pellets of taconite concentrate formed with a PAM/NaA/VA binding agent in a water-in-oil emulsion. The mole percent of PAM/NaA/VA is 47.5/47.6/4.9. The oil used in the external phase was Isopar® M. The concentration and test results are in Table VI below.

TABLE VI

	kg active polymer/ tonne	wet crush	wet drop	dry crush	dry drop	% H_2O
PAM/NaA/VA-Na_2CO_3*	0.35	3.3	6.2	6.8	4.3	9.8

---

* This is a 50/50 mixture; PAM/NaA/VA had an IV of 10.3 dl/g.

This Example shows that the dual addition of a 47.5/47.6/4.9 mole ratio of PAM/NaA/VA binding system with a lower molecular weight as evidenced by an IV of 10.3 in a water-in-oil emulsion along with Na_2CO_3 produces a taconite binder system which is superior to the current art employing combinations of hydroxyethylcellulose/Na_2CO_3 or carboxymethylcellulose/NaCl/Na_2CO_3. Note that wet drop number, dry crush and dry drop were all better with the PAM/NaA/VA-Na_2CO_3 binder system.

EXAMPLES C AND III

The procedures for preparing and testing the green pellets in these Examples were the same as described for Examples A and I. These Examples compare pellet strength resulting from varying concentrations of polymer binder systems. The concentrations and test results are in Table VII below.

TABLE VII

Example		total dose+ kg /tonne	Active polymer Dose kg/tonne	wet crush	wet drop	dry crush	dry drop	% H_2O
III	PAM/NaA/VA* Na_2CO_3	0.70	0.35	3.2	11.6	5.6	4.1	10.0
C	CMC/NaCl/ Na_2CO_3	0.70	0.48	4.6 3.4	2.9 2.7	5.4 5.3	2.4 2.0	8.3 8.8
III	PAM/NaA/VA* Na_2CO_3	0.53	0.18	3.6	3.4	4.2	2.2	8.7
C	CMC/NaCl Na_2CO_3	0.53	0.36	4.2	2.6	4.4	2.1	8.2
III	PAM/NaA/VA* Na_2CO_3	0.45	0.10	3.5	3.0	3.4	2.5	8.9
C	CMC/NaCl Na_2CO_3	0.45	0.31	3.9	2.5	2.9	2.1	8.5

+ kg active polymer plus kg Na_2CO_3.

* intrinsic viscosity 23, mole percent of 47.5/47.6/4.9.

These examples show that mechanical properties of taconite pellets formed with a PAM/NaA/VA binding agent in a water-in-oil emulsion improve with increasing dose. Comparison of the poly(acrylamide) based polymer binder system in Example III is made at each concentration to a CMC/NaCl/Na_2CO_3 binder system in Example C.

EXAMPLE IV

The procedures for preparing and testing the green pellets in this Example were the same as described for Example I. This Example compares the effect of intrinsic viscosity on pellet strength for a poly(acrylamide) based polymer binder system. The intrinsic viscosities and test results are in Table VIII below.

TABLE VIII

DOSE: 0.35 KG ACTIVE POLYMER/TONNE*

IV	wet crush	wet drop	dry crush	dry drop	% H_2O
10.8	2.8	8.1	5.4	4.3	10.3
23.0	3.2	11.6	5.6	4.1	10.1

---

* Mole percent of PAM/NaV/VA 47.5/47.6/4.9 and also contains 0.35 kg Na_2CO_3 per tonne.

This example shows that polymer binder systems of higher intrinsic viscosity produce better mechanical pellet properties with taconite concentrate when the polymer binder is a PAM/NaA/VA terpolymer.

EXAMPLE V

The procedures for preparing and testing the green pellets in this Example were the same as described for Example I. This Example compares the effect on pellet strength occurring when the mole ratios of a polymer's monomers are varied. The mole ratios and the test results are presented in Table IX below.

TABLE IX

Dose: 0.10 kg active polymer/tonne plus 0.35 kg Na_2CO_3 /tonne

Polymer Composition mole percent PAM/NaA/VA	wet crush	wet drop	dry crush	dry drop	% H_2O
47.5/47.6/4.9[1]	3.5	3.0	3.4	2.5	8.9
71/24/5[2]	4.1	4.0	4.4	2.0	8.5
80/15/5[3]	3.9	3.4	4.7	2.7	8.2
PAM/NaA[4]					
59/41	3.8	3.0	3.8	2.1	8.8

---

1. IV 23.0 dl/g, 29.5% active polymer
2. IV 20.0 dl/g, 30% active polymer
3. RV 17.5 dl/g, 30% active polymer
4. Approximately IV 20.0 dl/g, 30% active polymer

This Example shows that NaA between about 15 and about 47.6 mole percent was not critical to achieve satisfactory performance in an acrylamide polymer.

