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ORE PELLETIZATION PROCESS AND PRODUCTS

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This invention relates to an improved method for pelletizing metallic minerals and ores, resulting in pellets having increased strength and cohesiveness. More particularly, this invention is concerned with the use of amine humate salts as pelletizing aids in such a process, which salt inclusion aids to increase the overall efficiency of the pelletizing process and also produce pellets of such increased strength, cohesiveness etc., that they are attrition resistant and able to withstand mechanical and thermal shock.

In recent years, the metal refining industry has undergone striking changes in processing ores for refinery and/or smelting. In particular, emphasis has been placed upon production of pellets making a part or all of the ore charge since their use has resulted in immense increases in efficiency in operation of blast furnaces. In particular, the melting of such pellets in a blast furnace can be achieved at increased rates, with concurrent decrease in emission of small particles of flue dust which for most efficient operation must be collected and reused. Also, a permeable bed of pellets allows rapid transfer of the hot reducing gases through its entire dimension. In many instances up to 20% increases in efficiency have been noted when ore pellets are used in the blast furnace. The reduction of iron ore and manufacture of steel are particularly improved through use of such pellets.

While in some instances relatively pure ores containing a high percentage of the valuable mineral constituent have been pelletized after minor prior processing such as crushing, of more importance is the production of pellets from relatively impure ores, such as ores having a low content of iron oxide. Since these ores of necessity must be beneficiated, that is, increased in relative proportion of desired metal content, and since after such process of beneficiation the purified mineral is already in the wetted particulate state, a pelletization process is particularly suitable. The ore mass then can be easily and conveniently made into pellets for subsequent blast furnace use. Also, not only are the lower grade ore deposits such as finely divided hematite iron ore deposits more useful in such pelletizing process, but also "tailings" from prior ore processing, which have heretofore been discarded and stockpiled, can also be made into convenient pellet size. Thus, in the case of these relatively impure minerals or by-product fines, not only is it desirable to pelletize these materials, but in many instances it is also essential. For example, in the case of working low grade iron ores the products cannot be fed directly into a blast furnace due to the fact that the high content of impure materials would cause considerable slag with result of inefficiency of operation and repeated breakdown. Likewise, many of these relatively impure ore deposits are in such a fine state of aggregation that they would be lost through the flue of the blast furnace long before any liquification into a fluid state could take place. The same result occurs through use of flue dust, which, while it could be collected and reused, nevertheless in subsequent reuse without further processing would again be lost through the flue. Therefore, these fine particles must be processed into larger dense masses such as small integral units or pellets. Thus, it can be seen that the pelletizing process is admirably suited to use of the above type materials.

As is mentioned above, in the case of impure mineral deposits the valued or desired metal constituent in the

mineral must be concentrated prior to pelletization. For example, many impure iron ore deposits have an iron content as low as 30% or less. These deposits must be increased in iron content to above about 60% in order for them to be economically and efficiently employed in the blast furnace as pellets.

In general, these impure ore deposits are processed to the desired wetted particulate state prior to pelletization as follows: The first step normally involves crushing or comminution of the raw ore as mined or in the presence of a liquid media, most generally water, by means of successive reduction steps to the final particulate stage. In the crushing operation in which the final particles are usually ground to a fine or intermediate state, two general types of mechanisms are employed to apply gradual pressure to the particles. The first mechanism involves reciprocating breakers, that is, alternate approach and withdrawal of the crushing surfaces in the crushing zone to a substantially fixed predetermined minimum spacing. Reciprocating pressure breakers include such mechanisms as jaw, gyratory, cone and gyrasphere crushers. The continuous pressure breakers include rolls, single roll crushers and roller mills. Of lesser importance are impact crushers such as stamps, hammer mills and tumbling mills.

In order to concentrate the valuable or desired metal in the mineral, now in a particulate state, it is necessary to separate it from the impurities or gangue which normally contains a substantial amount of silica which is later discarded. One means by which the mineral may be separated from the gangue is by gravity concentration since the desired metal portion of the mineral and gangue differ appreciably in specific gravity. The theory or gravity separation depends upon a difference in movement in response to joint simultaneous actions upon the mineral and impurity or gangue by gravity and one or more other forces. This type concentration may be carried out by means of pulsated, shaken, or stirred beds, water impulse separators, pneumatic concentration, etc. Normally, water is employed as the impregnating fluid. Another method of concentration of the valuable mineral constituent is by means of flotation processes. Normally these consist either of froth flotation or agglomerate or table flotation. Another excellent method of concentrating the desired constituent is by magnetic means. This is effective only with magnetic iron oxide ores. In particular, magnetic iron ores such as taconite are admirably suited to beneficiating by treatment of the ores with electromagnets or magnets.

