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METHOD OF INHIBITING EROSION ON MOLD SURFACES

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The instant invention relates to an improved metal casting process. More specifically, the present invention is concerned with a method of increasing the life of mold bottoms used to cast ingots, and prevent adherence of these mold bases to subsequently formed solidified ingots which must be removed from within the mold walls.

All metal ingots are cast from molds. One popular type is a "big end down" mold. These molds rest on bases commonly known as "stools." The stools are merely large, normally rectangular, flat slabs of metal, commonly made of cast iron, which are used as support for the mold sides and also, of course, form the bottom portion of the mold. The mold inside surfaces generally taper up in diameter from bottom to top. Another type of mold is known as the "big end up" mold. The majority of these are ladle-like receivers for the molten metal, the bottom portion of which molds are integral, non-removable parts of the entire mold.

Various problems commonly occur in use of these molds and particularly with respect to the surface of their base portions. First, the unprotected metal surface quickly erodes and pits from the action of molten metals which are cascaded upon their surface. Large gouges in the base portions are produced due to the force and high temperature developed by the flowing molten metal which contacts the surface of the stool. Since many molds are generally approximately 5–10 feet in height, the metal must be poured from a height at least equal to that distance and quite often is poured from even greater heights. A considerable pressure head is also developed due to the mass of molten metal. Thus, the hot molten metal easily gouges gaping depressions in the base members under such force and at a temperature greater than the liquefaction temperature of the molten metal.

The molten metal upon solidification to an ingot thereby has a bottom form conforming to the undesirable eroded surface configuration of the stool or base member of the mold. Thus, a considerable amount of the ingot, when withdrawn from the mold and subsequently processed into slabs or blooms, is lost through a cropping of the irregularly formed end of the slab. This, of course, is highly undesirable, since it results in increase in scrap, which must be subsequently reprocessed. Thus, there is an overall reduction in yield.

Another extremely serious and costly problem results after the ingot in a big-end-down mold has solidified to a point where it can be removed from both the mold sides and its base platform member or stool. In many cases, if the surface of thes tool is unprotected, or inadequately protected, and erosion occurs as described above, the ingot has a greater tendency to remain tightly adherent to the stool. Thus, after the mold sides are removed from around the ingot, which process can normally be efficiently achieved with a minimal film of coating selected from a variety of coating agents, the ingot must be forcibly removed from the stool. This is normally achieved by raising both ingot and adherent stool, and thrusting them against some other larger object whereby the ingot is jarred loose. In many cases, the stool and ingot are merely dropped on the floor from some suitable height. In such a situation, the stool is often broken into two or more smaller pieces and cannot be subsequently reused in casting other ingots. Again, replacement cost of these stools

is high, making this aspect of the overall casting process somewhat disadvantageous. The same problem exists with respect to closed end big-end-up molds wherein sticking of ingots particularly occurs at their base portion. New molds of this type are especially vulnerable to sticking due to their smooth surface unprotected by any layers of metal oxides or scale. A tight metal-to-metal bond between mold bottoms and ingots then occurs.

Cracking of molds and particularly their base portions due to the above discussed rough handling occasioned by "stickers" between the base portions and ingots is also enhanced by thermal shock during ingot formation. Unprotected or inadequately protected bottom surfaces of molds are especially susceptible to such destructive shock.

Many prior art coating materials have failed to give adequate protection to the mold base members, and in some cases caused ancillary process difficulties. For example, some inferior coatings were washed off the surface of the base portion of the mold and were thereby included as an unwanted impurity in the ingots. Such inclusion oftentimes deleteriously affected desirable metal properties.

U.S. Patents 3,184,813 and 3,184,815 describe excellent methods of combatting the above described arduous problems. However, it would be of further benefit to the art if an additional method of stool coating were discovered which possessed added advantages of lower cost as well as enhanced efficiency. If the above described stools of big-end-down molds or base members of big-end-up molds could be protected from erosion by cascading molten metal in a more economical operation, such process would find ready acceptance in the art. Likewise, if the problem of adherence between a mold base member and subsequently formed ingot could also be overcome in a simple, efficient and economical method, the overall casting process would be materially benefited.