EXAMPLES D AND VI

The procedures for preparing and testing the green pellets in this Example were the same as described for Examples A and I. The concentrations and test results are in Table X below.

TABLE X
DOSE: 0.18 kg ACTIVE PAM COPOLYMER/TONNE
PLUS 0.35 kg Na_2CO_3/TONNE*

Example	Copolymer mole % PAM/NaA	wet crush	wet drop	dry crush	dry drop	% H_2O
VII	59/41[1]	3.4	5.5	4.4	2.5	9.1
VII	76/24[2]	3.3	4.2	4.6	2.8	8.5
VII	85/15[3]	3.7	4.9	4.8	2.3	8.1
VII	100/0[4] powder	3.4	2.5	4.4	3.3	8.0
D	CMC Peridur Control[5]	4.2	2.6	4.4	2.1	8.2

* (0.48 kg emulsion/tonne).
1. IV = approximately 20 dl/g.
2. IV = 17.3 dl/g.
3. IV = 16.2 dl/g.
4. IV = 15.4 dl/g, this powder is AD-10 sold by Rhone Poulenc.
5. 0.53 kg/tonne (containing 0.36 kg CMC polymer/tonne).

These Examples show that acrylamide copolymers containing 0 to at least 41 percent Na acrylate are effective as binding agents for taconite concentrate.

EXAMPLE VII

The procedures for preparing and testing the green pellets in this Example were the same as described in Example I. The concentrations and test results are in Table XI below.

TABLE XI

Dose: As shown + 0.35 kg Na_2CO_3/tonne

copolymer mole % PAM/NaA	active polymer dose kg /tonne	wet crush	wet drop	dry crush	dry drop	% H_2O
89/11	0.35	3.9	4.4	6.8	3.1	9.2
77/23	0.35	3.7	6.9	7.9	3.3	9.1

These Examples show that solid poly(acrylamide) based copolymers in powder form are effective binding agents for taconite concentrate.

EXAMPLES E AND VIII

The procedures for preparing and testing the green pellets in these Examples were the same as described in Examples A and I. The polymer binder system used and the test results are in Table XII below.

TABLE XII

Dose of PAM based polymers 0.18 kg active/tonne + 0.35 kg Na_2CO_3/tonne

Composition	wet crush	wet drop	dry crush	dry drop	% H_2O
PAM/N Decyl Acrylamide (99/1) nonionic	2.7	3.0	4.7	3.0	8.5
PAM/Sipomer Q5-80[1] 94/6 cationic	3.1	2.4	4.4	2.8	8.4
CMC/NaCl/ Na_2CO_3 (control)[2]	4.2	2.6	4.4	2.1	8.2

---

[1] Sipomer Q5-80 is Dimethylaminoethylmethacrylate/Dimethyl sulfate quaternary salt.

[2] 0.36 kg CMC/tonne.

These Examples show that emulsions of nonionic poly(acrylamide) based polymers with long chain hydrophobic groups and cationic modified PAM perform well as taconite binders when compared to CMC based products. The results obtained from these Examples demonstrate that an emulsion of PAM/NaA/VA is better than or roughly equivalent to a CMC/NaCl/Na_2CO_3 binding agent in both drop tests and compression tests.

EXAMPLE IX

The procedures for preparing and testing the green pellets in this Example were the same as described in Example I with the exception that the inorganic salt used in this example is applied as a 30 percent aqueous solution. The polymer binders in this example are in a water-in-oil emulsion. These tests were conducted on taconite ore concentrate and demonstrate the effect of applying the polymer binder emulsion and inorganic salt solution in different sequences to the mineral ore concentrate. When these liquids are applied to the mineral ore concentrate separately, the first liquid is mixed with the mineral ore concentrate in a muller. The second liquid is then added and the total composition is mixed for an additional 3 minutes. The test results are presented in Table XIII below.

