

ALIEN PROPERTY CUSTODIAN

REFRACTORY PRODUCTS

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Refractory products are generally obtained by mixing in presence of water a more or less finely granulated chamot, obtained by baking at high temperature raw materials apt to produce refractory products, with a binding agent, which, in most cases is of an inorganic nature; the mass resulting from this mixture is then transformed, by means of a pressure over pressure or modelling by hand or pneumatic hammer, into bricks or articles of the desired shape, which are dried and baked at high temperature. It has to be endeavoured in this manufacture, to use as little water as possible, because the evaporation of the water during the drying and the baking causes the formation of pores which decrease the density of the finished products; but it is not possible to lessen that quantity under a certain limit, limit determined for a given refractory composition, as otherwise the mass could no longer be moulded or modelled.

Now, we have found, according to the present invention, that the manufacture of refractory products was facilitated and that the physical and mechanical properties of the finished products was increased when the basis refractory material, constituted of a solid element having a high melting or softening point, was mixed, without emulsifying with air, with the binding agent in the presence of an aqueous solution of a wetting and dispersing agent, the solution containing either the binding agent or part of the latter if it is soluble or partially soluble in water.

Materials having a high melting or softening point which can be used for the realisation of the present process are generally all those which are used in the manufacture of refractory products, such as, for instance, oxides of silicium, of zirconium, of thorium, of beryllium, of aluminium, of magnesium, of chromium, the silicon hydrocarbon, the natural or artificial refractory silicates, for instance the aluminium silicate, the carbon, or the mixtures or natural combinations of these materials either together or with other materials.

The binding agents can be of inorganic or organic nature or composed of mixtures of substances of these various natures. Lime, silicates, clay, boric acid, phosphoric acid, magnesium chloride can be mentioned as inorganic binding agents, as well as all those used in the refractories industry. It has besides been found that it was possible to obtain particularly advantageous results in the application of the above mentioned process by incorporating to the binding agent used, or by using as binding agent itself, a small

proportion of bibarytic silicate. The latter forms, indeed, during the baking operation, with the constituents of the mixture which has to be agglomerated, complex silicates which have high melting points, and act as a cement joining very firmly together the particles of the material which has to be agglomerated. On account of the own refractory strength of the silicates thus formed and of the fact that the presence of a wetting and dispersing agent permits, by facilitating the repartition of the binding agent in the mass which has to be agglomerated, to decrease to a minimum the proportion of bibarytic silicate to be introduced in that mass to obtain the desired binding—and as a consequence the proportion of complex silicates formed—it is possible to obtain agglomerated bodies which, while having a high mechanical resistance, have a resistance to the heat almost of the same kind as that of the refractory material which has been used to compose them. Generally an addition of 0.5 to 4% (five tenth to four per cent) of bibarytic silicate by weight with respect to the mass which has to be agglomerated, will be sufficient to obtain good results. Dextrin, glues, albuminoids, residual lies of the sulphitation of cellulose materials, alginates, pitches, tars, for instance as emulsions or dispersions in a liquid, for instance water, linseed oil, natural or synthetic resins can be mentioned as organic binding agents. Pitches and tars are advantageously introduced as colloidal suspensions or aqueous emulsions. In that case the wetting and dispersing agent is used as emulsifying agent for the formation of the aqueous emulsion or suspension of pitch or tar.

By wetting and dispersing agent, it has to be understood a product which facilitates the mutual dispersion of the solid material and of the aqueous solution. Such products are, i. e. the products of condensation and sulphonation of aromatic hydrocarbons and their derivatives with the aldehydes, the alcoyl and aralcoyl-naphthalene sulphonates, the sulphonated derivatives of the fatty bodies, of the fatty alcohols, of the fatty acids, of the amids of fatty acids, of the esters of fatty acids, the products of the sulphonation of the residues of the distillation of the benzoic aldehyde, the substance soluble in water resulting from the action of the ethylene oxide on bodies insoluble in water and containing a reactive hydrogen and other similar substances. The alkaline alginates and the residual lies of sulphite cellulose, which have also a certain dispersing power, have already been used as bind-

ing agents in the refractories industry. Nevertheless, the use of these substances as dispersing agents, according to the present invention is also taken into consideration. In this case, in reality, they will be used in concurrence with one or several appropriated binding agents used as such, and in much lesser proportions than when they are themselves used as binding agents (i. e. in proportion of about 0.2 to 2% of the total weight of the refractory mass), that is to say in such conditions that they should effectively have the function of dispersing agents between the aqueous solution and the solid material and be unfit to fulfill the function of binding agents as in their previously known uses.