It therefore becomes an object of the invention to provide a method of casting metal ingots into metal molds whereby adherence of the base member of the mold to the formed ingot and erosion of the same base member diring ingot formation are substantially prevented.

A specific object of the invention is to inhibit such erosion and adherence by applying a film of coating material to the surface of the base member whereby these problems are overcome.

Yet another object is to provide metal molds used for casting ingots which have at least the base member of the mold protected by a film of material so that the above described problems of erosion of the base member and adherence of same to metal ingots no longer exists to any appreciable degree.

Other objects will appear hereinafter.

In accordance with the invention a method of casting metal objects from metal molds has been discovered, whereby adherence of the base member of those molds to ingots formed therefrom, and erosion of these same base members during such ingot formation are substantially inhibited.

In its broadest aspects, the invention comprises the steps of applying a slurry consisting of a binder and refractory to the surface of the base member of a metal mold. In order to best achieve dual purposes of prevention of erosion of base member and non-adherence to formed ingots, the slurry should consist of at least one refractory of the following types: vitreous silica, crystalline silica, magnesium silicates, aluminum silicates, alumina, graphite, zirconium silicates and clay. These materials are all well-known substances and are all commerically available. Typical aluminum silicates, for example, may include mica, a laminated type of aluminum silicate and mullite, an orthorhombic aluminum silicate available from the Island of Mull or other sources or

artificially made by heating andalusite, sillimanite or kyanite. Excellent magnesium silicates are forsterite or talc, while a useful zirconium silicate is zircon. A typical crystalline silica is quartz. The most preferred refractory, discussed in more detail hereinafter, is vitreous silica. The binder used with any one or more of the above refractories should comprise colloidal silica sol and a silicic acid sol, both of which will be fully described hereinafter.

The slurry is provided in an amount adequate to form a coating of sufficient thickness to prevent the above-mentioned adherence and erosion from occurring. After the slurry is allowed to dry with or without application of heat, whereby the liquid phase is driven from the surface of the base member, leaving a thin film of solid refractory coating, the molten metal is thereafter poured into the mold and on top of the now coated base member. The solidified ingot is then removed from the coated base member and mold sides.

The slurry coating is simply applied to the stool or bottom of the mold by a wide variety of methods. For example, the slurry may be applied by flowing it over the stool, by spray techniques, by coating the stool with some type of applicator, etc. Spray application is believed to be the most efficient and practical way of slurry application. The slurry may be applied to the stool portion of the molds before or after the metal mold sides are placed thereon.

Effecting removal of the liquid phase of the slurry from the solid refractory material may likewise be carried out in a variety of methods. For example, the bottom portion of the mold may be coated with the slurry and allowed to dry gradually. Another method of laying down a thin protective coating is to apply the slurry to an already heated stool or mold having an integral base portion. This is particularly preferred in that the stools and their metal mold sides or big-end-up molds are generally already hot before introduction of the molten metal due to the residual heat from the previous casting run, and in such a method drying time is a very minimum period.

Another way of applying the protective film is to coat the base member, and then heat it as slowly or rapidly as desired to drive off the liquid portion of the slurry. In any event all that is necessary is that the coating be laid down and dried in some manner after the slurry has been applied to the base member.

In the most preferred method the coating slurry is applied to stools or mold base members having a temperature ranging from that of room temperature to 1200° F., and more preferably from 200° F. to 800° F. Most preferably, best adherence of solid coating to stools is achieved by slurry application to the stools at a temperature range of 200–500° F. For best results, it has been determined that films should measure in thickness from 0.01" to 3" and most preferably from 0.01" to ⅛".

It is believed that the excellent coating success achieved by use of the above described slurries is due to their ability to form a strong ceramic coating even when affixed to the base members of the mold at relatively low temperatures, at least under mill conditions, of say about 500° F. or even lower. The coating becomes completely resistant to subsequent contact with water and stays tightly adherent to the base portions of the mold even under such washings.

