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SHELL MOLD COMPOSITIONS

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This invention relates to shell mold compositions, and has for its object the provision of improved shell mold compositions. More particularly, the invention aims to provide a novel and improved shell mold made by a process of double investment.

Shell molds have heretofore been commonly made of a mixture of a dry clean silica sand mixed with 3% to 8% by weight of resin, usually a thermosetting resin of the phenolformaldehyde type. The sand-resin mixture is discharged from a dump box onto a hot metal pattern. Upon contacting the hot pattern the resin fuses and the mix invests the pattern with a soft thin crust. The thickness of the crust may be controlled by the investment time or pattern temperature, or both. The pattern and invested crust are placed in an oven to complete the resin cure which serves to harden the crust into a shell. The cured shell is then stripped from the pattern.

The shell mold compositions of the invention are especially advantageous for the casting of metals of relatively high melting temperature, such as plain or low carbon steel, low and high alloy steels, gray iron, ductile iron, copper-base alloys and the like. While low carbon, low alloy and certain high alloy steels suffer from surface defects when cast in the heretofore customary sand-resin shell molds, runout difficulties are commonly experienced with such metals as gray iron, ductile iron and copper-base alloys. The invention provides shell molds of improved thermal resistance to minimize runout difficulties, and shell molds of chilling properties to cure surface defects on steel castings.

Basically, the cause of surface defects in steel castings appears to be an unfavorable time relationship between skin formation of castings and gas pressure build-up within the shell mold. Displacing this time relationship by retarding skin formation of the casting or by advancing gas evolution by the mold has been found to result in surface improvement. Similarly, it has been found that advancing skin formation of the casting with respect to the evolution of gas by the mold results in surface improvement. Substitution for the usual silica sand of chilling sands, such as zircon, chrome ore, olivine, forsterite and the like, has heretofore been demonstrated to have a strong chilling effect on the surface of steel castings (due to their high heat extracting ability), and consequently to diminish surface defects.

The present invention is based on our discovery that skin formation on shell mold steel castings can be advantageously advanced by the endothermic dissociation of granular limestone (or the equivalent thereof) when substituted in substantial amount for part of the silica sand in the heretofore customary silica-resin composition of shell molds. Thus, in its broad aspect, the invention involves a shell mold composition comprising essentially a mixture of refractory materials, resin and a substantial amount of a granular carbonate, like calcium carbonate (CaCO_3), which may exert a strong chilling effect by its highly endothermic decomposition taking place at relatively low temperature. Granular limestone is a suitable source of calcium carbonate, and dolomite (calcium-magnesium carbonate) and magnesite (magnesium carbonate— MgCO_3) may similarly be included in the mold composition, alone or mixed with limestone, to impart a chilling effect to the shell mold. The carbonate is in granular form, as contrasted with powder, and for the purposes of

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the invention the demarcation between granular and powder is drawn at 270 mesh (U.S. standard sieve series). A substantial amount (i.e. at least 5% by weight) of granular carbonate (e.g. limestone) is included in the mold composition. The inclusion of such an amount of carbonate in the composition is only practical when the carbonate is in granular form. Satisfactory shell molds cannot be made when 5% or more carbonate in the form of powder is included in the mold composition.

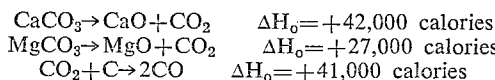
The substantial amount of limestone (or equivalent) included in the shell mold composition increases the heat absorbing ability of the mold. Consequently, the mold is characterized by considerably better thermal resistance than the heretofore customary sand-resin shell molds. This is of special advantage in minimizing runout difficulties, particularly with gray iron, ductile iron and copper-base alloys which are metals of long fluid life. When sufficiently large amounts of limestone (or equivalent) are included in the shell mold composition, such chilling effect on the casting is obtained as to completely eliminate surface defects heretofore commonly occurring on castings of low carbon (carbon content around 0.15–0.30%), low alloy (alloy content less than about 8%) and certain high alloy (alloy content exceeding about 8%) steels cast in sand-resin shell molds of the prior art. A further improvement in the surface of the casting may be obtained by adding up to about 5% iron oxide or manganese dioxide powder to the materials although such addition is not essential.