By using wetting and dispersing products of the aromatic series having a high wetting power as well as high dispersing properties, without giving rise to an important formation of foam—such as, for instance, neutralised products of condensation and sulphonation of phenols, of naphthaline, of chloronaphthalenes, of anthracene with aldehydes, of products of condensation of sulphonic naphthalene acids with formol, of neutralised products of sulphonation of sulphite phenols—it is possible to realise an excellent agglomeration with comparatively reduced proportions of emulsion or suspension of pitch or tar, which is advantageous from the point of view of the quality of the refractory products obtained as well as from the point of view of the economy realised in the manufacturing. The pitch or tar incorporated to the refractory mass, forms, indeed, during the baking, a coke net work which maintains the agglomerated mass, up to its pre-fusion, but disappears afterwards by combustion; the smaller the proportion of pitch or tar introduced, the smaller will also be the porosity of the products after this disappearance.

The preparation of pitch or tar emulsions can be made in a very simple way. For the tar, it is possible to proceed by adding to it, in the cold and by small portions, the wetting and dispersing agent to which a certain proportion of water has been added, while the mixture is submitted to a mechanical shaking or an air insufflation, and by finally introducing—with stirring—the complementary quantity of necessary water. For the pitch, it is possible to use solid pitch and to crush it, in the cold and in presence of the quantity of water in which it has to be emulsified, water to which the wetting and dispersing agent has been added. It is also possible to heat the pitch at a temperature not above 80° C., to flow in, while stirring, the wetting and dispersing agent to which water has been added and which has been heated to a temperature of about 70° C., then the complementary quantity of water also heated at 70° C. It is moreover possible to use the pitch as a solution, for instance in light fractions of tar, in which case the preparation of the emulsion is made as it is mentioned here above in the case of tar.

It is also possible to use an emulsion composed of pitch and tar; in that case an emulsion of pitch (in the cold or in the heat) and an emulsion of tar are prepared separately. They are then mixed.

To increase the stability of the emulsions, it may be advantageous to introduce in them small proportions of a stabilisator, such as, for instance, the casein, preferably little alkalised, the albumin of the blood or an alkaline resin.

In all cases, it is good that the wetting and

dispersing agent used according to the invention should be chosen in such a way that its properties will not unfavourably be influenced by the presence of a constituent of the refractory material; i. e. when the lime is the binding agent, a wetting and dispersing agent stable to the lime salts has to be chosen.

For putting the invention into practice, a non-foaming paste is preferably formed with the refractory material or materials, the binding agent or agents and the aqueous solution containing the wetting and dispersing agent and eventually the binding agent or part of it; it is of course possible to add other products to the composition of the paste in order to modify the properties of the finished products. This paste is modelled or moulded at a compression sufficient for the agglomeration; the articles obtained are dried and baked according to the normal technique.

The process which is the object of the invention permits to decrease the quantity of water used in the manufacturing of refractory products and therefore to manufacture products having a high density, a small porosity and a high mechanical resistance. Compared to refractory products obtained without wetting and dispersing agent, all other conditions being similar, the refractory products, according to the invention bear with more load at high temperature, have a better resistance to abrasion and a reduced penetration to the slag; as a consequence of their higher density, they will, under a similar volume, take in more calories and are therefore especially recommended for the filling of heat regenerators.

A particularly interesting method of carrying out the process which is the object of the invention consists to use as binding agent, a solution containing organic cold-binding agent, an organic hot-binding agent and a wetting and dispersing agent. By organic cold-binding agent it has to be understood an organic product capable, in aqueous solution or emulsion, to stick together at low temperature and especially at the atmospheric temperature, the particles of refractory materials in a way sufficient to permit the handling of the agglomerated body; such materials are, for instance: the dextrin, the glues, the casein, the natural or artificial resins. By organic hot-binding agent it has to be understood an organic product capable of being converted into caramel or coke at high temperature and which is consequently capable to unite together the particles of refractory materials by means of a kind of coke net work; such products are, i. e. the monoses, polyoses, sugars, molasses, raw products soluble in water coming from the hydrolysis of the wood. The thus obtained mixture of organic binding agents can be used alone or in concurrence with an inorganic binding agent.

When this method of carrying out is employed without inorganic binding agent, it is possible to obtain refractory products composed almost only of refractory materials. The organic binding agent gives rise, from about 500° C. up, to the formation of a sort of extremely fine coke net work which keeps its shape to the article during a certain phasis of the baking, this phasis being situated in an interval starting at the coking of the binding agent; this coke net work permits the evacuation, by capillarity, of the steam or of the gases coming from the eventual decomposition of certain components of the raw products and avoids the formation of pores in the mass, without however making particu-

larly porous finished articles, because, according to the invention, the addition of the wetting and dispersing agent decreases the porosity in a greater proportion.