After coating operations, molten metal is poured into

the mold, allowed to solidify into an ingot and the ingot is then separated from mold surfaces. The invention is not limited to use with specific mold sides or any particular metal mold bottom or to use with any particular molten metal. However, it has found specially preferred use in coating cast iron metal base members for molds which are used in forming ingots of steel.

One of the binder components used to form the slurries of the invention is a colloidal silica sol. These are well-known materials and are commercially available from several sources of supply. A typical group of commercially available silica sols that may be used in the practices of the invention are those silica sols sold under the name "Nalcote." Silica sols of this type are described below in Table I.

TABLE I

Silica Sol	I	II	III	IV	V	VI
Percent colloidal silica as SiO_2	15	30	35-36	21-22	49-50	35
pH	8.6	10.2	8.6	3.7	9.0	3.5
Viscosity at 77° F., cps	<5	<5	<5	<10	20-30	6.5
Specific Gravity at 68° F	1.09	1.205	1.255	1.06	1.385	1.255
Average Surface Area, m.² per gram of SiO_2	330-430	190-270	135-190	135-190	120-150	135-190
Average particle size, millimicrons	7.9	11-16	16-22	16-22	20-25	16-22
Density, lbs./gallon at 68° F	9.1	10.0	10.5	8.8	11.6	10.5
Na_2O, Percent	0.04	0.40	0.10	0.05	0.30	0.01

Other silica sols that may be used in addition to those above, may be prepared by using several well-known conventional techniques. Perhaps the most convenient method of making aqueous colloidal silica sols is described in Bird, U.S. Patent 2,244,325, wherein a dilute solution of an alkali metal silicate is passed in contact with a cation exchange resin in hydrogen form, whereby the silicate is converted to a dilute aqueous silicic acid sol. The dilute silicic acid sol may be both converted to a silica sol and concentrated to solids concentrations which are more economically usable from the standpoint of shipping costs and ultimate process use, by employing the techniques described in either Bechtold et al. U.S. Patent 2,574,902; Borge et al., U.S. Patent 2,680,721; or Alexander et al., U.S. Patent 2,601,235. Another type of silica sol which may be used in the practices of the invention is described in the specification of Reuter, U.S. Patent 2,856,302. While aqueous colloidal silica sols may be used, it will be understood that other forms of colloidal silica may be employed, such as for instance, sols which contain a major portion of polar organic solvents. Said sols may be generically referred to as organo sols, and are typified by the sols described in Marshall U.S. Patent 2,386,247. It is only necessary that the silica particles used can be dispersed colloidally in a hydrophilic substance, such as water or lower alkyl alcohols and other organic compounds possessing relatively high dielectric constants.

In some instances mixtures of water and organic substances compatible with water may be employed as suspending media for the colloidal silica particles. Particularly preferred organic substances are those which lower the freezing point of pure aqueous sols by their admixture with these aqueous silica sols. Such final product sols then are especially useful during the colder months of the year when they must be stored and/or used at relatively low temperature. Amines such as morpholine, diethyl amine, etc., and polyhydroxy organics as ethylene glycol, glycerine etc., are preferred materials in making up silica sols containing these substances as sole silica suspending media or as a portion of a mixture additionally containing water. A preferred sol, "winterized" against freezing contains 5–50 parts by weight of polyhydroxy compound such as ethylene glycol, 20–85 parts by weight of water and 10–60 parts by weight of silica.

Regardless of the method employed to produce the colloidal silica sol containing water, polar organic liquids or mixtures of these substances as a continuous suspending phase, it is desirable that said sols contain silica

particles which are dense, amorphous, and have an average particle diameter which does not exceed 150 millimicrons and is greater than 5 millimicrons. As evidenced by a reading of Table I, all the silica sols contemplated as starting materials have an average particle size diameter well below 150 millimicrons. Preferably, the starting silica sols have an average particle size diameter of from 10–50 millimicrons. The silica concentration in the sols may be between 0.1% and 60% by weight silica expressed as SiO_2. More preferred sols contain from 3.0 to 60% by weight of silica and most preferably 10–60% by weight. The molecular weight of the silica particles is in excess of 200,000 and may range as high as several million.