TABLE XIII

Dose: emulsion 0.50 kg emulsion[1]/tonne + Na_2CO_3 0.37 kg/tonne

Method of Addition	Total Minutes of Mixing	Wet Drop	Wet Crush	Dry Drop	Dry Crush	% Water
Emulsion[2] then	6					
Na_2CO_3 Solution	3	6.7	3.8	2.3	5.2	8.9
Na_2CO_3 Solution then	6					
Emulsion	3	8.4	3.7	2.0	4.0	9.1
Emulsion and Na_2CO_3 Solution Applied Together[3]	6	5.2	3.7	2.2	4.8	8.5

---

[1] The emulsion contains 27.6 percent active polymer.

[2] The emulsion was PAM/NaV/VA in a mole percent of 47.5/47.6/4.9.

[3] The emulsion and inorganic salt solution were applied concurrently to the taconite ore concentrate from separate containers.

This example demonstrates that an inorganic salt solution can be applied in conjunction with polymer binders to effectively agglomerate a mineral ore concentrate.

EXAMPLE X

This Example was conducted on taconite concentrate in the same manner as Example I. This example compares the effectiveness of a binding agent in a water-in-oil emulsion both with and without an inverting surfactant. This test involved a two-step addition. The Na_2CO_3 powder was added to the taconite concentrate and mixed for three minutes. The emulsion was then added and the entire composition was mixed an additional three minutes. The test results are presented in Table XIV.

TABLE XIV

	Wet Drop	Wet Crush	Dry Drop	Dry Crush	% Water
Emulsion* with inverting surfactant	5.1	3.9	2.0	4.4	8.5
Emulsion* without inverting surfactant	3.7	3.9	2.0	3.6	8.3

---

* Both emulsions contain PAM/NaA/VA in a 47.5/47.6/4.9 mole ratio at 0.50 kg of emulsion per tonne and 0.37 kg Na_2CO_3 per tonne.

This experiment demonstrates that acceptable green pellets are formed both with and without an inverting surfactant in the emulsion.

EXAMPLES F AND XI

The following Examples were conducted in full scale plant with a full size balling drum and kiln. In these Examples 55 tonnes per hour of taconite concentrate were conveyed to and processed in the balling drum. The selected binding agent systems were added by spraying onto the taconite ore concentrate just prior to entering the balling drum and by vibrating the Na_2CO_3 powder onto the taconite ore concentrate. The average contact time of the binders with the mineral ore concentrate before entering the balling drum was approximately 0.5 to 1 minute. The average size of the green pellets obtained were between approximately one-fourth to one-half inch in diameter.

In Example XI an anionic water-in-oil emulsion of PAM/NaA/VA in a mole percent of 47.5/47.6/4.9 was used as a polymer binding agent. The quantities of binding agents used and the results obtained by the poly(acrylamide) based polymer binding agents are detailed in Table XV. Comparative results for other binding agents are in Table XVI.

TABLE XV

Example	Test Number[1]	PAM/NaA/VA l/min	PAM/NaA/VA kg/tonne	Na_2CO_3 kg/min	Na_2CO_3 kg/tonne	Wet Compression Pa	Wet 457 mm (18") drop	Dry[2] Compression Pa
IX	1	0.55	0.68	0.33	0.36	---	---	---
IX	2	0	0	0.33	0.36	---	---	---
IX	3	0.55	0.68	0.00	0.00	---	---	---
IX	4	0.38	0.43	0.33	0.36	0.10×10^5	8.4	0.16×10^5
IX	5	0.42	0.48	0.17	0.18	0.11×10^5	7.0	0.12×10^5
IX	6	0.53	0.61	0.43	0.47	0.14×10^5	10.6	0.19×10^5
IX	7	0.45	0.51	0.77	0.84	0.14×10^5	9.6	0.21×10^5

TABLE XV CONTINUED

min

Test Number Cont.	Avg. Fired[3] Compression Pa	% of Fines That Break Under 13.8x10^5Pa (200 psi)	% FeO	% H_2O	457 mm (18 ") drop Min. after start of bin addition 10	 20	 30	
1	22x10^5	19	0.43	9.6	--	16.0	7.3	7.
2	--	--	--	9.2	6.0	4.2	3.6	--
3	--	--	--	10.1	4.5	11.1	9.3	--
4	13.4x10^5	63	0.35	10.1	8.7	7.8	8.5	--
5	16.8x10^5	50	0.31	9.4	8.0	9.3	8.0	--
6	8.1x10^5	85	5.1	--	10.5	18.7	13.2	6.
7	17.9x10^5	42	0.31	9.8	12.5	12.1	11.9	--

