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GREEN MOLDING SAND ADDITIVE

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This invention relates to additives for silica base green molding sands and more particularly relates to a green molding sand composition which includes material which prevents common types of casting surface defect.

One of the most serious problems in the metal casting art concerns the number of rejects which result from surface defects which are commonly referred to in the art as "rat-tails," "buckles," and "scabs." The art has long sought some means of preventing these surface defects and numerous attempts have been made to provide green molding sands which include a material which will eliminate the uneven expansion of the silica grains which comprise the greater proportion of green molding sands.

It is well-known that the expansion of the silica grains, due to the high coefficient of expansion brought about by the heating of the grains when molten metal is poured into a mold, create forces which have a tendency to set up stresses within the surface layer or the crust of the mold. In normal foundry operation, green molding sand compositions include clay which effects the bonding of the silica grains to produce the desired shape of the mold. When the total expansion of the sand grains in the surface layer or crust of the mold is such as to overcome the cohesive action of the clay, a rupture or a separation of the layer or the crust of the mold takes place. When the surface or crust of the mold ruptures or separates during the pouring of molten metal into the mold, the above-mentioned surface defects in the casting appear.

The principal object of this invention is to provide an additive to green molding sands which prevents a rupture or separation of the surface layer or crust of a mold when it is heated by a molten metal being poured into the mold.

A further object is to provide a material which, when added to green molding sand, gelatinizes at a temperature of above 140° F. when in the presence of steam or hot water.

A more specific object of this invention is to provide green molding sand compositions which include modified starches or starch derivatives that show no cold water adhesiveness or solubility, but which are able to form strongly cohesive gel structures in the presence of steam or hot water and which remain a cohesive element over a wide range of temperature and water content.

The above-mentioned problem of surface defects in castings is one which has been a constant source of difficulty for many years. In an attempt to eliminate these difficulties by providing a green molding sand composition, the mechanism of the mold failures resulting in rat-tails, buckles and scabs was studied using high speed motion picture techniques. The first attempt made in our study was to prepare mold compositions which were known to result in failures. Following a careful study of these failures by high speed motion pictures, we obtained a better appreciation of the causes of the failures. Various types of additives to green molding sands which have been employed in the trade were also used and the mechanism of their failure also was studied. Some of the cellulosics, including hard and soft wood flour, corn cob flour, flax seed hulls, and other commonly known were used as additives in green molding sands. It has commonly been the theory that these cellulosic materials are effective to relieve the stresses developed by the expansion of the silica grains. This result has been attributed to the fact that all of these materials burn out, leaving voids in the spaces between the sand grains which will accommodate the expansion which inevitably occurs. The proportions of the materials which have been used are designed to balance the net total expansion of the sand and thereby relieve the forces which result in the rupture or the separation of the mold and thus prevent a rupture or separation.

As is more fully set forth below, the prior art materials are effective to a certain degree but the prior art has not taken into account the basic reasons for the failures in the molds which result in the known surface defects.

For practical foundry reasons, green molding sands include silica grains bonded together by clay and temper water. The above high speed motion pictures studies resulted in the theory which is set forth below of the mechanism of the failure of the crust of the compacted sand made from this type of green molding sand. The crust or surface of the mold, and consequently the elements of the composition which make up the mold, are rapidly heated by the incoming molten metal. The form of heat transfer to the silica grains is either by conduction or by radiation. The rate and degree of heating is dependent on the proximity of the silica grains to the molten metal and the heat transfer conditions which prevail in the mold.

As the molten metal is poured, the temperature of the surface of the mold begins to rise very rapidly until its temperature reaches the boiling point of the temper water. Assuming a normal atmospheric pressure, the boiling point of the water will be 212° F. At this point the temperature of the sand will remain fairly constant for a period of time during which all of the free water present boils off as steam. When the last of the free water has been boiled off, the temperature will again start to rise to a point which is dependent upon the temperature of the molten metal and the distance of the sand mass from the source of heat and the heat transfer conditions which prevail. The heat and dehydration of the sand mass makes it become, in effect, an integral mass of sand and clay. Each grain of sand is bonded to its neighbor by a dry clay bond similar to a dry sand mold or core.

