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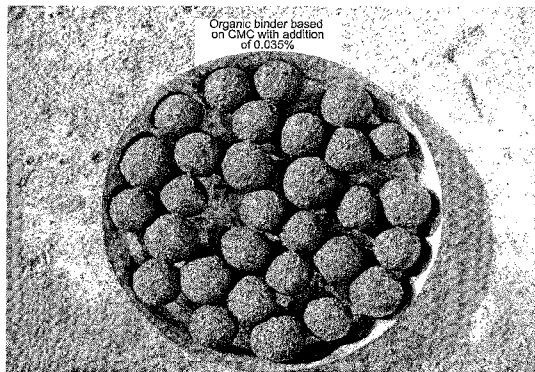
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(54) **Title:** BINDER COMPOSITION FOR PELLETIZING IRON ORE

Fig.1



(57) **Abstract:** The present invention refers to a binding composition containing bentonite for use in binding finely ground iron ore. The composition of the invention comprises bentonite and molasses. The invention also refers to process for preparing iron ore pellets wherein a composition comprising bentonite and molasses is used as binder.



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Title: "**BINDER COMPOSITION FOR PELLETIZING IRON ORE**".

The present invention refers to a binding composition for use in pelletizing minerals, more particularly iron ore, and its respective manufacturing method for use in pelletizing processes.

5 Background of the Invention

Ever since the discovery of steel and the introduction of the blast furnace as the main process for producing it, the exploitation of the raw material known as iron ore has become of vital importance for the development of humanity. During the World War I and chiefly during World War II, there was
10 a major increase in the consumption of steel to meet the military needs and after the wars, the increase in iron ore steadily continued to meet man's ever-growing demands intrinsically linked to the significant scientific and technological development of the twentieth century.

Initially, iron ore was exploited and consumed in the form of granules originating from crushing the mineral extracted from mines and separated from the sinter feed generated in crushing by sieving. These granules were directly fed into the shaft of the blast furnace to produce pig iron. Over the years, this practice led to a significant increase in stocks of ferrous sinter feed originating from crushing for the production of granules and in parallel
15 thereto the minerals suitable for crushing for use in blast furnace gradually became scarcer, causing pressure to use the sinter feed that was stocked and unused.

The problem associated to this sinter feed is that it cannot be used in a blast furnace process or in other shaft furnaces where hot reduction
25 gas is blown at high speed from the bottom upwards to transform the ferrous oxide into metallic iron. In these processes, the presence of sinter feed in the mineral bed to be reduced causes blockages and confinement of the load besides forming preferred paths, whereby hindering the processing of the load and worsening the quality of the final product.

30 This sinter feed was soon began to be used in a range that goes from 100 mesh up to 6.35 mm in the sintering processes and thereafter the portion of powder less than 100 mesh began to be used in pelletizing proces-

ses that transform the mineral powder into pellets.

Due to the good quality of the pellets produced, within a short period of time they supplanted the consumption of granules and with the successive increases in the demand for pellets they began to be produced not only with the residues of the granule production, but by implementing products exclusively dedicated to the exploitation of minerals for the production of pellets.

Various types of minerals have been used in the production of pellets, be they compact minerals or not, and being pure or mixed hematitic or magnetic, or containing iron-hydrated minerals. The known processes used commercialized to manufacture pellets are continuous, in which an iron ore concentrate pulp is vacuum filtered in rotary disk filters where the cake produced should have a suitable humidity for pelletizing. In the condition of controlled humidity, the concentrate receives a suitable amount of binder, is intensively mixed and then sent to pelletizing disks or drums to produce green pellets.

The green pellets thus produced are sent to a firing oven on conveyor belts and, therefore, must have sufficiently high mechanical resistance to withstand shocks and falls that may occur during transport. Consequently, the pellets should arrive at the furnace with their physical integrity intact so as not to compromise the physical quality of the fired pellets.

The types of problems that may occur with the green pellets during transport to the firing oven are:

- deformation of the pellet due to compression squashing
- deformation of the pellet due to impact squashing
- breakage or chipping of the pellet by compression
- breakage or chipping of the pellet by impact

The resistance of the green pellets depends on many factors that are directly related to iron ore and to materials that are added to aggregate chemical and/or physical properties to the green pellets, as well as to guarantee the physical and chemical properties of the fired pellets in close harmony with the steel manufacturing processes where they will be used.