After the desired mineral content has been increased to a relatively high content via any of the above means, the material must normally be partially dewatered either by draining or thickening. For best pellet formation the mass of the particulate mineral substance to be processed must be in a damp or wetted condition. Normally from 5–10% by weight of water content is required for efficient pellet formation. In conjunction with the dewatering process, normally the beneficiated ore must be filtered to give a wet ore mass having water in the above range. This filtration may be carried out by use of continuous vacuum, sand, pressure, vacuum-leaf, centrifugal, etc., filters. After such processing, the mineral is now in the desired state for pellet formation.

The concentrated, dewatered ore may be pelletized alone or flue dust may be added thereto and the resultant mixture pelletized. Likewise moist flue dust may be pelletized singly. Generally, prior to the pellet forming step, coke is added as a fuel media for use in the subsequent step of firing or setting the formed pellets to a hard mass suitable for mechanical handling and shipping. Normally since the bulk of the siliceous material has been removed in the separation of the gangue from valuable mineral constituent, no flux is necessary. However, in some in-

stances a small amount of calcium carbonate-containing material, preferably limestone, may be used as a flux. This flux intermingle in the pellet causes ore such as iron ore to melt more readily by dissolving the outside or surface impurities, thereby increasing the fluidity of the impure ore in bringing all of its components to a more intimate contact during the liquification step at the blast furnace.

In addition to sources of ore such as the low grade ores which have been processed as generally outlined above, ore flue dust or sludges may also be used. In the case of iron ore a convenient source is found in the use of sludge which is obtained in aqueous suspension or slurry, from flue gases which have been collected from blast furnace stacks, wetted in gas washers and then concentrated. Other iron ore sludges may be found, for example, in holds of iron ore barges or around iron ore shiploading areas. Also, in addition to use of flue dust as a by-product from the blast furnace melting process, cold and hot fines falling from a sinter process, and tailings from other iron ore processing may be used. For convenience sake these finely divided dry iron materials, generally in the form of impure iron oxides, may be referred to as iron dust. Again, these may be used alone, in combination with each other or with the beneficiated ore concentrate and/or the ore sludge.

In order to form an ore pellet of sufficient strength to hold its shape prior to the firing step, it is necessary, as mentioned above, that it contain sufficient water to form a damp mass suitable for formation of a cohesive pellet. Normally in the case of impure ore deposits which have been processed by the above stated steps, sufficient water remains after the filtration step so that no additional water need be added. In some cases though, it may be necessary that water be added to the material to be pelletized in order to give it more compactness in pellet-forming tendency. The water may be added directly to the material at any point prior to the pelletizing, and/or it may be introduced into the system by use of ore sludge. A burden form material to be pelletized is then available in a form for ready pelletization by means of known machinery.

The pelletization step itself may be carried out by such machinery as a disc or drum pelletizer. This machinery comprises a rotating inclined surface which agglomerates the burden material composite into pellets when the burden is flowed upon the revolving inclined surface. The burden therefore must be capable of being compacted into pellets by virtue of the centrifugal force imparted by the revolving pelletizers. Therefore, it is essential that the burden have sufficient adhesive qualities in order to form relatively large pellets of sufficient strength to withstand subsequent processing and transfer prior to their firing. Multiple-cone drum pelletizers are particularly desirable for the pelletizing operation. Another type of machinery available for this use is a pug mill which in its simplest form is a long trough containing two parallel counter-rotating paddle-bearing shafts, horizontally mounted in side by side relationship so that the paddles on respective shafts are moving upwardly and away from each other in the center of the trough. This paddle action tends to fluff the burden mix, and cause the dampened mass to be joined into cohesive particles. It is essential to the pelletizing process that the core either have some inherent natural binding tendency or be treated so that its binding tendency is increased to the point where pellets may actually be formed. Ores containing clay impurities have such natural binding tendency. However, these ores are becoming increasingly scarce and the harder to handle ore such as iron ores of relatively low iron content are becoming increasingly more important.

Therefore in order to give compression or "green" strength to the pellets with concomitant increase in pellet size, it has been proposed that substances be introduced into the burden material in order to act as binders both during the pelletizing step and subsequent thereto. Prior art substances such as pickle liquor, lime, starch and other naturally occurring organic materials, and the like have been tried with little success. These prior art binders either fail to impart the required green strength to the pellets or commonly fail to increase the pellet size to that sufficient for efficient utilization in the firing process and subsquent blast furnace operation. Many of these substances give a barely passable pellet only with increased retention time in the pelletizing process, thus increasing cost by reducing through-put.

