

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF MOLDED PRODUCTS

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The idea has already been had of manufacturing mastics and cements called "antacid," by using as an agglomerating agent sodium silicate in the presence of a catalyser causing the setting of the latter, such as, for instance, sodium fluosilicate, and a wetting agent. The sodium fluosilicate causes, as is well known, the decomposition of the sodium silicate with the formation of nascent silica and it is the latter which, once freed, combines with the silicious substances contained in the inactive powders utilized in the manufacture of these cements and mastics and ensures the agglomerating one to another of the various particles of matter. The wetting agent facilitates the preparation of the pastes, increases their fluidity and improves the adherence of finished cements and mastics.

These cements and mastics, which comprise, in practice, a high proportion of sodium silicate, are applied by means of a spatula or a trowel.

Now, it has been found, according to the present invention, that mixtures of this nature could be applied to the manufacture of molded products of high quality starting from pulverulent substances of diverse natures, by using particularly small proportions of sodium silicate. The invention ensures, notably, the obtention of molded products which have a high percentage of useful agglomerated substances and at the same time a strong reciprocal binding of their constituent particles. It allows, moreover, for the same molding pressure, the obtention of molded products presenting a compactness and consequently an apparent density which are higher than that of agglomerated bodies manufactured by most well known processes. Inversely, for the obtention for molded products of a given density, it offers the possibility of using a molding pressure substantially lower than pressures generally used in the agglomerating processes known up to now.

The process according to the invention is essentially characterized by the fact that the pulverulent mass to be agglomerated and molded is mixed with a solution of sodium silicate and with a substance capable of decomposing the latter thereby giving rise to the formation of nascent silica having the power to ensure the setting of the mixture, in the presence of a dispersing-wetting agent, and in that the mixture thus obtained is then molded.

The dispersing-wetting agent utilized in accordance with the invention diminishes the surface tension of the liquid and allows the uniform distribution, in an extremely thin layer, of the sodium silicate around all the particles of the substance to be agglomerated. Accordingly, by

operating in the presence of a dispersing-wetting agent, the proportion of sodium silicate to be used in order to obtain a good agglomeration may be considerably reduced with respect to that which would be necessary were the mixture effected without the presence of such a dispersing-wetting agent. In general when using a sodium silicate solution at 36° Bé., this proportion may vary from 2 to 8% by weight with respect to the pulverulent mass to be agglomerated.

The reaction of decomposition of the sodium silicate may be, notably, as it is known "per se," a catalytic reaction, in which case the substance which is added to the pulverulent mass to obtain this decomposition plays the unique or principal part of a catalyser. To that purpose, it is possible to use such substances as, for instance, fluosilicates, fluotitanates, fluotungstates, fluozirconates of sodium or of potassium. In certain cases, which will be specified hereafter, it is also possible, to attain the same object to use impalpable silica freshly ground. To allow the use of the smallest possible quantity of catalyser, it seems desirable that the ratio

$$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$$

of the sodium silicate be at least equal to 3,2. However, it is preferable that this ratio do not exceed the value of 3,35 so as not to hinder the reaction giving rise to the formation of nascent silica.

A real stoichiometric reaction may also be used by causing the flocculation of nascent silica by any reacting agent having a pH lower than that of the sodium silicate solution or containing or capable of liberating a molecule of free acid the acidity of which is at least equal to that of the silica. Along the same line of thought, it is possible to use, in order to obtain this reaction, bicarbonates or tricarbonates which, in the presence of water, give rise to free carbonic acid, or again, a sulphate, such as, for instance, aluminium sulphate which, in hydrolysing, produces sulphuric acid. It is also possible to use a sulphide capable of liberating, by hydrolysis, hydrogen sulphide which then acts as a weak acid, or an organic compound such as ortho or para-toluene sulphochloride which produces, by hydrolysis, one of several acids. Tests effected to this day seem to have revealed that, in the case of a reaction of stoichiometric decomposition, the ratio

$$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$$

of the sodium silicate may be lowered to about 2,5.

Depending upon the case, the reaction of decomposition of the sodium silicate may be more or less rapid. It is advisable that it be sufficiently slow to allow the operator to effect the necessary handlings before the setting be complete, but sufficiently rapid that the agglomerating time is reduced to a duration that corresponds to industrial needs. According to necessities, a catalyser acting more or less rapidly will be chosen.

The binding, one to another, of the particles of the pulverulent substance to be agglomerated may, depending upon the case, result from the fixation of the nascent silica—formed by the decomposition of the sodium silicate—on to constituents elements of the substance to be agglomerated or contained in the latter or on to bodies introduced for this purpose into the substance to be agglomerated. Thus, for example, when the pulverulent substance to be agglomerated contains silicious bodies (free silica or silicate), it is probable that the freed nascent silica will combine superficially with these ingredients to form complex silicates which will ensure the desired agglomeration. If it is desired to agglomerate a metal in powder form or in the form of filings, it appears that the nascent silica resulting from the decomposition of the soda silicate forms with the metal or with the oxide of the surface layer a small quantity of silicate but sufficiently large to bind together the metallic particles.