Nevertheless, in this same method of carrying out, when the wetting and dispersing agent produces a persistent foam, it is possible according to modification of the present invention, to form by thorough shaking or introduction of air, or by these two means, a stable emulsion of refractory materials, of organic binding agent and of air; the drying in moulds and the baking of the thus obtained foam, produces light and porous refractory products which are particularly suitable when it is desirable to decrease the weight of the refractory body or to obtain at the same time a calorifugal action. This result is notably obtained when saponine is used as a wetting and dispersing agent.

It has besides been found that, when the wetting and dispersing agent contains an alkaline metal under a combined form, i. e. in the case of an alkaline sulphonate, the application of the process which is the object of the invention permits to realize a kind of self-agglomeration of the refractory product at the temperature of the baking, whether the traces of alkaline oxides, (i. e. 0.02 to 0.05%) uniformly distributed on all the surfaces of the refractory particles owing the action itself of the wetting and dispersing agent, give rise to the superficial formation on these particles of alkaline silicates which join together the said particles, whether they determine a softening of the surfaces of contact of the refractory particles. If the wetting and dispersing agent contains no alkaline metal, it is possible to add to the binding solution a very small quantity of the compound of an alkaline metal; inversely, if the refractory contains no silica or silicates, it is possible to add to the initial mixture a very small quantity of a siliceous material such as crushed quartz.

Finally, the pitch or tar emulsions can be used for the agglomeration of refractory materials without the adjunction of any other binding agent, under the condition however, that, in case of solid pitch emulsions or suspensions the mixture of refractory materials should be submitted, before or during the moulding, or after it, to a temperature of 80° C to 100° C capable of bringing the pitch to a state at which it possesses a binding power sufficient to permit further manipulations of the agglomerated bodies. It is also possible to use these emulsions or suspensions in concurrence with a substance playing the part of cold-binding agent, according to the method of carrying out described above in which a cold binding agent and a hot binding agent are used simultaneously. The emulsion or suspension of pitch or tar composes then the hot-binding agent; as cold-binding agents it is possible to use, as said above, for instance, the dextrin, the glues, the gums, the casein, the natural or synthetic resins. On the other hand, if the emulsion has a sufficient binding power at low temperatures, but insufficient at high temperatures—which can be the case, for instance, of tars of a feeble content of pitch—it may be interesting to use that emulsion in concurrence with a material capable to act as hot-binding agent. It has been indicated above that it was possible to use, for fulfilling this condition, a certain number of materials, such as, for instance, the monoses, polyoses, sugars, molasses, as well as, notably, the raw products, soluble in water coming from the hy-

drolisis of the wood. In the various cases which have been considered, the complementary binding agent can be incorporated to the emulsion of pitch or tar during its preparation, or brought itself to the state of an emulsion or solution which is added to the emulsion of pitch or tar separately prepared.

In addition to the cases which have been mentioned, where it can be interesting to use the emulsion of pitch or tar with a complementary hot or cold-binding agent, it has been found, according to the present invention, that a particularly advantageous possibility was the use, as binding agent for the manufacture of refractory products, of an emulsion of pitch or tar, in connection with a fatty refractory clay, such as, for instance, the clay of Sézanne (Marne). The incorporation to the emulsion of pitch or tar of such a clay, permits to reduce notably the quantity of tar or pitch necessary to obtain the wanted cohesion at the various temperatures of manufacturing and use.

In the following non limitary examples, the parts by volume are taken so that, in the case of water, one part by volume is equal to one part by weight.

Example 1

90 parts by weight of mullite chamot granulated at the standard size,
10 parts by weight of white bauxite of high contents of alumina,
5 to 7 parts by volume of water in which 0.4 part by weight of the sodium salt of a sulphonated condensation product of naphthaline with formol, for instance of the product commercially known as "Diastorsol NDS", had been dissolved,

were mixed together.

The mixture was moulded and baked at 1500° C. The thus obtained refractory bodies had a porosity inferior to that of the refractory bodies manufactured without the use of a dispersing agent.

Example 2

90 parts by weight of dead burnt magnesia chamot,
10 parts by weight of caustic magnesia sifted through a sieve of 200 meshes per sq. inch, and
5 parts by volume of water in which 0.4 parts by weight of butyl-naphthalene-sodium sulphonate had been dissolved,

were mixed together.