The heating of the sand, which is now a clay bonded mass, will cause the silica grains to continue to expand and since the mass acts as an integral unit, the expansion of the individual grains is cumulative. The result of this cumulative effect is that a stress or force is created between the dry, heated mass and the green or un-dehydrated and unheated sand located at some distance from the surface of the mold. The stress or force created is the sum of the stresses exerted by the individual grains in the dry clay bonded integral mass which lies between the molten metal and the green sand.

The process of dehydration, resulting in the dry clay bonded mass, also results in the carrying of water as steam through other portions of the sand mass in a direction which is normal to the isotherms developed in the mold, which isotherms are governed by the geometry of the castings. The water driven off exists as steam until it reaches the 212° F. isotherm at which point the steam will condense to liquid water. This necessarily results in a greatly increased amount of water which is at or very near 212° F. isotherm in the mold. The increase of the moisture content of the sand at or near 212° F. isotherm is quite substantial. The effect of the increased water content is to weaken the bond strength of the bonding clay.

One reason for this is that clay, which is wetted to a point above its temper point, loses its bonding strength inversely with the water content. In fact, the clay will lose all of its bonding ability and slump if a certain

amount of moisture is exceeded. The point at which the clay loses its bonding ability is known in the art as the "slump point" of the clay. A second factor which must be taken into account is that clay, in the presence of hot water, loses bonding strength as the temperature of the water present exceeds 140° F. Therefore, the clay is largely ineffective as a bonding material above 140° F. when in the presence of excess water.

The loss of strength of the bonding clay at a zone defined by the 212° F. isotherm in the mold means simply that at that point the green molding sand composition is unable to resist the stresses created by the expanding heated and dehydrated integral sand mass. Thus, rupture in the surface of the mold takes place.

The study by high speed motion pictures of a cross-section of a mold into which molten metal was poured indicated to us that the relationship between the expansion of the heated crust with respect to the unheated mass of sand results in a failure in shear which occurs at the dividing line between the dry heated sand and the over-wetted sand. When the mold surface fails in the above described manner the casting defect known as a rat-tail is formed by the dehydrated sand mass shearing away from the green sand. The heated integral mass is thus free to slide up and over the green unheated mass. The cavity left by the displacement of the dehydrated sand mass will be filled by the molten metal and when the casting thus produced is examined the surface defect known as a rat-tail will be readily apparent.

When the above described failure of the sand mass takes place in the cope of the mold, the effect of gravity becomes apparent on the configuration of the surface defect on the casting. The action of gravity on the ruptured sand mass will, depending upon certain conditions, produce either a buckle or a scab.

A buckle on the casting resulting from a separation, due to gravity, of the dehydrated sand mass in the cope results from a separation or open crack in the dry clay bonded sand mass. Radiant heat normally produces the dry heated sand mass whose separation from the surface of the cope results in this type of defect. The force of gravity results in a rupture or separation but may not necessarily result in a complete breaking away of the crust. If the sand mass does not break away, the surface defect in the casting is that referred to by the art as a "buckle." If, however, a portion of the crust breaks away then the surface defect referred to by the art as a "scab" will result.

An explanation for the mold failure which produces a "scab" on the drag of the mold is as follows: The rupture of the crust, which occurs normally just past the metal front produces the integral dry clay bonded mass referred to above. If the molten metal recedes backwardly from its former front, adhesive conditions may prevail between the metal and the dehydrated sand mass. If such adhesive conditions prevail, the metal moving backwardly tends to peel up the ruptured sand layer. As the metal flow continues to fill up the mold, the void created by this sand mass which adhered to the molten metal is enclosed by additional metal. Thus the sand penetrates down into the casting proper and produces the surface defect which is known as a "drag scab."