TABLE XV CONTINUED

Size Distribution of Pellets

Test Number Cont.	+12.7mm	+11.11mm	+9.52mm	+8.73mm	+6.35mm	-6.35mm
1	2.2	43.2	43.7	7.8	1.4	1.8
2	13.6	57.1	19.9	4.8	2.1	2.5
3	2.9	33.5	40.8	14.3	4.8	3.7
	4.7	31.8	46.4	8.5	2.8	5.9
4	2.7	27.9	44.6	15.1	4.6	5.1
5	1.4	45.4	44.3	6.8	1.1	1.0
6	1.2	14.1	58.6	20.2	3.8	2.1
7	1.9	22.5	57.9	12.9	2.8	1.9

---

[1] Samples were obtained by (1) filling a basket with green pellets, (2) transporting the basket through the kiln operation, and (3) testing pellets from the top, mid-top, mid-bottom, and bottom of the basket.

[2] Pellets contain no moisture, samples are taken just prior to kiln operations.

[3] Samples are taken after drying in kiln.
\+ 48 MIN
++ 40 MIN

BAD ORIGINAL

Examples	Test number	Wet compression Pa	Wet 18"drop	Dry compression Pa	Average fired compression Pa	% of fines that breaks under 13.8×10^5 Pa (200 psi)	% water
F	CMC/NaCl Na_2CO_3 (control) 5kg /tonne	0.09×10^5(Apx.)	5.0(Apx.)	0.07×10^5	---	40	---
F	CMC/NaCl Na_2CO_3 (control) 9,5kg /tonne	0.09×10^5(Apx.)	5.0(Apx.)	0.24×10^5	17.3×10^5	---	---
F	Bentonite* (typical values)	0.15×10^5 to 0.18×10^5	7 to 10	0.34×10^5 to 0.41×10^5	30.3×10^5	<6	9.0

---

* Apx. 8.2 kg/tonne.

These Examples show that the 18 inch drop number for wet green pellets and the dry compression strength of dry pellets improve with increases in Na_2CO_3 concentration. Varying the concentration of Na_2CO_3 did not show a trend in the compression strength of fired pellets.

IN THE CLAIMS:

1. A process of agglomerating a particulate material comprising: commingling said particulate material which is preferably a mineral ore concentrate and more preferably an iron ore concentrate with a binding amount of water soluble, high molecular weight polymers, said polymers being adapted to be selectively usable in at least one of either of two conditions of use,

in a first condition of use being applied to said particulate material as a dry powder and, in a second condition of use being applied to said particulate material in a water-in-oil emulsion.

2. A process for manufacturing fired, agglomerated mineral ore, comprising:

(a) commingling a binding amount of powdered water soluble, high molecular weight polymers onto mineral ore concentrate to form a composition, said mineral ore concentrate having a sufficient moisture content to activate said polymers;

(b) agglomerating said composition to form green pellets by a means for pelletizing mineral ore concentrate; and

(c) firing said green pellets by a means for applying sufficient heat to indurate said pellets.

3. A process for manufacturing fired, agglomerated mineral ore, comprising:

(a) commingling a binding amount of water soluble, high molecular weight polymers dispersed in an aqueous phase of a water-in-oil emulsion onto mineral ore concentrate preferably iron ore concentrate, to form a composition;

(b) agglomerating said composition to form green pellets by a means for pelletizing mineral ore concentrate; and

(c) firing said green pellets by a means for applying sufficient heat to indurate said pellets.

4. The process of claim 1, 2 or 3 wherein said polymers are poly(acrylamide) based polymers.

5. The process of claim. 1, 2 or 3 further comprising commingling a binding amount of an inorganic salt with said mineral ore concentrate, preferably said inorganic salt being an alkali or alkali metal salt of carbonates, halides, or phosphates, and more preferably said inorganic salt is a member selected from the group consisting of sodium carbonate, calcium carbonate, sodium chloride, sodium metaphosphate, and mixtures of these.