The presence of silica in the feed to be pelletized entails drawbacks mainly concerning the quality of the pellets of direct reduction and the higher the content of silica in the material to be pelletized, the greater the need to treat this material to reduce the silica. The binder presently known and most used in pelletizing iron ore comprises a silico-aluminous clay mineral called bentonite and which contains about 50% to 60% of silica and 13% to 17% of alumina depending on other characteristics of the clay. Therefore, the use of bentonite as binder in the formation of pellets causes an increase in the content of silica and alumina, which leads to a drop in total iron content of the pellet, this being the material of economic interest and for which the iron ore pellets have minimum specification limits for acceptability on the market.

For this main reason, many studies have been carried out over the years to develop so-called organic binders which are free of silica and which have the objective of totally substituting the bentonite in pelletizing processes whereby avoiding the increase of the silica in the pellet. These organic binders are basically manufactured with industrial polymers originating from vegetable cellulose or polyacrylamide-based industrial polymers.

Brazilian patent PI 9605362-3 discloses a process for preparing iron ore pellets that comprises the use of molasses as principal binding material in an amount that, according to that document, would be considered very high by a person skilled in the art and that varies from 0.5 to 1.5% based on the total weight of the mixture to be palletized. Bentonite when present in the mixture to be pelletized, can vary from 0.4% to 0.6% which is also a concentration described as high because it adds silica and decreases the total iron content of the pellet.

Document US 4863512 discloses a binder for minerals comprising, among other components, a metal alkaline salt, carboxymethyl cellulose, together with a sodium tripolyphosphate. This type of binder was idealized to substitute bentonite but was not successful because it contained sodium tripolyphosphate which is a phosphorous contaminant that is highly harmful in steel production processes and for the steel itself. This type of binder

was rejected by the presence of phosphate which if not extracted during the process causes serious weakening of the structure of the resultant steel.

Document RU 2245930 describes a binding composition containing bentonite and an amount by weight of a polysaccharide as bentonite activator. In this document, a polysaccharide-based polyelectrolyte polymer is added to the iron ore concentrate in the range of 1% to 5% and it is disclosed that this amount should vary with the specific surface of the mineral concentrate. Considering the additions of 1% to 5%, it can be said that the polymer besides being used in variable amounts according to the specific surface of the mineral, has an excessively high use proportion. By virtue of the use of excessively high amounts of the polymer, a person skilled in the art could affirm that there is no activation effect of the bentonite which is described because the amount of polymer that should be added, being very high, does not justify activation.

Further, document RU 2227165 refers to a binding composition that comprises, in addition to bentonite, a compound containing sodium and a water-soluble polymer. This document teaches that the binder contains bentonite, a compound containing sodium and a soluble polymer that can be cellulose ether, starch or polysaccharide or polyacrylamides in water at a viscosity of 5000 to 20000 mPa.s. As revealed in this document, the composition of the binder may contain a sodium compound that can vary from 0.1% to 6% and a water-soluble polymer that can vary from 0.1% to 3%. Under these conditions, the concentration of bentonite in the binder can vary from 91.0% to 99.8%.

Document GB 1383368 discloses a mixture for sintering and pelletizing minerals in which the polysaccharide added to the mineral before sintering is selected from alginates, pregelatinized starches and galactomannan thickeners. An inorganic binder such as bentonite can also be present. The document clarifies that polysaccharide is added exclusively to improve the fluidity of the material and does not specify the amount of bentonite used but explains that bentonite improves the permeability and worsens the fluidity of the material.

In the present invention a new conception for a binder is proposed, designed to achieve a binder that contains bentonite together with other organic and/or mineral components and that displays the same or even better pelletizing characteristics that those of the organic or inorganic binders of the current state of the art. In the binder composition of the present invention, the bentonite exists in percentage quantities over 50% but tests show that its use in the process only causes a minimal increase in the silica content of the pellet.

So, the objective of the present invention is to provide a binder for pelletizing minerals and, more specifically, iron ore, which allows the use of bentonite together with other binders, without the drawbacks associated to the increase of silica in the pellets when using pure bentonite.

SUMMARY OF THE INVENTION

The present invention refers to binder compositions for use in pelletizing iron ore which composition comprises, based on the total weight of the binder, at least a clay that in this case is preferably bentonite in a concentration of from 30% to 80%, and from 10% to 30% of molasses, the percentages being by weight based on the total weight of the binding composition.

The present invention also refers to a process for pelletizing iron ore using a binding composition as defined above as a binder added to said iron ore prior to the pelletizing step.

BRIEF DESCRIPTION OF THE FIGURES

Figures 1 to 3 present photographs of iron ore pellets obtained through the use of prior art binding compositions whereas figures 4 to 7 show pellets obtained with the binder of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention refers to binding formulation for use in pelletizing iron ores containing in their composition at least from 30 to 80%, by weight of bentonite based on the total weight of the binding composition, preferably between 45% and 60% by weight, and from 10% to 30%, by weight based on the total weight of the binding composition of molasses.