With the above background in mind, it will be understood why previous attempts to counteract the occurrence of surface defects have been largely unsucessful. Most, if not all, previous attempts to include cellulosic additives to green molding sands have relied upon the theory that, by creating a sufficient amount of void space to accommodate the expansion of the sand, the stress created by such expansion will be relieved to an extent sufficient to prevent a rupture or separation of the surface layer of the mold. Our tests and studies neither disprove nor support the theory that the inclusion of such additives is completely beneficial. However, in order to test the effectiveness of the material of this invention, molds prepared from prior art materials were made and the resultant castings compared with castings made in molds using the materials of this invention.

We found that the ability of the above mentioned cellulosic materials to reduce the water content in the critical zone was extremely minor. It was found that these materials shift the slump point of the clay very slightly and not sufficiently far in order to overcome the stresses which are normally produced in the surface layer of the mold. Furthermore, as is above mentioned, these materials cannot produce any additional bonding strength in the critical zone where the shear between the green sand and the dehydrated sand mass occurs.

The prior art cellulosic materials have secondary effects which are, in fact, deleterious to the molding sand. They are known to affect adversely the green properties of the sand. Thus the inclusion of much more over 1 to 1½% of such cellulosic materials has an embrittling effect. This embrittling effect produces a very delicate sand from the standpoint of molding and handling.

A further adverse effect that cellulosic materials have on green molding sand is that they cause it to dry out exceedingly fast, especially upon the surface. The drying out of the surface of molds produced from green sands including cellulosic materials results in loose sand on the surface of the mold when patterns are being drawn therefrom or when any abrading action is applied to the surface of the mold. These loose sand particles are difficult to remove and if not removed lead to various of the other types of casting defects.

A third deleterious effect in the use of cellulosic materials in green sand molds is that, in severe cases, where a great amount of expansion takes place such large quantities of the materials must be used, that in burning off, they produce a volume of gas which is so excessive that it leads to other types of molding and casting defects associated with excess volatile material being present.

Because of the above, we have developed an additive for green molding sands which eliminates most, if not all, of the shortcomings of other materials. The additive materials which we prefer are those materials which are related to modified starches and starch derivatives which show no cold water adhesiveness or solubility but are able to form highly viscous and highly tenacious gel structures in the presence of steam or hot water.

A preferred formulation for our additive is as follows: 25 to 100 parts of an additive composed of the sodium salt of ungelatinized low-substituted starch acid ester derivatives containing carboxylic and sulfonic acid groups. This material is a poly-electrolyte exhibiting anionic properties and having a very pronounced hydrating capacity. This material may be used alone or may be mixed with 100 to 25 parts of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. This material should not show any adhesive property below 150° F. Either of these two materials acting alone will stop green molding sand expansion but the combination of the two is more desirable.

The additive of this invention is preferably added in the form of a mixture of the two types of materials in an amount between 1/10 to 2% by weight to a normal green molding sand of average composition. A typical synthetic green molding sand composition consists of 85% to 97% washed and graded silica sand, A.F.S. fineness 30 to 250; 3% to 15% bonding clay such as bentonite, fire clay and the like; to which is added an amount of temper water to suit the particular mold being produced. To this mixture is added either the above-mentioned mixture of the two types of materials or either one of the two materials separately in an amount between 1/10 to 2% by weight. Green molding sand compositions made in accordance with this invention have been found to be eight times more effective in preventing surface defects in cast-

ings of the "rat-tail", "buckle", and "scab" types, as compared to green molding sands which include the cellulosic materials employed by the prior art.

The advantages in using the additives of this invention are as follows. When the additives of this invention are admixed in the molding sand they have no effect and are dormant at ambient temperatures. In other words, they do not in any way affect the green properties of the molding sand. Any green properties the molding sand had prior to adding our new materials are not changed by the addition of the mixture of the two materials or either of the two materials separately. There is no embrittling effect nor is there any increase in the drying out qualities of the molding sand. Furthermore, since only a small quantity of the additive materials of this invention is necessary to be effective, when the resulting gel formation is burned off, very little gas is produced. Therefore, the casting defects resulting from the large volume of gas generated when cellulosics are used are eliminated.