In its more complete aspect, the invention involves a composite shell mold made by a process of double investment and comprising a thin facing of resin-bonded refractory materials and a backing of the composition herein described. The mold facing, which comes into contact with the metal poured, is preferably formed with resin-coated materials instead of a dry mixture of resin powder and facing materials which tend to segregate. The facing materials may include zircon, sillimanite, mullite, silica sand or equivalent refractory, with a fineness number between 80 and 150 (A.F.S. classification system), corresponding approximately to $-50 +270$ mesh, advantageously with a small amount (up to 5%) of powdered iron oxide (preferably Fe_2O_3) or manganese dioxide admixed therewith. It is believed that these metal oxides react with the free hydrogen released by the pyrolysis of the binder and stabilize it in the form of water vapor (H_2O), completely inhibiting what appears to be hydrogen porosity in the surface of castings. Resin-coated silica sands are commercially available. Other refractories may be coated with resin in an alcohol-water solution (cold coating) or with molten resin or hot refractory (hot coating). Basically, the same types of resin are used for coating sand and other refractories as are used in the shell mold composition, but generally less resin (2–4%) is necessary.

With all type steels, cast in composite shell molds of the invention, advantages result from the fact that there is no metal penetration into the mold and practically no refractory adherence to the casting, and consequently the casting has an exceptionally smooth surface finish, requiring a minimum of cleaning effort. Metal penetration into the mold and adherence of molding refractory to the casting are almost completely inhibited due to the fact that heating of the fine refractory facing to high temperature is prevented by the endothermic reactions taking place in the mold backing composition. In addition both (1) the protection given the resin binder in the outer part of the mold by the internal absorption of heat and (2) the compensation of silica expansion by the decomposition of the carbonate contribute to the greatly improved thermal resistance of the mold, which is of special advantage to prevent runout difficulties. The pro-

tection given the resin binder and the compensation of silica expansion result from the inclusion in the mold composition of a substantial amount of granular limestone (or equivalent).

The heat extracting ability and chilling properties of the mold composition of the invention result from the endothermic dissociations of calcium carbonate and/or magnesium carbonate plus the further endothermic reaction of the carbon dioxide (CO₂) resulting from such dissociation with carbon released by the resin binder in the shell mold, as indicated by the following reactions with their resulting changes of enthalpy:



The amount of granular limestone (dolomite or magnesite) included in the mold composition depends upon the effect sought. From 5 to 8 percent is normally sufficient when only improved thermal resistance of the mold is desired. When seeking a chilling effect, from 8 up to 15 percent may be included in the composition coming in contact with the metal poured (plain mold). Additionally, the mold composition contains 3 to 7% of resin and the balance silica sand. In composite shell molds the amount of granular limestone (or equivalent) included in the backing composition may be as high as 95 percent, but 15 to 50 percent is normally sufficient.

The particle size of the granular limestone (or equivalent) may also vary with the application. Thus, when the mold composition comes in contact with the molten metal being cast (as in a plain shell mold), the limestone is preferably relatively fine, that is, mainly minus 50 and plus 270 mesh. When the mold composition is part of a composite shell mold, that is, the mold has a thin facing of resin-bonded silica sand (or other refractory) and hence the backing composition does not come in contact with the molten metal, the limestone is preferably coarser, mainly minus 10 mesh and plus 50 mesh. However, finer material can be used in the backing composition provided a greater amount of binder is included.

The thickness of the resin-bonded refractory facing is a factor controlling the efficiency of the chilling effect of the composite shell mold composition. This facing should be as thin as practicable. As short an investment as can be made on the hot pattern usually yields a facing layer of about $\frac{1}{16}$ inch in thickness. Although possible, it is difficult in commercial practice to invest a layer thinner than $\frac{1}{32}$ inch thick. On the other hand, if the facing is thicker than about $\frac{3}{32}$ inch the chilling effect of the carbonate is lost, and the casting has bad surface defects. In practice, the total thickness of the composite shell mold usually runs from about $\frac{9}{32}$ to $1\frac{1}{32}$ inch but in the case of large castings, a thickness of up to 2 inches is utilized, hence the thickness of the backing composition will then run from about $\frac{3}{32}$ to nearly 2 inches (and more usually from about $\frac{9}{32}$ to $1\frac{1}{32}$ inch).