The work was carried out as in the above example and similar results were obtained.

Example 3

100 parts by weight of mullite chamot suitably granulated, and
5 to 7 parts by volume of an aqueous solution containing, per litre,
250 gr. of dextrin,
250 gr. of molasses, and
50 gr. of the sodium salt of a sulphonated condensation product of naphthaline with formol, for instance of the product commercially known as "Diastorsol NDS",

were mixed together.

The mixture was moulded and baked at 1500° C; the thus obtained refractory body was essentially composed of self-agglomerated mullite.

Example 4

100 parts by weight of dead burnt magnesia chamot containing less than 4% of Fe_2O_3 , and of appropriated granulometry, and 5 parts by volume of the solution used as in Example 3, were mixed together.

The mixture was moulded according to the technique of over compressed refractory bodies and baked at 1500° C. Magnesia bricks were obtained having a density of 3 to 3.15, an apparent porosity in volume of 11 to 15% and the absorption of water of which by weight was of 3.75 to 4.75%.

Example 5

200 parts by weight of zirconium oxide chamot of a granulometry of 0 to 0.5 mm, were mixed with

20 to 25 parts by volume of an aqueous solution containing, per litre,
200 gr. of dextrin,
100 gr. of molasses, and
200 gr. of butylnaphthalene-sodium sulphonate.

The mass was thorough shaken, up to the formation of a persistent foam, then placed in moulds of the desired shape, cautiously dried in the open air or in a drying oven at a temperature below 100° C and baked at 1500° C. Bricks of an apparent density of 1.25 to 1.50 were obtained.

Example 6

94 parts by weight of dead burnt magnesia chamot,
4 parts by weight of caustic magnesia sifted through a sieve of 200 meshes, and
2 parts by weight of bibarytic silicate,
were mixed with

5 parts by volume of water in which 0.4 part by weight of butylnaphthalene-sodium sulphonate had been dissolved.

The mixture was moulded and then baked at 1500° C. The refractory bodies obtained had a porosity inferior to that of refractory bodies manufactured without dispersing agent.

Example 7

98 parts by weight of zirconia chamot (oxide of zirconium), and
2 parts by weight of bibarytic silicate,
were mixed with

4.5 parts by volume of water in which 0.25 part by weight of a sodium salt of a sulphonated condensation product of naphthaline with formol, commercially known as "Diastorsol NDS" had been dissolved.

Work was carried out as in Example 6.

Example 8

96 parts by weight of dead burnt magnesia chamot,
3.5 parts of bibarytic silicate, and
5 to 7 parts by volume (according to the granulometry of the chamot) of water in which 0.5 part by weight of dextrin and 0.25 part by weight of "Diastorsol NDS" had been dissolved,
were mixed together.

The mixture was moulded and baked at 1500° C as in Example 6.

Example 9

94 parts by weight of a chamot of aluminous silicate were mixed with
5 6 parts of a cold emulsion prepared by kneading 50 parts by weight of pitch in presence of 50 parts by volume of water to which 0.1 part by weight of "Diastorsol NDS" had been added.

The work was carried out afterwards as in Example 6

Example 10

95 parts by weight of zirconia chamot
15 were mixed with

5 parts by weight of an emulsion prepared by adding little by little to 50 parts by weight of coal tar, 1 part by volume of an aqueous solution of 50% (fifty per cent) of "Diastorsol NDS", then 49 parts of water.

Work was carried out as in Example 6.

Example 11

90 parts by weight of a chamot of aluminous silicate,

30 were mixed with

10 parts of an emulsion composed of:
20 parts by weight of fatty clay of Sézane (melting point about 1800° C),
20 parts by weight of tar (or pitch), and
60 parts by weight of an aqueous solution of 5% (five per cent) of "Diastorsol NDS".

The mixture was moulded and then baked at 1500° C, as in Example 6.

Example 12

The heavy tar usually employed as agglomerating material for the manufacturing of an oven hearth made out of sintered dolomite or of zircon (zirconium silicate), was replaced by an equal quantity of an aqueous emulsion of pitch containing only 50% (fifty per cent) of pitch prepared as in Example 9.

Work was then carried out as usually.

Example 13

For the manufacturing of cellular refractory bodies:

81 parts by weight of a chamot of sintered magnesia,
4 parts by weight of bibarytic silicate, and
60 15 parts by volume of water in which 10% (ten per cent) of saponine were added,

were mixed together.

The mixture was beaten up to the formation of a persistent foam, then placed into moulds of the wanted shape, afterwards cautiously dried in the open air, and the products obtained were baked at 1500° C.

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