At steam temperatures, or in the presence of steam or hot water above a temperature of 140° F., either of the additive materials of this invention or a mixture of them gelatinizes. This creates a tenacious bond that is insensitive to water over a wide range of temperature. This means that the newly formed bond aids, if in fact it does not completely replace, the bonding duties of the clay at the time and place at which the clay bond normally begins to fail. This gel type of bond remains completely effective in the presence of water and is effective as a bond throughout a decreasing concentration of water, all the way up to and including dryness.

The effect of the gel bond is as follows. At high concentrations of water at elevated temperatures the bond is a gel which has strong bonding qualities. As dehydration of the gel begins to take place it rapidly increases in viscosity until it finally becomes a solid when all of the water present in the gel system has been removed. The solid which results has strong film-forming properties and thus produces an effective bonding of the sand grains. In other words, the additive material of this invention provides an effective bond throughout the transition period from high moisture concentrations, to moisture at steam temperatures, to dehydration and to the completely dry state while effectively maintaining all of its bonding ability during these separate stages.

The bond is also effective in the heated zone. That is, the zone which is heated directly by the molten metal. In this area the temperature of the sand grains and the other materials present in the surface of the mold can become elevated to above 1000° F. The gel bond at these temperatures, being an organic compound, will be consumed and will effect a volume decrease in the sand. This latter effect is secondary and is not nearly as important as the effect of strengthening the weakened, overwetted clay bonded zone. However, this slight increase in the available void space into which the sand grains can expand does exist and does to a degree aid in the total effect of preventing the expansion of the silica grains from creating mold surface separation or rupturing.

In the above mentioned studies we have found that on a weight per weight basis the additive materials of this invention, either separately or when admixed in the proportions mentioned, are eight times more effective in preventing the surface defects in castings, as compared to the prior art cellulosic materials.

Both of the additive materials have the common properties of showing no cold water adhesiveness or solubility and both form gel structures in the presence of steam or hot water. Of the two materials, the sodium salt of ungelatinized low-substituted starch acid ester derivatives containing carboxylic and sulfonic acid groups is the preferable material to be used alone. However, this material is considerably more expensive than the cross-bonded corn starch of high potential viscosity and the added efficiency of the low-substituted starch material is not that much greater to warrant the extra expense. In view of the relative expense of the two materials and substantial similarity of their properties, a mixture containing a larger proportion of the cross-bonded corn starch material is preferred since the resulting mixture is highly effective and quite economical.

Typical sand formulations using the additives of this invention are set forth in the examples below.

Example 1

A green sand formulation using the materials of this invention for preparing light gray iron, aluminum and bronze is as follows:

Jersey silica sand A.F.S. fineness 140–160	lbs.	100
Southern bentonite	lbs.	5
Seacoal	lbs.	4–5
A sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups	lbs.	1–2
Moisture	percent	4.5

Example 2

A green molding sand composition for preparing medium weight castings for gray iron is as follows:

Old sand	lbs.	50
Jersey silica sand A.F.S. fineness 70	lbs.	50
Western bentonite	lbs.	3
Seacoal	lbs.	4
A cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F	lbs.	1–2
Moisture	percent	3–3.5

Example 3

A natural sand molding composition for gray iron is as follows:

Albany sand grade #0	lbs.	100
Seacoal (fine)	lbs.	2
A mixture in equal amounts, of cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups	lbs.	1–2
Moisture	percent	4.5–5.5

Example 4

A typical composition for a skin dry molding sand is as follows:

Heap sand	lbs.	60
Grade "C" Jersey silica sand	lbs.	40
Western bentonite	lbs.	2
Pitch	lbs.	1
Mixture of the additives containing 25% of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and 75% of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups	lbs.	1–2
Moisture	percent	3.5

It should be noted that the expansion stopping additives of this invention were used in this particular molding sand to insure the stability of the mold sections which will be re-wetted due to the driving off of steam by the molten metal in the portions which are remote from the surface of the mold cavity.