Other sols which may be employed as binders for the silica refractory are those known as "salt-free" silica sols. These are particularly preferred when the suspension media of the silica particles in the binder itself is solely a polar organic liquid or a mixture of water and polar organic liquid. Since many of the above described sols usually contain alkali metal compounds as stabilizers, they are generally not compatible with organic systems due to the fact that the salts present in the aqueous sol cause gelation or precipitation of the silica particles when the aqueous phases are exchanged for polar organic solvents. This can be avoided by use of "salt-free" aqueous silica sols as starting materials in preparation of pure organosols or mixtures of water and organic as silica carriers. In order to avoid this gelation effect, it is necessary that the causative cations be removed from the surface of the colloidally dispersed silica particles and from the liquid phase of the sol. This may be readily accomplished by treating typical silica sols of the type described in Bechtold et al. U.S. Patent 2,547,902, with a cation exchange resin in the hydrogen form and a strong base anion exchange resin in hydroxide form. This treatment tends to produce a finished aqueous sol in which both the continuous aqueous phase of the sol and the particles of silica are considered "salt-free." Typical commercially available silica sols which may be deionized to produce "salt-free" silica sols are those which are described in Table I above. These aqueous "salt-free" silica sols may be either used as such in combination with the silicic acid sol and with one or more of the named refractories to constitute a slurry coating material or may be modified whereby the aqueous phase is completely or partially exchanged for a hydrophilic polar liquid such as an alcohol or the alcohol is mixed with aqueous sol in desired proportions. The "salt-free" pure alcosols or aqueous-alcoholic silica sols may then be easily combined with silicic acid sols and a refractory and the resultant slurry used to coat the stools.

When the particle sizes of the silica sols described above are within the ranges specified, the silica particles present in the starting aqueous or organic sol have specific surface areas of at least 20 $m.^2/g.$, and usually in excess of 100 $m.^2/g.$ Further, when dionized sols are employed as a binder, they generally have a salt content expressed as Na_2SO_4, of less than 0.01%.

The particular silicic acid sols used as a binder component may be produced by a wide variety of methods. All of these particular sols have average molecular weights below about 90,000. More preferably these acid sols contain silica particles having an average molecular weight of from about 1,000 to 46,000. The pH of these acid sols is below 5.5 and more preferably they lie within the range of 2.5 and 3.5. The average particle diameter is less than 5 millimicrons and generally 1–4 millimicrons.

One method of preparing such acid sols is to neutralize water glass with a mineral acid. In using this method to form the acid silica sols it is necessary, however, to remove the major portion of the salts formed by neutralization reaction. This may be accomplished by dialysis or electrodialysis, but these procedures are not adaptable to large scale economic production. An improved method for preparing acid sols has been described in Bird U.S. Patent 2,244,325. By utilizing the teachings of this patent, the preferred starting acid sols are produced. According to the Bird method, a water glass (alkaline silicate) solution is passed through a column of cation exchange material in the hydrogen form whereby the alkali metal in the water glass is exchanged for hydrogen and the resultant product is an acid silica sol of unusual purity. Generally, the pH of the sols so produced lie within the range of 2.0–4.0. In addition, the average molecular weight of the silica particles is well below 90,000. Also, silicic acid sols generally have a SiO_2 solids content ranging from about 2% to about 10%.

Other acid sols suitable for use in the invention may be prepared by a variation of the Bird method described above. In this embodiment the effluent from the Bird process may then be further treated by passing it through a weak base resin in the free base form. The resultant product is then substantially stripped of any ions and is generally known as "deionized." Still another variation of the technique is to employ a mixed resin bed, that is, a bed containing a weak base resin in the free base form and a strong acid resin in the hydrogen form whereby the silicic acid sol is formed simultaneously with exchange of its companion ions to produce a substantially deionized polysilicic acid sol.