The composition of the present invention allowed the obtention of

a binder having a considerable content of bentonite, that is, up to 60% and
event 80% by weight, without the showing drawbacks found in the natural
bentonite binders, said drawbacks being associated with the high percentage
of silica in the bentonite. The inventor noted that the use of a binder compo-
5 sition according to the present invention results in an insignificant increase of
silica in the pellet when compared to the use of pure bentonite.

The binder composition of the present invention may preferably
contain other optional components that add further advantages to the results
achieved. For example, the binding composition may comprise from 0 to
10 10% by weight of a polysaccharide, preferably a starch polysaccharide. The
polysaccharide used in the present invention can be selected from the group
of natural starches of corn, potato, manioc and rice.

Said binder composition may contain solid and water-soluble or-
ganic polymers such as anionic polyacrylamide, synthetic polymers derived
15 from natural polysaccharides such as carboxymethyl cellulose (CMC).

Preferably, in addition to the bentonite and molasses as defined
above, the binder composition of the present invention comprises a polyacr-
ylamide, preferably linear and anionic, having a molecular weight in the range
of 11,000,000 to 14,000,000 with reference to the carbon 12 and present in a
20 range of 2 to 10%, preferably from 4 to 9%, by weight based on the total wei-
ght of the binder.

The composition may also comprise a synthetic polymer derived
from natural polysaccharides such as carboxymethyl cellulose (CMC) or mo-
dified starches present in an amount of up to 10%, preferably from 4% to 8%,
25 by weight based on the total weight of the binding mixture. Carbonates and
bicarbonates of alkaline metals or soluble hydroxides from alkaline metals
such as carbonates, bicarbonates or hydroxides of sodium, lithium or potas-
sium may be present in a percentage of up to 20%, preferably from 7 to 20%,
by weight of the binder.

30 A particularly preferred binder comprises:

- from 45 to 60% of bentonite;
- from 10 to 20% of molasses;

- from 4 to 9% of a polyacrylamide;
- from 0 to 10% of a starch polysaccharide;
- from 0 to 20% of a natural or synthetic **carbonaceous** compound containing some of the following ions: lithium, sodium or potassium.

5 So, the present invention provides:

- a binder that is a mixture of bentonite with other conventional binders and that is an efficient substitute for pure bentonite in the processes for production of iron ore pellets that have limitations of reduction of silica of the iron ore, as well as in any processes of production of pellets in general;
- 10 • high efficiency in growing the pellets and so increasing productivity of the pelletizing process;
- maintenance of the quality characteristics of the green pellet in comparison with the prior art binders with the objective of guaranteeing their physical integrity during the process of transport to the firing oven and whe-
- 15 reby to guarantee the quality of the fired pellet;
- significant reduction of the surface humidity of the pellets;
- significant improvement in the surface finishing of the pellets as shown in the photos of figures 4 to 7 in comparison with prior art binders;
- significant reduction in the increase of silica of the pellets in
- 20 comparison with the use of pure bentonite;
- tests carried out on compositions of the present invention proved the synergic action of the components of the binding mixtures on the physical properties of the green pellets.

25 The tests to evaluate the quality of green pellets in general are not regulated, but are standardized by the pellet-producing companies. This is why the **drop** tests were carried out in conformity with the standard procedure used in pelleting industries where the pellets are dropped from a height of 45 cm onto a cement or metal surface with the measurement of the number of drops that the pellet withstands from falling from this height without

30 showing cracks. Similarly, the compression tests of the pellets were performed by breaking them with a press having a capacity of 0 to 20 kg suitable for the resistance that green pellets normally present.

Table 1 below shows results of the tests carried out on pellets produced with each of the binder compositions according to the present invention. The same table presents for comparison the corresponding results for an organic binder manufactured based on carboxymethyl cellulose (CMC) but which may also contain in its formulation inorganic salts of alkaline cations from groups of carbonates and various organic salts and for bentonite which currently represent the state of the art in binders. Also presented are the results of increase in the silica content due to addition of each kind of binder of the present invention, which is noted to be insignificant.