Another material which has been used as a binder is bentonite, a naturally-occurring clay. However, this material has the important disadvantage of adding silica to the burden mixture. To combat this problem, additional amounts of limestone are required to remove the silica contained in the bentonite during the blast furnace operation. This silica creates large amounts of unusable and deleterious slag in the blast furnace operation. Another disadvantage of such material is that relatively large quantities must be used to give the required binding effects.

It would therefore be an advantage to the art if a binder could be introduced into burden material which is to be pelletized, which binder would increase the pellet size of the burden, allow a rapid pelletization, and increase the "green" or compression strength of the formed pellets, thereby allowing considerable physical handling without breakdown in pellet size or shape. Another advantage would be realized if this binder was relatively inexpensive, imparting no deleterious impurities into the burden and resultant fired pellet product, and could itself be used as a source of fuel during the firing where the formed pellet is fixed into a hardened state.

It therefore becomes an object of the invention to provide a method of increasing efficiency of pelletizing metallic minerals and improving the pellet product thereof by addition of a novel binder into the ore burden prior to its pelletization.

Another object is to provide an organic binder of a relatively inexpensive nature, which can be efficiently fed in low amounts into a mineral burden without introducing impurities which would adversely affect the subsequent process of firing or the use of resultant products thereof as a blast furnace feed.

Another object of the invention is to provide ore pellets, and particularly iron ore pellets having improved green strength and ability to withstand considerable handling prior to their firing and fusing, the thermal shock during such firing.

Another object of the invention is to provide organic salts which may be used as pelletizing aids in ore refining and related process.

In accordance with the invention, it has been found that certain novel organic salts comprising amine humate salts are extremely useful as binders for metallic mineral ore pellets. Use of such salts as binders increases the ability of ore composites to be pelletized into relatively large pellet sizes, with the resultant pellets having sufficient compression or green strength to withstand handling and transferring prior to their firing to a fused mass. Generally speaking, the process of the invention comprises addition of at least a binding amount of amine humate salt to a wetted mass of comminuted metallic mineral whereby a composite is formed and then pelletizing the composite into integral units or pellets.

The processing of impure mineral ores into their final hardened pellet stage generally includes the step of comminution of a mineral ore to particulate size, concentrating from this impure ore the valued or desired mineral constituent thereof to any desired increased purity by treating the mineral such as by gravity concentration, flotation, or magnetic separation, etc., in order to obtain a wetted particulate mass, pelletizing this wetted mass into intregal or individual pellets and finally firing the formed pellet units to a hardened fused state for use in blast furnace operations. The particular improvement

in this method, comprising the invention, is addition of an amine humate salt during or before the pelletization step whereby pellets are easily and efficiently formed due to the binding effect of the humate salt to a point where they have sufficient strength and adhesiveness to withstand the mechanical handling, prior to firing and the thermal shock during the actual fusion of the bound pellets.

Almost any type of metallic mineral desired to be pelletized may advantageously be acted upon by the amine humate salt binders. For example, the predominant desired metal constituent of the mineral may be chosen from among lead, copper, nickel, zinc, uranium, iron, etc. Mixtures of the above or any other metal occurring in the free or molecularly combined natural state as a mineral, or any combination of the above, or other metals which are capable of pelletization may be acted upon by the amine humate salts. While particularly effective results are realized in pelletization of minerals predominantly containing iron, it is understood of course that the invention encompasses enhancing the binding into pellets of any mineral containing a variety of metals or containing a single constituent in high abundance. For purpose of simplicity, the following discussion relating in more specific detail the pelletization process of the invention will be limited to processing of iron ores. It is understood that this is merely illustrative and the invention cannot be considered to be limited thereto.

As mentioned above, the burden or material to be pelletized may contain iron ore deposits coming directly from the mining site, from ore "tailings," flue dust, cold and hot fines from a sinter process or iron ore which may be found in a sludge condition as aqueous iron ore concentrates from natural sources or recovered from various processes. For example, flue gases containing fine flue dust particles may be caught, wetted in gas washers and then concentrated by coagulation-type clarifiers into a relatively concentrated wet sludge which may be employed in the pelletizing operation. Any one of these sources of iron or any possible combination thereof may be employed according to their availability and particular process setup of the pelletizing unit, normally existing at the mine site itself. Iron ore or any of a wide variety of the following minerals may form a part of the burden: magnetite, hematite, limonite, goethite, siderite, franklinite, ilmenite, chromite, pyrrhotite, cholcopyrite, pyrite, etc.