6. A process of producing pellets comprising:

(a) preparing a premixture of a poly(acrylamide) based polymers,

said polymers being adapted to be selectively usable in at least one of either of two conditions of use,

in a first condition of use being applied to a mineral ore concentrate as a dry powder and in a second condition of use being applied to said mineral ore concentrate in a water-in-oil emulsion,

said polymers being water soluble;

(b) mixing separately with said mineral ore concentrate for a sufficient amount of time to form a bound composition:

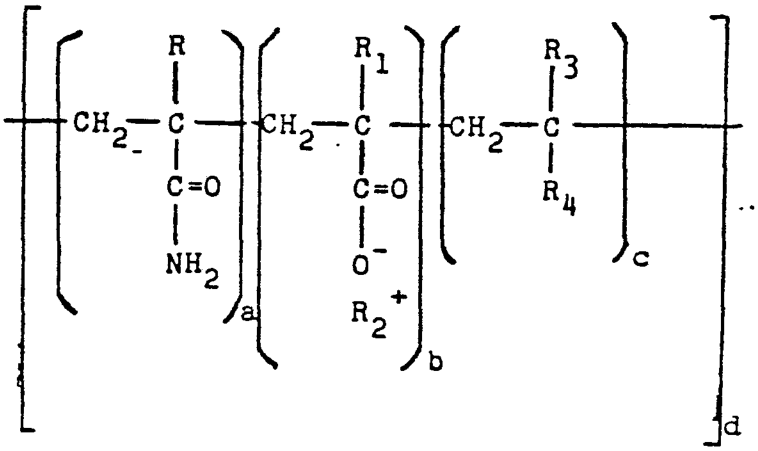
(i) a binding quantity of said premixture; and

(ii) a binding amount of an inorganic salt;

(c) pelletizing in a balling drum said composition to form green pellets;

(d) indurating said green agglomerates with heat.

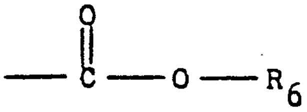
7. The process of any one of claims 1 to 4 wherein said polymers are of the following general formula:



$$\left[\left(-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{NH_2}}}{\overset{\substack{R\\ |}}{\mathrm{C}}}-\right)_a\left(-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{O^-}\\ R_2^+}}{\overset{\substack{R_1\\ |}}{\mathrm{C}}}-\right)_b\left(-\mathrm{CH_2}-\underset{\substack{|\\ R_4}}{\overset{\substack{R_3\\ |}}{\mathrm{C}}}-\right)_c\right]_d$$

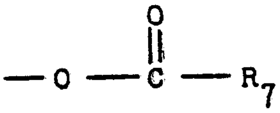
wherein R, R_1, and R_3 are independently hydrogen or methyl, R_2+ is an alkali metal ion, such as Na+ or K+, R_4 is either

(1) $-OR_5$, wherein R_5 is an alkyl group having up to 5 carbon atoms;

(2) 

$-\overset{O}{\overset{\|}{C}}-O-R_6$

wherein R_6 is an alkyl group having up to 8 carbon atoms;

(3) 

$-O-\overset{O}{\overset{\|}{C}}-R_7$

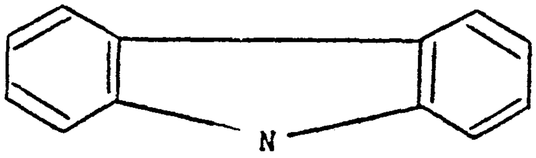
wherein R_7 is either methyl or ethyl;

(4) phenyl;

(5) substituted phenyl;

(6) -CN; or

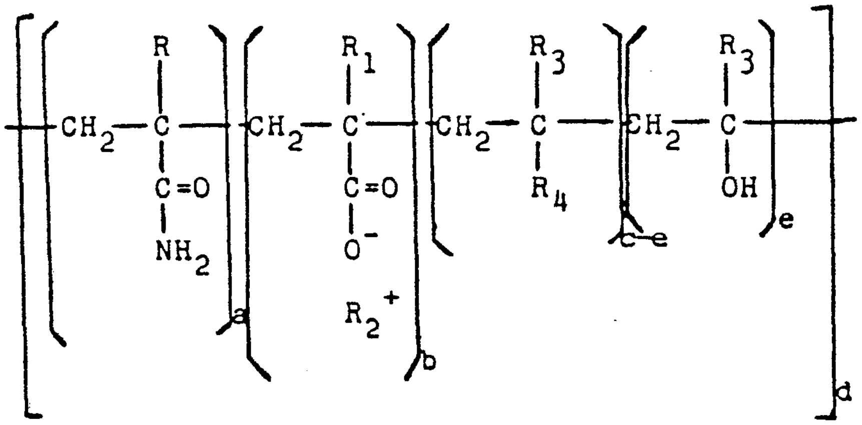
(7)



; and

wherein (a) is from about 5 to about 90, perferably from about 30 to about 60 percent, (b) is from 5 to about 90, preferably from about 30 to about 60 percent, (c) is from about 0 to about 20 percent with the proviso that (a)+(b)+(c) equal 100 percent, and (d) is an integer of from about 1,000 to about 500,000.

