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CROSS REFERENCE

EXAMINER
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FOUNDRY SAND COMPOSITIONS AND METHOD OF CASTING

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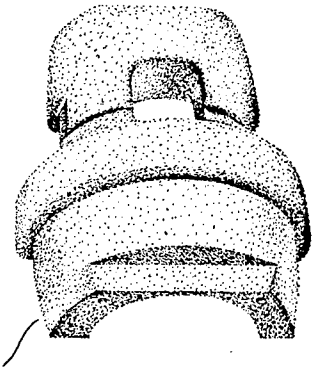

Foundry core bonded with alkali metal silicate binder containing a minor proportion of an organo-silicon additive.

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FOUNDRY SAND COMPOSITIONS AND METHOD OF CASTING

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This invention relates to the use of certain organosilicon additives in sodium (and other alkali metal) silicate-containing sand compositions to improve the physical properties of foundry cores and molds (especially the former) fabricated therewith for use in metal casting operations. It also relates to an improved method for casting metals, particularly ferrous metals, in molds fabricated from the improved sodium silicate bonded sand compositions of the present invention.

Sodium silicate is a well known binder material for foundry sands. It has been extensively employed for this purpose, particularly when foundry cores (as well as certain molds) are being fabricated for specialty applications. Equivalent results can generally be obtained with other so-called artificial alkali metal silicates, including potassium silicate and lithium silicate.

There has in recent years been developed an improved method for the utilization of aqueous solutions of sodium silicate as a binder in sand compositions suitable for fabrication of foundry molds and cores. This method, which is well known, is generally referred to as the Carbon Dioxide (CO_2) Process. The CO_2 process permits cores and molds to be made with a mixture of sand and an aqueous solution of sodium (or other alkali metal) silicate and hardened in very short order by passing carbon dioxide gas through the wet composition after it has been fabricated into a desired shape. The gas combines chemically with the silicate binder of the sand composition to form a silicic acid gel which cements the sand grains together and accomplishes the desired bonding in periods of time that may be as short as several seconds. Of course, the actual optimum gassing time may vary with the size and weight of the article being fabricated, as well as with the particular quantity of the silicate binder that is involved. Sodium (and other alkali metal) silicate bonded cores and molds that have been made by the CO_2 process can be used for metal casting very soon after the gassing of the fabricated structures. The CO_2 process has been described at page 33 of "Modern Castings" for August 1956 and at page 111 of "Steel" for August 6, 1956.

The major disadvantage encountered in the employment of silicate bonded sand compositions in foundry molds and cores, including those that have been prepared by the CO_2 process, is that of poor collapsibility after the metal has been poured into and solidified in the mold. In contrast to organic binders, sodium (or other alkali metal) silicate does not burn out at low temperatures. Instead, it sinters with the sand at high temperatures to form glasses. Such sintering begins to occur at a temperature of about 1475° F. and increases rapidly above about 1560° F. As a consequence, collapsibility and shakeout features are generally very poor and frequently inadequate in sand molds and cores bonded with sodium silicate and the like and the castings may be disadvantageously difficult to remove.

While better collapsibility may be obtained in cores and molds of the indicated compositions by reducing the quantity of silicate that is employed as a binder, such practice is generally undesirable for the reason than when

compositions containing less than about 2–3 percent by weight of silicate binder (taken as the weight of the aqueous solution or dispersion of silicate employed) are involved, the resulting molds and cores become exceedingly friable and, frequently, may not be acceptable for general foundry usage. Collapsibility in sodium (and other alkali metal) silicate bonded sand compositions may also be benefitted to a minor extend by incorporating as an additive in the compositions minor proportions (usually in the neighborhood of 2 to 6 percent by weight, based on the weight of the silicate bonded sand compositions in which the additive is incorporated) of certain filler or burn out materials, including such substances as asphalt emulsions, cellulose fibers, cereal binders, gilsonite, graphite, sea coal, pitch, wood flour, dextrine, iron oxide and the like. Such conventionally employed materials, however, are usually a nuisance to work with and difficult to handle in the formulation of the sand compositions. In addition, they oftentimes possibilitate only limited success since they frequently increase the friability of the molds and cores fabricated from compositions in which they are contained, despite the fact that they may exert a beneficial influence on collapsibility. Use of a coarser sand also tends to help collapsibility. Such practice may not always provide a desirable expedient for the reason that it may result in a poor surface finish being obtained in the resulting castings.