If, on the contrary, the substance to be agglomerated does not contain bodies capable of constituting combination points for the freed nascent silica, it is possible to add to this substance bodies adapted to perform this function, for example, fine impalpable, freshly ground silica. In this case, the silica introduced in this state into the substance to be agglomerated appears to act the part, not only of combination points for the nascent silica, but also that of a decomposing catalyser for the sodium silicate. It is also possible—if it is desired to agglomerate a pulverulent fuel, for example, and although this measure may appear at first sight to be formally counter-indicated—to add to the latter a small quantity of cinders in order to cause the formation of combination points for the freed nascent silica.

By the process according to the invention, it is possible to agglomerate, generally speaking, substances not having a tendency to swell up, and particularly: ferrous metal filings (cast iron, steel, etc.) as well as non-ferrous ones (copper, bronze, zinc, aluminium, magnesium, etc.); inactive substances containing or mixed with free silica or a silicate; pulverulent ores or ores in the state of flottation powders or the like, with or without the additions necessary for their use in metallurgy, such as coal or reducing coke, substances for correcting slags in view of the elimination of impurities out of the finished metal, etc.; the dusts of blast furnaces or of furnaces for white metal, containing or not-containing coke dusts or other dusts; materials and products for refraction linings such as silica, silico-aluminous materials, zircon (zirconium silicate) etc.; graphite, treated or not, with or without the addition of other substances; mica in small pieces or in powder form; cold setting cements; fuels not having a tendency to swell, such as charcoal, certain coals and in general all carbonaceous materials distilled at a high or low temperature.

As wetting and dispersing agents for carrying out the invention, it is possible to use, for ex-

ample, condensation and sulfonation products of aromatic hydrocarbons and of their derivatives with aldehydes, alcohol—and aralcoyl—naphthalene sulphonates, sulphonated derivatives of fatty bodies, fatty alcohols, fatty acids, amides of fatty acids, amines derived from fatty acids, esters of fatty acids, sulphonation products of the residues resulting from the distillation of benzoic aldehyde, products soluble in water resulting from the action of ethylene oxide on substances insoluble in water and containing a reactive hydrogen, and other analogous products; substances of vegetal origin possessing dispersing and emulsifying properties such as licorice, saponin, products resulting from the hydrolysis of albuminoid substances, residual lyes resulting from the treatment of ligneous substances by means of sulfites.

The weight of the catalyser, if recourse be had to a catalytic reaction, and the weight of the wetting agent are (within certain limits) practically independent of the weight of sodium silicate employed. The more wetting agent and the more catalyser there are, within limits which are not excessive, the greater will be the density of the compressed substance obtained and the quicker will the setting take place. In general, a good agglomeration is obtained—in a period of time allowing manipulations, without having to hasten excessively—with 6% of catalyser and 2% of wetting agent calculated with respect to the weight of the sodium silicate at 36° Bé.

For carrying the invention into practice it is possible to mix the pulverulent substance to be agglomerated with the catalyser for setting, with the dispersing-wetting agent, and eventually with the substance destined to form the combination points for the nascent silica (if the substance to be agglomerated does not contain any by itself) and then add the sodium silicate.

By a molding or slubbing operation, or by other similar methods, the mixture thus obtained is shaped into molded objects according to the invention.

It will be advantageous to vibrate or pervibrate (slightly or much) the mixture before subjecting it to compression. Preferably vibrating machines having a vertical reaction will be used for this purpose.

If it is desired to obtain agglomerated bodies having a high density, it is advisable to so choose the granulometry of the pulverulent substances entering into the composition of the mixture to be agglomerated that the smallest particles be capable of filling to the greatest extent possible the empty spaces existing between the largest particles. It is to be noted that, thanks to the invention, the pressure necessary to the obtention of agglomerated bodies of high density is substantially reduced in comparison to that of heretofore known agglomerating processes. Thus it is that in many cases an ordinary hand-press, such as the one used for making bricks of slag mixed with a hydraulic binder, is sufficient.

Certain examples of carrying out the invention will now be given by way of indication.

Example 1

To obtain bricks of coke dust, a coke dust is taken the granulometry of which lies between extra fine and 2 m/m particles, and a weight of sodium silicate at 36° Bé equal to about 4 or 5% of the weight of the mass of coke dust is then added under the conditions predescribed as well as 6% of sodium fluosilicate and 2% of the dispersing wetting agent commercially known under

the name of "Diastorsol NDS", with respect to the weight of the silicate. The mixture is then compressed into pellets by a pressure of 200 kgs/cm².

If the coke dust is wet, solid sodium silicate is used instead of a solution of this silicate for the water of the coke acts, in this case, as a dissolving agent. The silicate being little soluble in cold water, the difficulty is avoided by using a silicate which is richer in soda, but in this case, more catalyser is added, thus neutralizing the excess soda which has facilitated the dissolving of the silicate.

Example 2

To agglomerate pig iron filings, these filings were mixed with 6% of sodium fluosilicate and 2% of sulphonated lauric alcohol, with respect to a weight of sodium silicate equal to 3% of the weight of the filings. Once a thorough mixture was effected, this mixture was stirred with the 3% of sodium silicate at 36° Bé, until a thorough mixture was obtained.