While the above described methods are preferably to produce the starting acid sol, it must be understood that any appropriate method for producing an acid sol of a requisite molecular weight and pH may also be used. For example, minute amounts of the stabilizer such as alkali metal hydroxide may be used without departing from the scope of the invention as long as the pH is not raised above the operative limits described above.

The binder itself should be composed of 40–90% colloidal silica sol and 10–60% silicic acid sol. More preferably, each component ranges from about 40% to about 60%. A 50%–50% mixture was found to exhibit excellent performance in its intended end-use. All expressed percentages are weight percents.

As mentioned above, the most preferred refractory materials are those generally referred to as vitreous silicas. These are glassy modifications of silica, obtained by the fusion of selected low temperature crystalline forms, and are frequently referred to as quartz glass or silica glass. Specific vitreous silicas include those particles made from fused quartz glasses, silicate glasses, silica glasses such as the well-known Vycor materials and fused silica glasses. With respect to all of these materials the thermal expansion coefficients are relatively small in proportion to other refractories such as those of the soda-lime and lead glass types. Generally, they have thermal expansion coefficients smaller than 5×10^{-6} cm./cm./° C. Also, the silica content of these granular siliceous refractory materials is generally greater than 96% silica expressed as SiO_2 and may range as high as 99.8% SiO_2. Thus, by the term "vitreous silica" is meant a refractory comprising a silica glass having a thermal coefficient of expansion and SiO_2 content within the above range.

It has been determined that for best results in coating stools the refractory used in the silica slurry should be able to withstand severe heat shocks. Due to the extreme hot temperature of the molten metal as compared to that of the stool even when the latter is heated, an exceedingly abrupt change in temperature occurs when the metal contacts the stool. The coating must itself be able to withstand this heat shock to impart necessary protection to the stool base. It has been theorized that failure of some prior art materials was due, at least in part, to their inability to withstand this sudden increase in heat, thereby resulting in cracking of the coating and subsequent exposure of the metal surface to the cascading molten metal poured into the mold.

In view of the above it is generally thought that the most preferred refractories are those which have the highest purities concomitant with the lowest thermal coefficient of expansion. These properties are particularly possessed by vitreous silicas and more particularly those of the fused silica types. The latter materials have a silica content greater than 97% silica expressed as SiO_2 and a thermal coefficient of expansion not greater than about 6×10^{-7} cm./cm./° C.

A typical fused silica of the type described above which is extremely useful in the practice of the invention, having a thermal coefficient of expansion of about 5×10^{-7} cm./cm./° C., has the following typical analysis:

TABLE II

Ingredients:	Percent by weight
SiO_2	97.3
Al_2O_3	1.7
Sub-oxides of silica	1.0

The above type silica products are readily prepared by grinding very pure fused silica glasses. Likewise, the borosilicate glasses and Vycor silica glasses may be also ground to produce extremely useful refractories.

The particle size of the refractory may vary over a wide range. It is preferred, however, that the refractory particles be sufficiently small so that a uniform dispersion of refractory and binder may be made. The smaller the particle size the longer a slurry made up of binder and refractory, remains in a homogeneous state. It has been determined that particles ranging in size from 100 mesh to as low as a fraction of a micron may be employed. Preferred refractory materials have an average particle size ranging from a fraction of a micron to 500 microns in particle diameter, with particles corresponding to the lower range diameters being most preferred. Specific vitreous silica substances, marketed under the name, "Nalcote" fall within the above preferred particle size range and have been employed with much success in preventing erosion of base portions of molds and adherence of same to the formed ingots.