10 Table 1:

Binder	Addition	Humidity of pellet (%)	Surface humidity (%)	Number of falls	Wet compression (g/bel)	Dry compression (g/bel)	Surface finishing	Increase in SiO ₂ in pellet (%)
Organic CMC base	0.035	9.43	0.24	5	1810	4500	Very good	0.00
Bentonite	0.10	10.05	0.71	4	1672	2540	Poor	0.06
Bentonite	0.35	9.07	0.23	4	1840	4600	Good	0.22
BUN 6	0.13	9.52	0.27	5	1790	4790	Good	0.04
BUN 7	0.13	9.28	0.17	5	1930	4390	Very good	0.04
BUN 8	0.13	9.11	0.24	5	1975	4020	Very good	0.05
BUN 9	0.13	9.14	0.11	5	1950	4270	Good	0.04

For the examples from BUN6 to BUN9, were utilized the binder compositions in accordance with the present invention, as indicated in Table 2:

Table 2:

	Bentonite	Polyacrylamide	Molasses	Polysaccharide starch	Alkaline Carbonate
BUN 6	51%	9.2%	20%	-	20%
BUN7	54%	6%	20%	-	20%
BUN8	60%	-	20%	-	20%
BUN9	50%	-	20%	10%	20%

Figures 1 to 3 present images of the surface finishing of the pellets produced with the binder compositions of prior art wherein figure 1 refers to a CMC-based organic binder and figures 2 and 3 to binders of pure bentonite. Figures 4 to 7 refer to pellets produced with the binders of the present invention BUN 6, BUN 7, BUN 8 and BUN 9, respectively.

The pellets obtained with the binder composition of the present invention present high resistance to drops, high compression also (all had dry compression above 4000 grams) and, moreover, have an extremely flat outer surface, that is, a very good surface finishing that has a highly positive influence on the physical properties of the fired pellets. The photographs of figures 4 to 7 also show the surface finishing factor of the pellets as an important aspect of the quality of the pellets manufactured and show the importance of the binding characteristics to produce the desired finishing on the pellets.

It was also possible to demonstrate that with the use of the binder compositions of the present invention, in spite of the high bentonite content, the increase in silica is insignificant when compared to the use of organic binders as shown in table 1.

The examples also demonstrate a significant reduction in the surface humidity of the pellets as shown in table 1 particularly in examples BUN7 and BUN9.

Comparative tests were also carried out with binding compositions of the present invention and compositions such as described in the state of the art, more specifically in document PI 9605362-3. The results are illustrated in Table 3 below:

Table 3

Composition	Binder additions	Humidity of the pellet	Surface humidity	Number of drops	Wet compression (g)	Dry compression (g)
A	0.5% Bentonite	9.80	0.49	No pellets for tests		
	0.5% Molasses					
B	0.5% Bentonite	9.70	0.47	5	1250	4020
	1.5% Molasses					
C	0.0% Bentonite	9.22	0.68	4	1240	3030
	0.5% Molasses					
D	0.0 Bentonite	9.35	0.63	4	1130	4220
	1.5% Molasses					
E	0.13%BUN6	9.84	0.33	10	2320	5105
F	0.13%BUN7	9.68	0.37	9	2290	5050

In the case of the compositions A to D prepared according to quantitative ranges described in document PI 9605362-3, pellets preferably grew in lower size ranges (from 12.5 to 9.5 mm). In tests with compositions containing 0.5% of bentonite and 0.5% of molasses, there was an increased tendency towards small pellets. There was no formation of sufficient pellets for physical tests and they ended up with highly irregular surfaces.

On the other hand, for the compositions E and F, the pellets homogeneously grew in the ranges of 16 to 12.5 and 12.5 to 9.5 mm. Due to the lower surface humidity, said pellets presented better finishing.

Tests were also carried out with the binding compositions BUN6 and BUN7 of the present invention containing CMC in the place of the polyacrylamides. The results shown in Table 4 below indicate that when the CMC is used in binders in substitution of the polyacrylamides, the same trends in improvement of the quality of the pellets are noted.

Table 4

Binder sample	Additions	Humidity of the pellet	Surface humidity	Number of drops	Wet compression (g)	Dry compression (g)
BUN6 with CMC	0.13%	9.47	0.3	8	2080	5260
BUN7 with CMC	0.13%	9.52	0.24	7	2200	5100

CLAIMS

1. Binder composition for use in pelletizing iron ore characterized by comprising from 30% to 80% by weight of bentonite and from 10 to 30% of molasses based on the total weight of the binding mixture.

5 2. Binder composition according to claim 1, wherein the bentonite is present in an amount from 45 to 60%, by weight based on the total weight of the binding mixture.

 3. Binder composition according to claim 1 or 2, also comprising a starch polysaccharide in an amount up to 10% by weight based on the total
10 weight of the binding composition.

 4. Binder composition according to claim 3, wherein the polysaccharide is starch and is present in an amount of 10% by weight based on the total weight of the binding mixture.

 5. Binder composition according to any of claims 1 to 4, also
15 comprising a compound selected from anionic polyacrylamide, from synthetic polymers derived from natural cellulosic polysaccharides or from modified starches, from alkaline metals carbonates and bicarbonates, from soluble alkaline metals hydroxides, or mixtures thereof.