These filings were then compressed into small brickets by exerting a pressure of 500 kilos per square cm.

Example 3

Pulverized coal was agglomerated by mixing the coal dust with 8% of sodium silicate at 36° Bé with a quantity of sodium fluosilicate and of butyl-naphthalene sulphonate of sodium the total of which was equal to 6% of the weight of the sodium silicate.

The agglomerating pressure was 300 kgs/cm².

Example 4

Pulverulent anthracite was also agglomerated by using from 7 to 8% of sodium silicate at 36° Bé with respect to the weight of the anthracite and, in addition, 6% of calcium sulphide and 2% of the wetting agent commercially known as "Tibalene NAM" with respect to the weight of sodium silicate used. The same pressure as in the preceding example was used.

Example 5

The agglomerating of pulverulent flottation ores (of lead, zinc, iron and of other flottation ores) has been obtained with quantitles of sodium silicate at 36° Bé varying from 3 to 8% with respect to the weight of the ore, the proportions of catalyser and wetting agent employed being respectively 6% and 2% with respect to the weight of the sodium silicate. The compression pressures were of the same value as those of the preceding example.

In the case where the ore was very wet it was possible to effect the agglomerating with solid sodium silicate under the same conditions as those in example 1) above concerning the agglomerating of coke dust.

Example 6

For agglomerating graphite, it has been proceeded, generally speaking, in the same manner, but by providing a preliminary preparation of the graphite. By means of any one of the well known processes, the graphite was transformed into graphitic acid which was washed and dried, then heated to red hot (about 1000° C) while being sheltered from air. The graphite swelled and assumed a volume about twenty-six times greater than before heating.

Once the swelling up was effected, the graphite was compressed into lozenges under a pressure of 50 to 100 kgs/cm² and the said lozenges were heated to about 500° C, which operation gave

rise to a much less intensive swelling. The lozenges increased from one to three times in volume and were disintegrated to some extent but remained agglomerated nevertheless with a tendency to recover the foliated structure. Finally, by means of an easy crushing effect, the lozenges thus treated were ground and the powdered graphite thus obtained was mixed with 2 to 4% of sodium silicate at 36° Bé after having also been thoroughly mixed with 6% of sodium fluosilicate and 2% of the product sold under the commercial name of "quicltan", with respect to the weight of the sodium silicate.

Agglomerated bodies were then obtained by pressures which have varied between 25 and 1000 kgs per cm², these agglomerated bodies already having a very satisfactory hardness for a corresponding pressure of 25 kgs. The hardness increased as the pressure became higher.

Agglomerated bodies of graphite of this kind heated to 1000° to 1200° C have remained unchanged and appear to be appropriate for the fabrication of electrodes, retorts, muffles, crucibles and other objects of which graphite forms a part.

In all the cases where the catalyser utilized has been sodium fluosilicate, the setting was complete at a temperature of 15 to 20° C. after about six hours. In the case where the ambient temperature falls below 15° C the setting may be hastened by bringing the molded products in a stove to a temperature under 60° C until the inner temperature of the products attains about 40° C. Preliminary tests have permitted to determine the stoving time necessary in each particular case.

Example 7

The agglomerating of refractory substances has also been obtained in order to allow the substitution to dinas bricks (which contain a very high proportion of silica and a few percent of lime) of bricks containing practically only silica.

Quartz was taken and ground at the granulometry usually adopted for the fabrication of dinas bricks and was then agglomerated by means of sodium silicate, a catalyser and a wetting agent by using from 5 to 6% of sodium silicate at 36° Bé with respect to the weight of the silica, and on the other hand, 6% of catalyser and 2% of a wetting agent with respect to the weight of the sodium silicate. The mixing of these ingredients was effected along the general lines specified hereabove.

The mixture obtained was molded into brick shapes under a pressure of 500 to 2000 kgs/cm² and said bricks were subjected to a slow baking at a temperature gradually increased to 1500° C. The reaction which occurred in the course of the operation gave rise to the formation of nascent silica which united the quartz grains one to another whereas the volatile products of the catalyser progressively distilled due to the high temperature and escaped. As a result, the bricks obtained contained only silica grains, in the form of tridymite or criptobalite, soldered one to another, so to speak.

Example 8

Instead of using a fluosilicate as catalyser, it is also possible, as has been specified hereabove, to use freshly ground fine silica which also plays the part of an element permitting the combination of the nascent silica produced by the decomposition of the sodium silicate.

In this line of facts agglomerated bodies of zirconia have been produced by thoroughly mix-

ing 100 parts by weight of chamot of zircona with 2.5 parts by weight of freshly ground silica passed through a sieve of 300 meshes and 0.1 part of Diastersol NDS; then by adding to this mixture 5 parts by weight of sodium silicate at 36° Bé. The mixture thus obtained was molded into bricks under a pressure of about 500 kgs per cm²

and, in this case, the products were dried in free air for several days. Then the products were baked under the conditions usually adopted for the manufacture of refractory materials of this kind.

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