To the burden may be added a flux material chosen from a number of substances. In most cases due to the fact that silica and related impurities have been removed in the processing prior to pelletization, a flux material is not needed. However, if such is necessary, a calcium carbonate containing substance is generally employed because of availability and relatively low cost. Among these, limestone or an impure source of limestone, such as calcite are suitable. Calcite is also known as calcspar which is a hexagonal, normally colorless, rock-forming mineral composed of both crystalline species, such as Iceland spar, corn spar and satin spar, and amorphous varities including chalk, marble, limestone, stalactite and baryte. Also spongy and flake-like calcium-containing mineral forms, such as mountain milk and schifer spar may be employed.

Another element in the burden, normally essential in order to fire and fuse the formed burden pellets after pelletization, is a source of fuel. Generally coke is employed, but any other inexpensive source of fuel may be included in the operation. A particular advantage in the use of amine humate salts as a binder is that concurrent with its action in building up larger pellets and giving greater compression strength, is its ability to burn and thereby enhance the fuel value of coke or any other fuel used in the firing step. A typical sample of amine humate salt has a fuel value of 6,000–10,000 B.t.u./lb. Therefore the amine humate binder not only helps to form pellets of requisite size and strength, but also volatilizes in the firing step thereby acting as a minor source of fuel without forming any deleterious slag deposits during this particular step of the process.

As outlined above, in order to promote compactness in adhesiveness of the pellets so that they may withstand handling subsequent to their formation and prior to the firing step, it is necessary that they be moist and in condition for ready and efficient pellet formation. It is necessary, then, that water in some form be added to the burden prior to the pelletization. The added water operates in conjunction with the amine humate salt to give good binding action. In the wet processing of impure ores, whereby the desired metal constituent is increased to a usable amount, sufficient water for good compaction generally remains after the completion of this beneficiation. However, in some cases water may be conveniently added by use of aqueous ore sludge, or may itself be added at any point in the overall pelletizing process either before or after the binder has been added to the burden to form a composite thereof.

It is preferred that the aqueous content of the burden prior to pelletization comprises 2–20% by weight of water based on the weight of the burden. More preferably the water content of the burden forms from 5 to 10% by weight of the entire mixture. In its most favorable aspect a burden composition comprises 6–9% by weight of an aqueous liquid primarily composed of water. Whether the above percent weight range is based on the weight of the burden alone or the composite comprising the burden and binder is immaterial, due to the relatively insignificant weight of the binder in comparison to the burden weight.

The amount of amine humate salt added to the burden may be varied according to the particular needs of the pelletizing operation. It has been determined that excellent results are obtained when from 0.1–100 pounds of amine humate salt per ton of burden are employed. More preferably, 0.5–10 pounds of amine humate salt are added per ton of burden with the most preferable results, from a standpoint of efficiency, and cost being obtained in the range of 0.5–5.0 pounds per ton. When measured in terms of parts of binder per million parts of burden it is preferred that the binder be added in the range of from 50–5000 p.p.m. and more preferably from 50 to 2500 p.p.m.

The amine humate salt may be added at any place prior to the pelletization operation. In the normal operating procedure the finely divided iron ore in any of its various forms and the coke, and, if necessary, flux material, which components when combined with the above required amounts of water comprise a mixture known as a burden, are mixed together first. The binder may be added in at any spot of the operation, before, during or after addition of any of the components of the burden. It is preferred, however, that the burden be prepared first and that the binder subsequently be added in required amounts. Partial mixing may be effected by transfer of the burden and binder, but more nearly complete mixing is effected during the balling step itself, in order to give a fairly homogeneous iron ore composite.

Any of the many well-known types of pelletizing apparatus may be used in this operation, but the preferred embodiment involves the use of what is known as a revolving disc or revolving drum-type pelletizing machine. In this type of operation the composite comprising the burden and binders flow over revolving surfaces, and are retained thereon for a sufficient amount of time, generally only a few seconds or so, to impart a centrifugal force to the composite and form or "ball" it into numerous agglomerates or pellets. These pellets spinning off the surface of the revolving drum or disc are then caught on a conveyor belt for transfer to the firing furnace. In the case of revolving discs the surfaces are normally set at

an angle of inclination ranging from 40° to 60°. Additional water may be added to the rotating pelletizing disc in order to promote better pellet formation.

As mentioned above, the ore-containing materials may also be composed of fines, hot or cold, or flue dust. In another embodiment of the invention these fines are added to the already formed pellets, and are held in contact with the moist adhesive-type pellets prior to entrance into the ignition furnace.