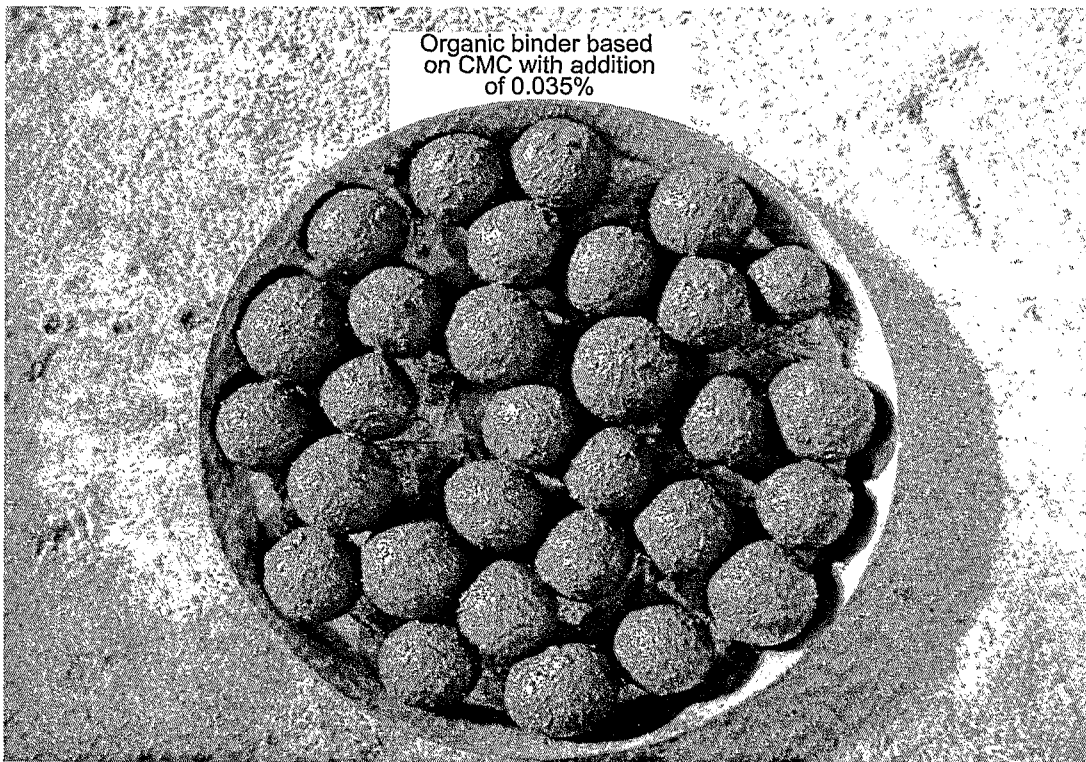
 6. Binder composition according to claim 5, wherein the polyacrylamide is present in a range of 2 to 10% by weight based on the total weight
20 of the binding mixture.

 7. Binder Composition according to claim 6, wherein the polyacrylamide is present in a range of 4 to 9% by weight based on the total weight of the binding composition.

25 8. Binder composition according to claim 5, wherein the synthetic polymer derived from natural polysaccharides is selected from carboxymethyl cellulose or from modified starches and is present in an amount up to 10% by weight based on the total weight of the binding mixture.

 9. Binder composition according to claim 5, comprising alkaline
30 metals carbonates e bicarbonates or alkaline metals soluble hydroxides in a percentage of up to 20% by weight of the binder.