The amount of binder making up a portion of the coating slurry must be such that it is present in an amount sufficient to bind the refractory particles together to thereby form a tightly adherent, continuous and unbroken coating which is securely bonded to the surface of the stool. Without proper amount of binder in relation to refractory, the resultant coating, after application and drying of slurry, exhibits a "pan-cake" effect with numerous undesirable holes appearing in the coating, thereby exposing portions of the stool or mold base surface. To achieve this, it has been determined that the slurry is preferably composed of from 10 to 70% by weight of refractory, and from 30 to 90% by weight of binder. Most preferably the slurry contains from 20 to 60% by weight of refractory and from 40 to 80% by weight of binder.

The following examples show typical ways of carrying out the aims of the invention and advantages over prior art processes. It is understood, of course, that these examples are merely illustrative, and that the invention is not limited thereto.

Example I

In order to particularly test the efficiency of the binder component of the invention, a laboratory test was devised which simulated a commercial stool coating operation. Six binder test blends were prepared having the following make-up: 90% silica sol-10% silicic acid sol; 80% silica sol-20% silicic acid sol; 70% silica sol-30% silicic acid sol; 60% silica sol-40% silicic acid sol; 50% silica sol-50% silicic acid sol and 40% silica sol and 60% silicic acid sol. The colloidal silica sol contained 35% silica solids, and the silicic acid sol was made up of approximately 5% solids. The binders were applied to a cast iron plate heated to about 325° F., and the coatings then inspected. In all cases, the above described binder compositions gave a hard adherent coating. Application of the colloidal sol alone also gave an acceptable coating. However, it was surprising to note that the combination of silicic acid sol and colloidal silica sol with an overall solids content of 17% was equal to or even slightly superior to the colloidal silica sol alone, having a solids content of 30%, or almost twice the solids content of the combination binder. Since the ultimate strength of the coating is derived solely from the silica solids contained in the binder with the liquid portion of the binder being volatilized off, it was entirely unexpected that the above results would be forthcoming. It is believed however that the excellent results obtained via use of the binders of the invention are attributable to the situation of a relatively wide range of silica particle sizes donated by the combination of binder ingredients.

Example II

In this case, an actual mill trial was effected. A binder of the invention was formulated by mixing in equal weight proportions a 30% aqueous colloidal silica sol corresponding to silica sol No. 2 whose physical characteristics are tabulated in Table I, and a 5% aqueous silicic acid sol prepared according to the teachings of Bird, U.S. Patent 2,244,325. A silica slurry was made by addition of equal part of the above binder and fused silica refractory. This latter material has a wide range particle size distribution in which 100% will pass a 100 mesh sieve, 75% will pass 325 mesh, 30% is smaller than 10 microns and the smallest particles are a fraction of a micron in size. The refractory and binder were thoroughly mixed and then coated onto a number of cast iron stools. The coatings had excellent adherence, and surface hardness and as well, were easy to apply. In comparison runs, a 30% silica sol in combination with fused silica, also at a 1:1 weight ratio, also yielded a coating having the above described excellent characteristics. However, in some instances employment of the binder composition of the invention yielded an even more adherent coating than a binder containing only the silica sol component. Again, such results were surprising and unexpected in view of the fact that the solids content of the combination binder of the invention was almost one-half that of a binder containing silica sol as the sole ingredient.

The coatings derived from the slurries of the invention and containing a binder of the type described herein substantially prevented erosion of the stools or base members of the metal molds during pouring of molten metal thereon. Moreover, adherence of the subsequently formed ingots to the base member after metal solidification was also substantially reduced. In addition, subsidiary good effects were also noted. For example, since erosion has been reduced to a minimal effect, life of mold bases is substantially increased. Likewise, since generally no adherence of the mold base portions to the ingots occurs, no resort need be taken to physically contacting the two adherent articles against a third larger object such as a floor, to separate the united objects and recover the ingot. As mentioned above, not only is this separation procedure time-consuming and costly, but it frequently results in cracking or complete disintegration of the stool, making it completely unsuitable for further use. Also, since little or no erosion occurs from the molten metal, the amount of metal required to be cropped from the ingot is substantially reduced. As an overall advantage, the mold inventory necessary for efficient operation may be substantially reduced through use of the slurries of the invention.