It is an object of the present invention to provide improved silicate bonded sand compositions, particularly sodium and other alkali metal bonded sand compositions, including, in particular, those for use in the CO_2 process, that are capable of being fabricated into excellent quality foundry cores and molds having high strength and excellent collapsibility or shake-out characteristics and features.

Another object of the invention is to provide an improved process for casting metals in molds and cores made of the silicate bonded sand compositions modified in accordance with the present invention.

These and corollary objects and associated benefits and advantages may be achieved by practice of the present invention which comprises uniformly incorporating in a foundry sand composition for the preparation of molds and cores which contains an aqueous dispersion or solution of sodium or other alkali metal silicate as a binder, a minor proportion of an additive that is an organosilicone compound (or an organosubstituted polysiloxane) which is compatible with the aqueous silicate solution and which has at least about 1 percent by weight of silicon-bonded groups therein and an average of from about 0.9 to 1.7 monovalent aliphatic hydrocarbon radicals (advantageously 1 to about 4 carbon atom alkyl groups) per silicon atom in the polymer molecule and wherein there is contained at least about 3 percent by weight of organic substituents consisting of alkoxy radicals (advantageously 1–6 carbon atom alkoxy groups). The compatibility of the organosilicone additive with the aqueous silicate solution can be easily determined by routine testing to observe the dispersibility of the additive, without gel formation, in the silicate solution. Advantageously, the quantity of the organosilicone additive that is incorporated in the sodium or other alkali metal silicate-containing sand composition in the practice of the present invention is an amount between about 1 and 15 percent by weight, based on the weight of the silicate solution. Preferably, the amount of the additive that is employed is an amount that is between about 0.1 and 0.6 percent by weight of the total composition, including the sand therein.

The organosilicone resin additives that are used in the practice of the present invention may be incorporated in the sand compositions in any desired manner, in-

cluding directly mixing or mulling the siloxane additive in a silicate-containing sand mixture. It is most convenient, however, to incorporate the organosilicone additives that are employed by dispersing or dissolving them in the aqueous dispersion or solution of sodium or other alkali metal silicate that is used as a binder for the sand prior to the mixing of the silicate solution with the sand in order to form the foundry core and mold compositions. Care should be taken during the preparation of the sand compositions to avoid drying out of the silicate solution in the process. To this end, it is better for the sand to be mixed cold and for abbreviated mulling or mixing times to be observed. Dispersions or solutions of the organosilicone resins in the aqueous silicate compositions are easy to handle and have good shelf life. Ordinarily, they may be stored without difficulty for extended periods and employed thereafter with as much benefit as freshly made compositions. In some cases, the prepared mixtures may separate on standing and may require some agitation just prior to use.

Advantageously, the silicate bonded sand compositions of the present invention may be employed for making molds and cores according to the above indicated CO_2 process by passing the gas through the composition after it has been fabricated into a desired shape for foundry use. If desired, however, the sodium or other alkali metal silicate bonded compositions can be permitted to harden in the normal maner without reliance on carbon dioxided by letting them become set up in air or subjecting them to heat at an elevated temperature, as by baking them in an oven according to the usual well known techniques and procedures.