Fig.1



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Fig.2

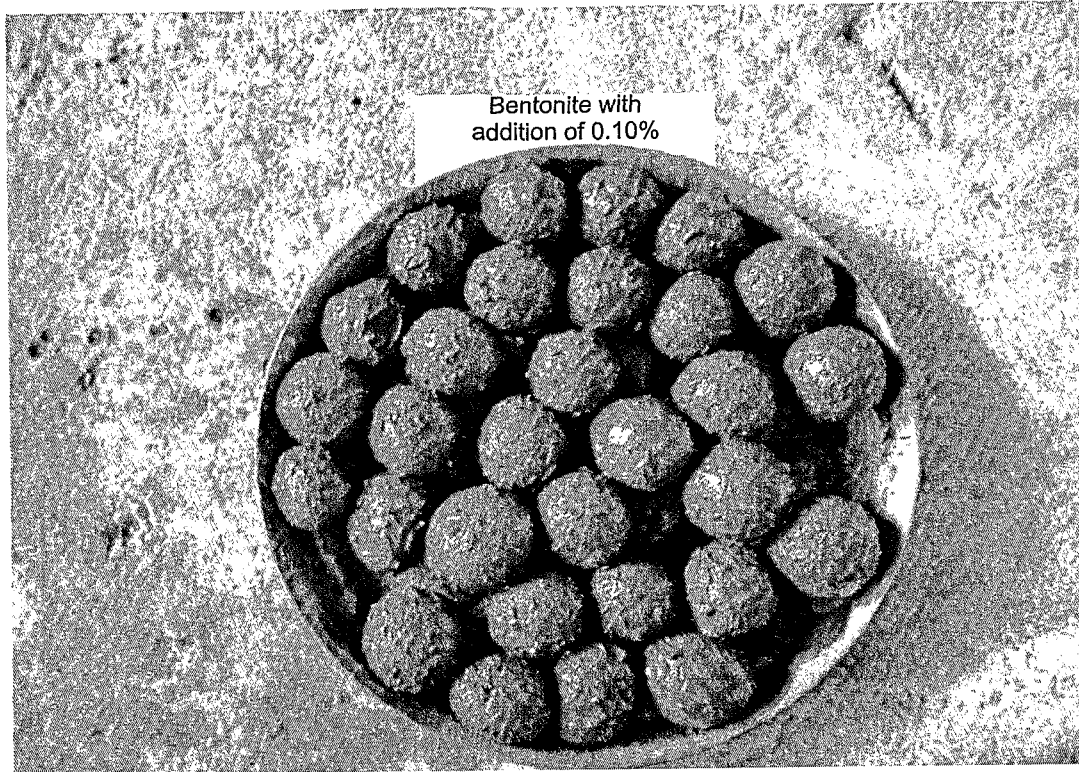
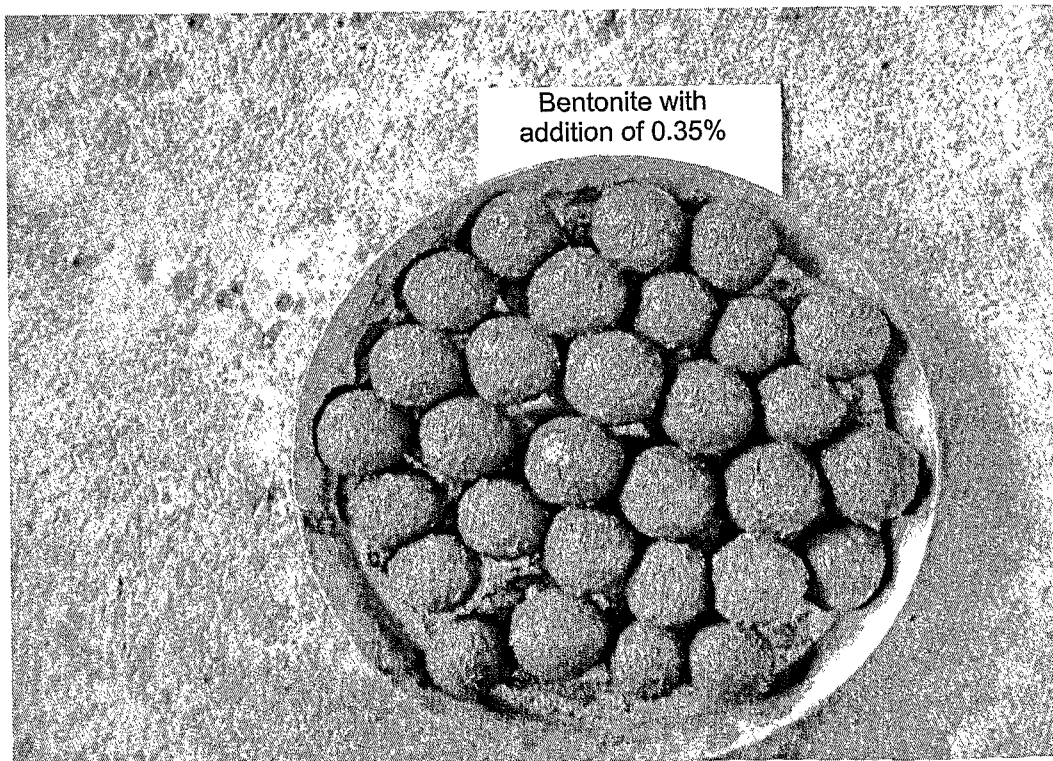