8. The process of claim 7 wherein said polymers are tetrapolymers of the following general formula:



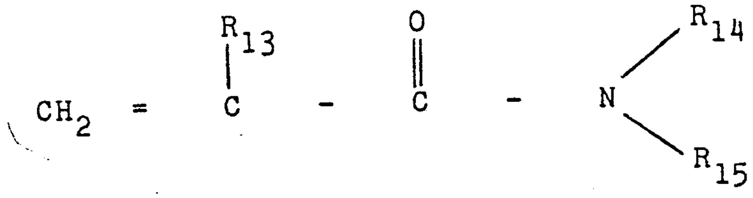
$$\left[\left(CH_2-\overset{R}{\underset{\underset{NH_2}{C=O}}{C}}- \right)_a \left(CH_2-\overset{R_1}{\underset{\underset{\underset{R_2^+}{O^-}}{C=O}}{C}}- \right)_b \left(CH_2-\overset{R_3}{\underset{R_4}{C}}- \right)_{c-e} \left(CH_2-\overset{R_3}{\underset{OH}{C}}- \right)_e \right]_d$$

wherein R, R_1, R_2+, R_3, a, b, and d are as defined in claim 7 R_4 is $-OR_5$ or $-O-\overset{O}{\overset{\|}{C}}-R_7$ wherein R_5 and R_7 are as defined in claim 7, c is from about 0 to about 20 percent, and e is from about 0.1 to about 20 percent.

9. The process of claim 7 wherein said poly(acrylamide) based polymers are derived from monomer units of acrylamide, sodium acrylate, vinyl acetate, and mixtures of these, preferably from monomer units of acrylamide and sodium acrylate and more preferably from monomer units of acrylamide, sodium acrylate, and vinyl acetate.

10. The process of any one of claims 1 to 6 wherein said binding amount of said polymers is applied to said mineral ore concentrate at an active polymer concentration on said concentrate between about 0.001 percent and about 0.3 percent by weight of dry concentrate.

11. The process of any one of claims 1 to 3 or 6 wherein said polymers are derived from monomer units of acrylamide and methacrylamide and derivatives thereof of the formula



$$CH_2=\overset{\displaystyle R_{13}}{\overset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-N\begin{matrix}R_{14}\\R_{15}\end{matrix}$$

wherein R_{13} is a hydrogen atom or a methyl group; R_{14} is a hydrogen atom, a methyl group or an ethyl group; R_{15} is a hydrogen atom, a methyl group, an ethyl group or $-R_{16}-SO_3X$, wherein R_{16} is a divalent hydrocarbon group having 1 to 13 carbon atoms and X is a monovalent cation.

12. The process of claim 6 wherein said inorganic salt is a member selected from the group consisting of sodium carbonate, calcium carbonate, sodium chloride, sodium metaphosphate and mixtures of these.

13. The process of any one of claims 5 or 12 wherein said inorganic salt is applied to said mineral ore concentrate in a concentration on said concentrate between about 0.001 percent and about 0.5 percent by weight.

14. The process of any claim of claims 5 or 12 wherein said inorganic salt is applied to said mineral ore concentrate in an aqueous solution.

15. A product of the process of any one of claims 1, 2, 3, 5 or 6.

16. The process of any one of claims 1, 3 or 6 wherein said water-in-oil emulsion has an oil phase, said oil phase is benzene, xylene, toluene, mineral oils, kerosenes, paraffinic hydrocarbons, petroleum, Isopar® M, or mixtures of these.

17. The process of any one of claims 1, 3 or 6 wherein said

emulsion contains an inverting surfactant.

18. The process of any one of claims 2, 3 or 6 wherein said sufficient heat to indurate said pellets is of a temperature of at least 982°C (1800°F) and preferably 1,538°C (2800°F).