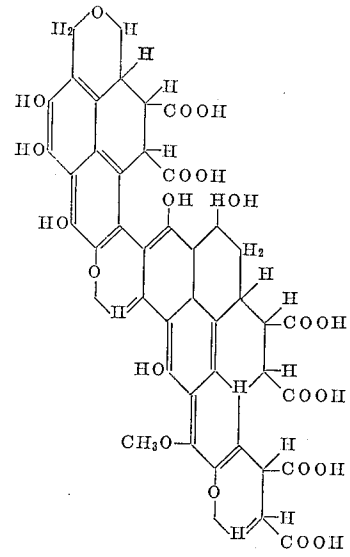
The mechanism by which the amine humate salt accomplishes its pelletizing action is not known for certain. However, it is believed that the binder imparts a degree of adhesiveness to the burden, but even more importantly it develops a compressible fluid bond at the particle interfaces of the burden. Since the binding action is dependent upon formation of thin surface films, rather than upon slurry formations, the amount of necessary moisture comprising a portion of the burden-binder composite will be less than normal, which reduction materially benefits the overall efficiency of the pelletizing process. The advantages of the use of the amine humate binders in the invention are many and varied. For example it was noted in trials, that much larger pellets were formed than was normal with no binder being applied. In fact, the average pellet size was much greater than that resulting from use of prior art binders. Due to the excellent pelletization action, the entire operation was able to be speeded up to a rate considerably above that which is considered normal. Also, it was possible to make up the burden to comprise a high amount of flue dust, utilization of which is a considerable economic advantage. Prior to invention of the process of addition of the amine humate salt compositions of the invention, substantial flue dust content in the burden could not be present without tending to have adverse effects on the firing operation.

In addition to the above advantages derived from the use of the binders of the invention, a further important effect was noted in trials, that is, increase in compression or "green" strength of the formed pellets, so that they were able to withstand handling subsequent to the pelletizing operation. A high compaction is necessary in order for the pellets to retain their characteristic shape, so that they may be mechanically handled and transferred to the firing furnaces without crumpling or complete breakdown of pellet formation. The ability of amine humate pelletizing aids to increase significantly the compressive or "green" strength of the formed pellets will be discussed in more detail hereinafter.

PELLETIZING AIDS

The amine humate salts, of course, are the resultant products from reaction of a source of humic acid which is a generic term for acids derived from humus or the top layer of the soil containing organic decomposition products of vegetation etc., with an amine. Sources of the humic acid may be from peat, brown coal, lignite, and the like. Of course, the invention contemplates salts prepared from the above raw materials containing varying amounts of humic acid. In fact, it is preferred that the impure or just mined material be used as a starting reagent due to low cost, availability, and lack of need for costly processing prior to salt formation.

One of the preferred sources of humic acid as used in preparing the pelletizing aids of the invention is leonardite, often found in association with lignite. This is a specific organic substance named after A. G. Leonard who was associated with its discovery. It is considered to be more in the nature of a chemical useful in various additive processes rather than as a fuel, due to its relatively poor combustibility and low B.t.u. content per unit weight. Leonardite is primarily mined from the Harmon bed in Bowman County, North Dakota, and Divide County, North Dakota, and in and around Alpine, Texas. Although physically similar to lignite, leonardite has a much richer oxygen content than does ligite, ranging in oxygen content from 27–33% by weight, whereas lignite contains about 19–20% oxygen by weight. The high oxygen content of leonardite is ascribed to the presence of carboxylic acid and phenolic groups in the leonardite molecule. Spectral analysis has indicated that leonardite is generically speaking a mixture of humic acids and salts thereof which upon excitation for such analysis, causes certain distinctive spectral patterns to appear. Although not proved conclusively, leonardite is probably a large condensed ring polymeric molecule containing carboxyl groups. The following structural formula has been proposed as a representative-type molecule defining leonardite. This formula, of course, is not meant to be conclusive but has been tendered in order to show the complex problems in defining such sources of humic acid as leonardite, and other humic acid-containing materials. Reference to their mining source is often the most convenient route to precise definition.



A typical leonardite sample normally said to be comprised of calcium, sodium, magnesium, potassium, etc., salts of complex organic acid and free organic acid is partially analyzed as follows: Ash, 14.01; C, 48.75–53.98; H, 3.79–4.70; N, 1.25; O, 31.99; CH_3, 1.26; CH_3O, 0.44; CH_3CO, 0.38.

The equivalent weight of the above sample of leonardite was determined to be 256.