Fig.3

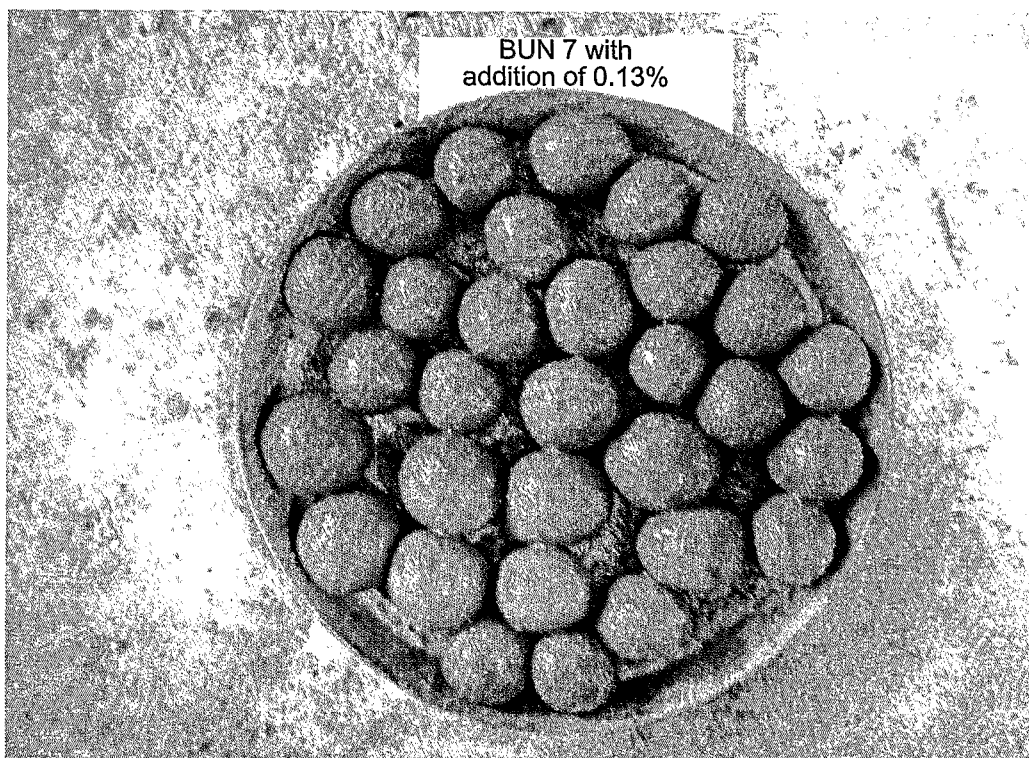


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Fig.4

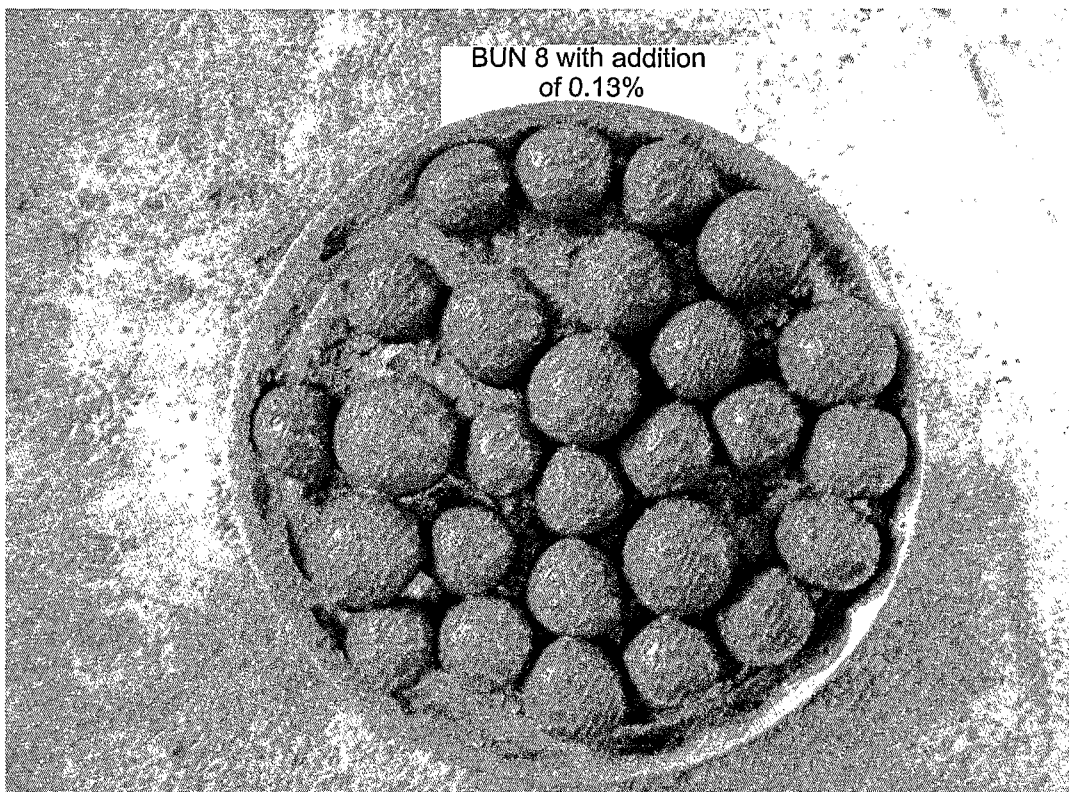


Fig.5



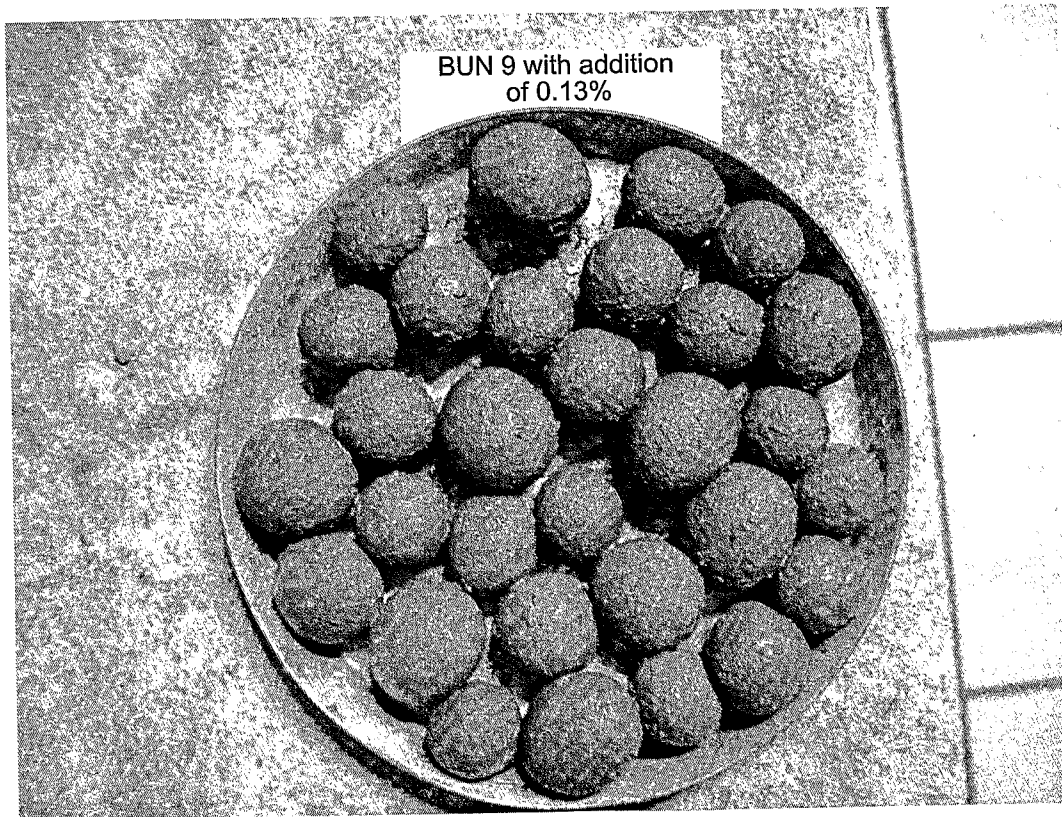
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Fig.6



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Fig.7



INTERNATIONAL SEARCH REPORT

International application No
PCT/BR2009/000057

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22B1/24 C22B1/243 C22B1/244

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B

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

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

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 976 977 A (JOHNSON MARK S [US] ET AL) 11 December 1990 (1990-12-11) column 2, line 33 - line 41 -----	1-3
X	US 4 224 119 A (DECRAENE DENIS F) 23 September 1980 (1980-09-23) examples 2,3 -----	1-3
A		4-9
X	US 4 369 062 A (STRANGE ROBERT R [US]) 18 January 1983 (1983-01-18) table 2 -----	1-3
A		4-9
A	US 3 751 241 A (SLOUGHFY J ET AL) 7 August 1973 (1973-08-07) column 4, line 10 - line 17 -----	1-9

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

18 June 2009

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4976977	A	11-12-1990	NONE
US 4224119	A	23-09-1980	BR 8008786 A 09-06-1981 CA 1162508 A1 21-02-1984 EP 0033344 A1 12-08-1981 MX 153818 A 19-01-1987 WO 8100421 A1 19-02-1981
US 4369062	A	18-01-1983	NONE
US 3751241	A	07-08-1973	NONE