Steels of different compositions have more or less a tendency to chill or to rapidly form a permanent skin when poured in sand molds. The remelt of the initial skin formed upon contact of the molten metal with the mold will depend upon the composition of the metal, the degree of superheat and the section size of the casting. Depending on conditions, therefore, chill type shell molds of the invention containing a granular carbonate will prevent the initial skin from remelting or will advance the time at which a second skin will form. Accordingly, the intensity of the chill effect required, and hence the amount of granular carbonate to be included in the mold composition, will depend upon the composition of the steel, the superheat of the metal, the section size of the casting and whether the mold is a plain or composite shell mold.

The following mixtures illustrate mold compositions of the invention for securing different thermal effects and

are intended merely as explanatory and in no sense as limiting the scope of the invention.

Percent

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| (1) For securing a chilling effect; | |
| (a) Where the mold composition comes in contact with the metal poured (plain mold): | |
| Silica sand (AFS fineness No. between 80 and 150)----- | 79-89 |
| Granular (fine) limestone (dolomite or magnesite) ----- | 8-15 |
| Powdered resin ----- | 3-6 |
| (b) Where the mold composition does not come in contact with the metal poured (composite mold): | |
| Silica sand (AFS fineness No. between 40 and 80)----- | 44-82 |
| Granular (coarse) limestone (etc.)----- | 15-50 |
| Powdered resin ----- | 3-6 |
| (2) For improved thermal resistance; | |
| May be used with either plain or composite shell molds: | |
| Silica sand: as above depending on whether mold is plain or composite-- | 86-92 |
| Granular limestone (etc.); fine or coarse depending on whether mold is plain or composite ----- | 5-8 |
| Powdered resin ----- | 3-6 |

The following examples illustrate various practices of the invention:

(1) Castings of low carbon steel were made in plain shell molds with 5, 10 and 12% granulated limestone (mainly minus 40 mesh and plus 270 mesh) included in the silica sand-resin composition. With 5% limestone, cast sections of 1 inch thickness were free of the heretofore usual surface defects while considerable improvement resulted in 2 inch thick sections. Two inch thick sections were completely free of surface defects when the mold composition contained 10 and 12% limestone.

(2) Castings (2 inch thick sections) of low carbon steel were produced free of the formerly usual surface defects in plain shell molds with 10 and 15% granulated dolomite (42% MgCO₃), of mainly minus 40 mesh and plus 270 mesh, included in the mold composition.

(3) Castings of low alloy steel (1.5-2.0% Ni, 0.5-0.8% Cr and 0.4% Mo) and castings of high alloy steel (11.5-14.0% Cr and 0.5-1.0% Ni) produced in plain shell molds with 10% granulated limestone (mainly minus 40 mesh and plus 270 mesh) were free of the formerly usual surface defects.

(4) Castings of low carbon steel produced in composite shell molds having a thin resin-bonded refractory facing and a backing composition containing 20 and 25% of coarse granulated dolomite (mainly minus 10 mesh and plus 50 mesh) were free of the formerly usual surface defects and had exceptionally good surface finish.

(5) Castings of low carbon steel produced in composite shell molds having a thin resin-bonded refractory facing containing 1-1½% Fe₂O₃ and a backing composition containing 20-25% of coarse granulated dolomite (mainly minus 10 mesh and plus 50 mesh) were free of the formerly usual surface defects and had a surface finish even superior to those of the foregoing example.

(6) Substantially the same result as in Example 5 was accomplished when 1% MnO₂ was used instead of the Fe₂O₃.

(7) A casting of low carbon steel free of surface defects was produced in a composite mold having a thin facing of resin-coated silica and a backing composition containing 95% granulated dolomite (mainly minus 40 mesh and plus 270 mesh).

Castings made from all of the molds described in the foregoing examples had surfaces which were outstandingly superior to those of castings made from conventional

molds. Even more impressive were castings obtained from molds containing the specified metal oxides in the facing material.