In order to synthesize the amine humate pelletizing aids of the invention it is only necessary to add an amino component to the above humates. The salt-forming reaction is preferably carried out in the presence of water. A wide variety of amines may be employed as reactants, but it is greatly preferred that amines be employed whose reaction products with the humus materials be water-soluble or water-dispersible. For best effectiveness the amine humate salts must have the ability to be solubilized, or at least must have sufficient hydrophilic character to be colloidally dispersed in water. Among those preferred amines are monoamines, and more preferably amines containing at least one hydroxyl group. Amines which have been employed with much success include methyl amine, ethyl amine, diethyl amine, morpholine, butyl amine, isopropylamine, di-isopropylamine, N-methyl morpholine, triethylamine, aminoethyl ethanolamine, diethanolamine, diethyl ethanolamine, di-isopropanolamine, dimethyl ethanolamine, dimethyl isopropanolamine, N-hydroxy ethyl morpholine, N-methyldiethanolamine, monoethanolamine, monoisopropanolamine, triethanolamine, tri-isopropanolamine, 1,1-dihydroxymethyl ethylamine, 1,1-di-

hydroxymethyl n-propylamine and polyglycolamine. A preferred species of the last amine listed has a general formula, $H_2NCH_2CH_2(OCH_2CH_2)_nOH$ where n may vary from 1 to 10.

The method of preparation of amine salts by reaction of the respective salt-forming ingredients may be considerably varied. A representative method is to dissolve the amines in water, mix thoroughly with the leonardite, and then allow the salts to air-dry from the liquid media. The drying step may also be conveniently carried out in drying ovens. The resultant salt is then broken up somewhat and is immediately ready for pelletizing use. The mode of addition of reactants to water or to each other is immaterial. For example, the humus material may be first dispersed in water and the amine added thereto. Likewise, an aqueous amine solution may be prepared, to which is added the humic acid material. During the reaction the basic amine groups react with the carboxyl groups existing on the humic acid, in order to form salts having requisite water solubility.

In preparation of the above amine humate salts, it is preferred that from 0.1 to 1.0 equivalent of amine be used for each equivalent of humic acid. The equivalent weight of the particular humic acid material employed is the weight required to react with one mole of sodium hydroxide, depending in turn upon the number of reactive groups available.

If desired, the above salt forming reaction may be carried out either at room temperature or at elevated temperatures. The amount of time necessary to effect the reaction is quite minimal and usually reaction is considered complete in times varying from 2–60 minutes.

An embodiment of the invention also includes the use of both amine humates and alkali metal or ammonium humate salts in combination. While the amine humate salts are clearly superior to the alkali metal or ammonium humate salts, in some instances it may be preferable to employ a combination of the two in order to lower the total cost of treatment. One expedient of this combination is to form separately the amine humate salts and alkali metal or ammonium humate salts and then combine the respective ingredients in one composition. It is preferred that such a composite contain at least 10% by weight of amine humate salt and more preferably from 20 to 80%. In another expedient the same source of humic acid may be first treated with alkali metal, alkaline earth metal or an ammonium base such as ammonium hydroxide and then treated further with a source of any one or more amines as represented above. Likewise, the humic acid material may be first treated with an amine and then reacted subsequently with the alkali metal, alkaline earth metal or ammonium.

The inorganic metal salts of the humic acid material, and preferably sodium leonardite, when used in combination with the amine humate salts as leonardite amine salts, achieve best results when the inorganic humic salt has been prepared by reaction of humic acid material with ammonium hydroxide or an alkali metal or alkaline earth metal hydroxide, such ass odium hydroxide, calcium hydroxide, magnesium hydroxide, or potassium hydroxide in order to give a product which has a pH greater than 7.0, measured as a 10% dispersion in water. Preferably samples of humic acid such as leonardite give better results as a binding agent in combination with the amine humate salts when they have pH's as a 10% aqueous solution, of between 8 and 12. Most preferably inorganic humate salts such as leonardite salts having a pH greater than 9.0 are employed in the pelletizing operation when used as one of the components in a composite with the amine humate salts or amine salts of leonardite. It is believed that the more highly basic humic salt material has better dispersibility and mixing tendencies when added to the moist burden.

The following examples below illustrate the typical methods of preparing the amine humate salts of the invention:

Exampe I

32 grams (0.27 equivalent) of tris (hyroxymethyl) methyl amine were dissolved in 50 mls. of water. This solution was then mixed with 100 grams of leonardite humic acid (0.4 equivalent). The resultant mixture was then agitated until no further evolution of heat was noted from the salt forming reaction. After cooling, the salt product was dried overnight in the open atmosphere and then pulverized. This amine humate salt had a moisture content of 8.4%. The above product was designated as Composition A.