Example 5

A typical green molding sand composition including the materials of this invention for preparing castings for light malleable iron is as follows:

Jersey silica A.F.S. fineness 70–80	lbs.	66
McConnellsville bank A.F.S. fineness 110–110	lbs.	33

Western bentonite	lbs.	4
Southern bentonite	lbs.	4
Seacoal	lbs.	4
Mixture of the additives containing 75% of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and 25% of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups	lbs.	1–2
Moisture	percent	4

While two specific groups of materials have been mentioned hereinabove as additives to be used singly or in mixture, it will be recognized by the art that any other material having the properties of forming gel structures in the presence of steam or hot water and which show no cold water adhesiveness or solubility will perform the same function as the materials which have been specifically mentioned.

We claim:

1. A green molding sand composition consisting essentially of from 85% to 97% sand, 3% to 15% clay, water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are substantially insoluble and substantially non-adhesive in cold water and form gel structures in the presence of steam and hot water, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

2. A green molding sand composition consisting essentially of from 85% to 97% sand, 3% to 15% clay, water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are insoluble in cold water, are non-adhesive in cold water and form gel structures in the presence of steam and hot water, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

3. A green molding sand composition consisting essentially of from 85% to 97% sand, 3% to 15% clay, water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are substantially insoluble and substantially non-adhesive in cold water and form gel structures in the presence of steam and hot water substantially effective to prevent the surface of a mold made from said composition from rupturing when molten metal is poured into said mold.

4. A green molding sand composition consisting essentially of from 85% to 97% sand, 3% to 15% clay, water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are insoluble in cold water, are non-adhesive in cold water and form gel structures in the presence of steam and hot water substantially effective to prevent the surface of a mold made from said composition from rupturing when molten metal is poured into said mold.

5. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, water and an amount of an additive which is substantially insoluble and substantially non-adhesive in cold water and forms a gel structure in the presence of hot water and steam consisting essentially of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

6. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, water and an additive which is substantially insoluble and substantially non-adhesive in cold water and which forms a gel structure in the presence of hot water and steam consisting essentially of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups, said additive being present in an amount between 1/10% to 2% by weight of said mixture.

7. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, water and an amount of an additive which is substantially insoluble and substantially non-adhesive in cold water and which forms a gel structure in the presence of hot water and steam consisting essentially of a cross-bonded corn starch of high potential viscosity, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

8. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, water and an amount of an additive consisting essentially of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and which is substantially non-adhesive and substantially insoluble in water at a temperature below 150° F., said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

9. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, water and an additive which is substantially insoluble and substantially non-adhesive in cold water and forms a gel structure in the presence of hot water and steam consisting essentially of a cross-bonded corn starch of high potential viscosity in an amount between 1/10% to 2% by weight of said mixture.

10. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, water and an additive consisting essentially of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and which is substantially non-adhesive and substantially insoluble in water at a temperature below 150° F., said additive being present in an amount between 1/10% to 2% by weight of said mixture.

11. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, temper water and an additive which is substantially insoluble and substantially non-adhesive in cold water and forms a gel structure in the presence of hot water and steam consisting essentially of an admixture of from 25 to 100 parts of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups and 100 to 25 parts of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and is non-adhesive at temperatures below 150° F., said additive being present in an amount from between 1/10% to 2% by weight of said mixture.

12. A green molding sand composition consisting essentially of from 85% to 97% sand, 3% to 15% clay, water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are substantially insoluble and substantially non-adhesive in cold water, form strongly adhesive materials in the presence of hot water and form gel structures upon further heating in the presence of steam and hot water, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

13. A green molding sand composition consisting essentially of a mixture of from 85% to 97% silica sand, 3% to 15% bonding clay, temper water and an additive which is substantially insoluble and substantially non-adhesive in cold water and forms a gel structure in the presence of hot water and steam selected from the group consisting of: a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups, a cross-bonded starch of high potential viscosity, and an admixture of 25 to 100 parts of said sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups and 100 to 25 parts of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and is non-adhesive at temperatures below 150° F.; the amount of said additive in said mixture being between 1/10% to 2% by weight of said mixture.