Other advantages are to be noted. For example, since semi-permanent coatings on stools may be maintained by formation of the coating film, more ductile stools may be utilized. Also, lighter stools may be employed, cutting down on track weight and track maintenance, since stools are normally carried by means of flat cars on rails to the point of pouring of metal. Again, since the coating appears to withstand a wide range of temperatures, it is possible that severe temperature surface applications may be per-

formed which were heretofore impossible due to failure of prior art coatings. Many other advantages of the mold forming process of the invention are apparent.

It is understood, of course, that the binders of the invention may be utilized with other known binders such as ethyl silicate, aluminum phosphate, sodium silicate, etc.

The invention is hereby claimed as follows:

1. A method of inhibiting erosion of the surface of the base member of a metal mold used to cast ingots, which erosion normally occurs during contact of said surface with flowing molten metal, while subsequently preventing adherence of said ingots to said base member upon ingot formation; which comprises the steps of applying to said surface a slurry comprising a refractory suspended in a binder, said slurry being applied in an amount sufficient to form a coating of sufficient thickness to inhibit said erosion and prevent said adherence and allowing said slurry to dry whereby a protective solid coating is formed upon said base member, said slurry comprising at least one refractory selected from the group consisting of vitreous silica, crystalline silica, aluminum silicate, alumina, graphite, zirconium silicate, magnesium silicate and clay suspended in a binder comprising a colloidal silica sol and a silicic acid sol, with said binder being present in an amount sufficient to bind the refractory particles together to thereby form a tightly adherent coating which is bonded to said surface.

2. The method of claim 1 wherein said base member is cast iron, and said ingots cast are composed of steel.

3. The method of claim 1 wherein said slurry comprises 10–70 parts by weight of vitreous silica and 30–90 parts by weight of said binder.

4. The method of claim 3 wherein said vitreous silica is fused silica which is characterized as having a silica content not less than 96% silica, expressed as SiO_2, and a thermal coefficient of expansion less than 5×10^{-6} cm./cm./° C.; and said binder is composed of a colloidal silica sol containing 10–60% by weight of substantially discrete, dense, non-agglomerated particles of silica colloidally dispersed in an aqueous liquid and a silicic acid sol containing 2–10% by weight of silica particles having an average molecular weight of less than 90,000 dispersed in an aqueous liquid.

5. In a method of casting metal ingots from a metal mold whereby adherence of the base member of said mold to said formed ingots and erosion of said base member during formation of said ingots are substantially prevented; which comprises the steps of applying to the surface of said base member, a slurry comprising at least one refractory selected from the group consisting of vitreous silica, crystalline silica, aluminum silicate, alumina, graphite, zirconium silicate, magnesium silicate and clay suspended in a binder comprising a colloidal silica sol and a silicic acid sol, said slurry being applied in an amount adequate to form a solid coating of sufficient thickness to inhibit said erosion and prevent said adherence, allowing said slurry to dry whereby the liquid phase of said slurry is driven from the surface of said base member leaving a thin film of refractory, pouring molten metal into said mold, allowing said metal to solidify into an ingot, and removing said ingot from said coated base member in said mold, said binder being present in an amount sufficient to bind the refractory particles together to thereby form a tightly adherent coating which is bonded to said surface.

6. The method of claim 5 wherein said coated base member is composed of cast iron and said ingots are steel.

7. The method of claim 5 wherein said slurry comprises 10–70 parts by weight of vitreous silica and 30–90 parts by weight of a binder containing a colloidal silica sol comprising 3.0–60% by weight of silica colloidally dispersed in a hydrophilic continuous phase and a silicic acid sol containing 2–10% by weight of silica particles havinng an average molecular weight less than 90,000 dispersed in an aqueous liquid.

8. The method of claim 7 wherein said vitreous silica is fused silica which has a silica content not less than 96% silica, expressed as SiO_2, and a thermal coefficient of expansion less than 5×10^{-6} cm./cm./° C.

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