Example II

This preparation followed the procedure outlined generally in Example I, with the exception that 20 grams of triethanol amine was employed as the amine reactant. The final product had a moisture content of 12.1%. This product was designated as Composition B.

Example III

In this example the procedure of Example I was followed with the exception that 30 grams of triethanolamine were employed as the neutralizing base. The product was labeled Composition C.

In order to determine the efficacy of the invention, the amine humate salt pelletizing aids were tested for their utility in producing the large size desired pellets, and particularly for ability to impart to the formed pellets the essential character of green strength or pellet strength before firing. Without sufficient green strength the formed pellet tends to crump or disintegrate partially or wholly before being fused. Thus only pellets of inferior quality are formed. The test unit employed to pelletize a burden was a rotating disc pelletizer. The disc was fitted with a 4″ sleeve allowing burden charges up to 5 pounds in weight to be placed on the disc without spillage. The particular burden pelletized in this case was taconite ore which had been previously beneficiated by means of a magnetic separation until iron content of approximately 60–70% was reached. The burden had a moisture content of between 8 and 10%. Five pounds of burden were placed on the disc pan along with the binder to be tested and rotated for 3 minutes. The agglomerate was then removed and sieved through a series of screens to determine the size distribution. The 4 mesh size pills were then also tested for green strength by a simple test described in detail below.

Compositions A, B and C, were added to the above burden in order to give a binder addition calculated as 5 pounds per ton of burden. Also a blank without any additive was run, as well as a run involving the use of 16 pounds per ton of bentonitic clay, a well-known commercial binder used to agglomerate many ore materials. Table I below shows that the amine humate salt pelletizing aids showed considerably greater activity in promoting the production of the desired large size pellets, when compared to the blank and even in relation to the known bentonite clay pelletizing aid. Its effectiveness when compared to that of bentonite is particularly striking in view of the fact that the amine humate salt is used at an additive dosage of less than ⅓ that of bentonite. The amine humate salts produced a higher number of ⅜″ pellets and pellets which are screened through the relatively large size sieves, for example through series having mesh sizes of 4 (0.187″) 5, and 7, etc. Use of the bentonite clay as an agglomerating agent resulted in a high percent of fines or material being screened through a 20+ mesh size screen, that is, one allowing a screening only of those particles less than 0.0331″ in diameter. Other tests involving bentonite yielded as high as 30% fines. The larger sized pellets of course are desired, and give most efficient results as blast furnace feed after fusion. On the other

hand, fines or micro-pellets have a tendency to be blown through the flue and lost, or must be subsequently recovered and reagglomerated.

TABLE I

Aid	3/8	4 mesh	5 mesh	7 mesh	10 mesh	20 mesh	20+ mesh
Composition A	4.7	31.4	11.3	19.2	23.6	9.8	0
Composition B	4.4	27.8	12.0	17.8	25.8	12.2	0
Composition C	4.8	29.3	10.6	12.6	20.2	22.7	0
Bentonite	2.5	27.1	8.0	10.9	10.2	25.3	16.0
Blank	1.3	28.4	12.1	16.2	20.2	21.7	0.1

In order to determine the very essential property of green strength, the pellets treated with the above agglomerating agents and the blank material which was retained in the 4 mesh size screen, were then evaluated by means of a "Drop Test." This test consists of dropping these 4 mesh pellets from both 18 and 36 inch heights upon a hard surface. At 18" a total of 20 pills were dropped up to three times each, depending upon when each breaks. A score of 3, 2 and 1 respectively is assigned to each pill, corresponding to the number of drops each survives. A perfect score then is 60. For the 36" drop test, a test with no cracks is assigned 1, a cracked but not broken pill 0.5; and 0 for those pellets which break. A perfect score in this case then is 20. The latter 36" test is particularly meaningful in determining which pellets have the necessary green strength to withstand the handling subsequent to pelletizing prior to the fusing process. Not only must pills of sufficient diameter be produced, but also these pellets must be able to maintain their integral character without breakdown or crumpling. The drop test and particularly the 36" drop tests are excellent criteria in determining the strength or ability to maintain formed integral character.