14. A process for preparing a green molding sand composition which consists essentially of the steps of mixing together an amount of silica sand which is from 85% to 97% of the total weight of said composition, from 3% to 15% by weight bonding clay, temper water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are insoluble in cold water, are non-adhesive in cold water and form gel structures in the presence of steam and hot water, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

15. A process for preparing a green molding sand composition which consists essentially of the steps of mixing together an amount of silica sand which is from 85% to 97% of the total weight of said composition, from 3% to 15% bonding clay, temper water and an additive material selected from the group consisting of modified starches, starch derivatives and mixtures of said modified starches and starch derivatives, said additive material being insoluble in cold water, non-adhesive in cold water and forming gel structures in the presence of steam and hot water, said additive being present in an amount between 1/10% to 2% by weight of said composition.

16. A process for preparing a green molding sand composition which consists essentially of the steps of mixing together an amount of silica sand which is from 85% to 97% of the total weight of said composition, from 3% to 15% bonding clay, temper water and an additive consisting essentially of a cross-bonded corn starch of high potential viscosity which is substantially insoluble and substantially non-adhesive in cold water and which gelatinizes at a temperature between 160° F. and 212° F. and which is non-adhesive below 150° F., said additive being present in an amount between 1/10% to 2% by weight of said composition.

17. A process for preparing a green molding sand composition which consists essentially of the steps of mixing together an amount of silica sand which is from 85% to 97% of the total weight of said composition, from 3% to 15% bonding clay, temper water and an additive which is substantially insoluble and substantially non-adhesive in cold water and forms a gel structure in the presence of hot water and steam consisting essentially of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups, said additive being present in an amount between 1/10% to 2% by weight of said composition.

18. A process for preparing a green molding sand composition which consists essentially of the steps of mixing together an amount of silica sand which is from 85% to 97% of the total weight of said composition, from 3% to 15% bonding clay, temper water and an additive which is substantially insoluble and substantially non-adhesive in cold water and forms a gel structure in the presence of hot water and steam selected from the group consisting of: a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups, a cross-bonded starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and is non-adhesive at temperatures below 150° F., and an admixture of 25 to 100 parts of said sodium salt of ungelatinized low-substituted starch acid ester derivative and 100 to 25 parts of a cross-bonded corn starch of high potential viscosity, the amount of said additive in said mixture being between 1/10% to 2% by weight of said composition.

19. A green mold sand composition consisting essentially of sand, bonding clay, temper water and an amount of an additive material selected from the group consisting of modified starches and starch derivatives which are substantially insoluble in cold water, are substantially non-adhesive in cold water and form gel structures in the presence of steam and hot water, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

20. A green mold sand composition consisting essentially of sand, bonding clay, temper water and an amount of an additive material which is substantially insoluble in cold water, is substantially non-adhesive in cold water and forms gel structures in the presence of steam and hot water consisting of sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of molten metal in said mold.

21. A green mold sand composition consisting essentially of sand, bonding clay, temper water and an amount of an additive material which is substantially insoluble in cold water, is substantially non-adhesive in cold water and forms a gel structure in the presence of steam and hot water consisting of a cross-bonded corn starch of high potential viscosity, said amount of said additive being effective to prevent overwetting the clay bond in a green sand mold made from said green molding sand composition during the casting of the molten metal in said mold.

22. A green mold sand composition consisting essentially of sand, bonding clay, temper water and an additive material which is substantially insoluble in cold water, is substantially non-adhesive in cold water and forms a gel structure in the presence of steam and hot water consisting of an admixture of from 25 to 100 parts of a sodium salt of ungelatinized low-substituted starch acid ester derivative containing carboxylic and sulfonic acid groups and 100 to 25 parts of a cross-bonded corn starch of high potential viscosity which gelatinizes at a temperature between 160° F. and 212° F. and is non-adhesive at temperatures below 150° F., said additive being present in an amount from between 1/10% to 2% by weight of said mixture.

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