All of the molds used in the foregoing examples showed considerably improved thermal resistance. Additional castings of gray iron and bronze with mold compositions of the invention definitely established the advantageous mold feature of better thermal resistance.

Throughout the specification and appended claims mesh is expressed in terms of the U.S. standard sieve series. Coarse granular limestone (or equivalent) consists mainly of minus 10 mesh and plus 50 mesh material, and fine granular limestone consists mainly of minus 50 mesh and plus 270 mesh material. "Mainly," in connection with mesh sizing, means at least 90%, i.e. "mainly of minus 10 mesh and plus 50 mesh" means that at least 90% of the material passes the 10 mesh sieve and at least 90% remains on the 50 mesh sieve. Percentage figures of the constituents of the mold composition are by weight based on the dry weight of the mixture, and "essentially" means the necessary and indispensable constituents of the composition.

It is to be understood that the term "mold" as employed in the claims hereof is to be construed to include structures usually termed cores in factory parlance.

This application is a continuation-in-part of our co-pending application Ser. No. 748,812, now abandoned, filed July 16, 1958.

Having thus described our invention, we claim:

1. A dry, investment type shell mold consisting essentially of a hardened layer composed essentially of a mixture of particulate refractory material, thermosetting resin, and a granular carbonate selected from the group consisting of limestone, dolomite, magnesite, and mixtures thereof, the particle size of said granular carbonate being mainly in the range between about minus 10 mesh and about plus 270 mesh, the amount of said granular carbonate being from about 5% to 15% by weight, the amount of said resin being about 3 to about 8% by weight and the balance essentially being said particulate refractory material.

2. A shell mold according to claim 1 in which the refractory material is selected from the group consisting of silica sand, zircon, sillimanite, mullite and mixtures thereof.

3. A shell mold according to claim 1 in which the granular carbonate has a particle size mainly within the range of minus 50 mesh and plus 270 mesh and constitutes from 5 to 15% of the weight of the mixture.

4. A shell mold according to claim 1 further characterized by the inclusion therein of a minor amount of up to about 5% by weight of the mixture of a powdered metal oxide selected from the group consisting of iron oxide, manganese dioxide and mixtures thereof.

5. A composite shell mold comprising a thin facing of resin-bonded refractory material of between about $\frac{1}{32}$ " and about $\frac{3}{32}$ " in thickness and a backing composition consisting essentially of a mixture of particulate refractory material, cured thermosetting resin and

at least about 15% by weight based on the total dry weight of said backing composition, of a granular carbonate selected from the group consisting of limestone, dolomite, magnesite and mixtures thereof, the particle size of said granular carbonate being mainly in the range between about minus 10 mesh and about plus 270 mesh, the amount of said thermosetting resin being about 3 to 8% by weight based on the dry weight of said backing composition, and the balance of the dry weight of said backing composition essentially being said particulate refractory material.

6. A shell mold according to claim 5 in which the granular carbonate has a particle size mainly within the range of minus 10 mesh and plus 50 mesh and constitutes from 15 to 95% of the weight of the backing composition.

7. A shell mold according to claim 5 further characterized by the inclusion in the facing or the backing composition of a minor amount of up to about 5% by weight thereof of a powdered metal oxide selected from the group consisting of iron oxide, manganese dioxide and mixtures thereof.

8. A composite shell mold as defined in claim 5 in which the refractory material is selected from the group consisting of silica sand, zircon, sillimanite, mullite and mixtures thereof.

9. A composite shell mold according to claim 5 in which the thickness of the backing composition is within the range of $\frac{3}{32}$ and 2 inches.

10. A shell mold according to claim 5 further characterized by the inclusion in the facing and in the backing composition of a minor amount of up to about 5% by weight thereof of a powdered metal oxide selected from the group consisting of iron oxide, manganese dioxide, and mixtures thereof.

11. A shell mold according to claim 1 in which the said thermosetting resin is a phenolformaldehyde resin.

12. A shell mold according to claim 5 in which the amount of said granular carbonate is less than 50% by weight of total dry weight of said backing composition.

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