Table II below shows that the taconite burden when pelletized through the aid of the amine humate salts formed excellent pellets having green strength or compression strengths heretofore unobtainable using prior art aids. In particular, those pellets agglomerated in conjunction with the amine humate salts of the invention scored high in the stringent 36" drop test. All of the amine humate salts of the invention showed clearly superior activity in promoting green strengths of pellets formed therewith, over those corresponding size pellets formed through the aid of bentonite or formed without aid of any treatment whatsoever. Thus, even though the pill size distribution obtained with no additive appeared passable, the subsequent low strength of such untreated pellets demonstrates the need for pelletizing. This need was not satisfied through use of the bentonite material, which not only resulted in a large amount of fines when employed, but the formed pellets were extremely soft when compared to like sized pellets formed through the aid of amine humate salts.

TABLE II.—PILL DROP SCORES

Aid	18" Drop	36" Drop
Composition A	29	13.8
Composition B	26	10.2
Composition C	31	13.3
Bentonite	20	8.5
Blank	16	4.7

Sodium salts of leonardite were also synthesized and used as pelletizing aids. The size distribution and strength of the pellets were likewise evaluated, and while the sodium salts of leonardite gave excellent activity in comparison to the blank and even considerably greater pelletizing activity when compared to the bentonite material, these salts did not measure up to the high degree of efficiency as shown by the amine leonardite salts. However, various combinations of alkali metal humates such as the sodium salt of leonardite and Compositions A, B and C, showed nearly as efficient pelletizing activity as did the amine salts alone.

We claim as our invention:

1. In a method of producing improved metallic mineral pellets which comprises the steps of comminution of a mineral ore to particulate state, concentrating the valued mineral constituent thereof to an increased purity, treating said mineral to obtain a wetted particulate mass, pelletizing said mass to form integral units and firing said formed pellet units to a hardened state; the improvement which comprises the step of adding to said wetted mass prior to pelletization at least a binding amount of an amine humate salt whereupon pellets are produced having increased strength and cohesiveness.

2. The method of claim 1 wherein said amine humate salt is an amine salt of leonardite.

3. The method of claim 2 wherein said amine humate salt is an hydroxyamine salt of leonardite.

4. The method of producing improved metallic mineral pellets of increased strength and cohesiveness which comprises the steps of adding at least a binding amount of an amine humate salt to a wetted mass of a comminuted metallic mineral to form a composite and pelletizing said composite to form integral units thereof.

5. The method of claim 4 where said amine humate salt is an amine salt of leonardite.

6. The method of claim 5 wherein said amine humate salt is an hydroxy amine salt of leonardite.

7. The method of claim 4 wherein said wetted particulate mass comprises finely divided iron ore.

8. The method of claim 4 wherein said wetted particulate mass comprises finely divided iron ore and iron dust added thereto.

9. The method of claim 4 wherein said units are fired to a hardened fixed condition while maintaining their integral character.

10. A metallic mineral pellet having improved green strength and cohesive character which comprises a major portion of a metallic mineral and a minor portion of a binder comprising an amine humate salt.

11. The pellet of claim 10 wherein said amine humate salt is an amine salt of leonardite.

12. The pellet of claim 11 wherein said amine humate salt is an hydroxy amine salt of leonardite.

13. The pellet of claim 8 wherein said metallic mineral comprises iron dust.

14. The pellet of claim 10 wherein said binder is present in an amount varying from 50–5000 p.p.m. and said mineral is taconite.

15. As a pelletizing aid an amine humate salt.

16. The composition of claim 15 wherein the said salt is an amine salt of leonardite.

17. The composition of claim 15 wherein said salt is an hydroxy amine salt of leonardite.

18. In a method of producing improved metallic mineral pellets which comprises the steps of comminution of a mineral ore to particulate state, concentrating the valued mineral constitutent thereof to an increased purity, treating said mineral to obtain a wetted particulate mass, pelletizing said mass to form integral units, firing said formed pellet units to a hardened state, heating said units to a liquid mass and cooling said liquid mass in molds whereby metal ingots are formed; the improvement which comprises the step of adding to said wetted mass prior to pelletization at least a binding amount of an amine humate salt whereupon pellets are produced having increased strength and cohesiveness.

19. The method of claim 18 wherein said amine humate salt is an amine salt of leonardite.

(References on following page)

References Cited by the Examiner

UNITED STATES PATENTS

1,536,033	4/1925	Stillman	75—3
2,274,807	3/1942	Rawlins et al.	260—501
2,668,105	2/1954	De John	75—3
2,810,633	10/1957	Cooper	75—5
2,816,016	12/1957	De Vaney	75—5

2,992,093	7/1961	Burdick	260—515
3,030,412	4/1962	Higuchi et al.	260—515
3,149,958	9/1964	Ward	75—5

OTHER REFERENCES

Leonardite: A Lignite Byproduct, RI5611 Bureau of Mines Investigations (1960), 12 pages.

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