The silicate bonded sand compositions which contain the organosilicone additives in accordance with the invention may be fabricated into excellent foundry cores and molds having improved physical qualities including high bond strength and very good collapsibility and shake-out features. As has been indicated, they may be used with particular advantage for preparing molds and cores according to the CO_2 process. The sand mixtures have excellent flowability. This permits the sand mixture to flow easily into desired cavities wherein it may be rammed or blown readily into good and solid structures. The presence of the organosilicone additive in the sand mixture also tends to minimize requirements for cleaning of mixing equipment, storage hoppers and mold patterns and to avoid fouling thereof and sticking thereto. The resulting molds and cores may be employed for the casting of any desired metal, including iron and other ferrous alloys, to provide excellent results in the casting operations. The molds and cores fabricated from the compositions of the present invention permit good quality castings to be obtained that are precisely formed and have desirable surface finishes. In addition, the mold and core structures prepared from the compositions of the invention have excellent shelf life prior to actual use for casting due to their inherent moisture resistance, again by virtue of the presence of the organosilicon additive.

The silicate bonded sand compositions that are improved by practice of the present invention may be pursuant to the heretofore known compositions for such purposes. Thus, the usual quantities of aqueous sodium or other alkali metal silicate solution may be employed for providing the binder. For example, amounts of an aqueous alkali metal silicate dispersion, such as an aqueous sodium silicate solution, between about 2 or 3 and 10 percent by weight, preferably on the order of from 4 to 6 percent by weight, based on the weight of the resulting wet sand composition, may be advantageously utilized in the composition as the binding constituent therefor. As has been indicated, the silicate dispersions or solutions which may be employed are the silicates of the alkali metals of atomic number from 3 to 19, i.e., lithium, sodium and potassium. For most purposes, it

is generally advantageous to utilize sodium silicate solutions or dispersions in water in order to bond the sand compositions. The solids content of the silicate dispersion or solution that is employed may be of any concentration that is adapted to provide for the efficient and effective bonding of the sand compositions. It is ordinarily beneficial for the concentration of the aqueous silicate dispersion or solution to be at least about 10 percent by weight (generally, approximately 10° Bé). Usually it is desirable to employ more concentrated solutions or dispersions of the silicate, such as those whose concentration is at least in the neighborhood of 30 percent by weight (usually approximately 30° Bé). Preferably, between about 45 and 50° Bé., particularly when solutions of sodium silicate are involved in which the SiO_2 to Na_2O ratio is greater than 2. It is usually unnecessary to employ the silicate solutions or dispersions in concentrations much greater than about 50–55 percent by weight, even if they are available in such strengths. As is evident, it is usually most advantageous to employ sodium silicate solutions of the indicated concentrations. These are usually the commercial meta silicates, in which the ratio of SiO_2 to Na_2O is greater than 2. If desired, however, the ortho-sodium silicates, in which the ratio of SiO_2 to Na_2O is as low as 0.5:1, may be utilized even though it is generally necessary to employ them in aqueous dispersion due to their insolubility or only partial solubility in water.

Any ordinary sand or other refractory material may be employed in the practice of the invention. Advantageously, the sand or its equivalent that is employed has a fineness in accordance with the values proposed by the American Foundrymans Society (AFS) that is in the numerical range between about 25 and 180. Such sands, for example, as the types which are known as Berkeley Float Sand, Juniata Sand, Lake Sand, Vassar Sand, Wedron Sand and the like are quite suitable. It is not necessary in the practice of the present invention that clean sand be utilized. In many cases it may be more advantageous to utilize a sand having a AFS fineness number from about 50 to 125. Very frequently sands that have a AFS fineness number in the neghborhood of 50–75 may be preferable for foundry cores and mold making operations.

By way of further illustration, and to demonstrate several of the specific types of organosilicon additives that are useful in the practice of the present invention, a series of sodium silicate bonded sand mixtures were prepared in accordance with the present invention by individually incoporating minor proportions of different compatible and operable organosilicon additives therein. The additives were incorporated in the compositions by dispersing them in the aqueous sodium silicate solution that was employed as a binder prior to maxing the silicate solution with the sand. E. I. duPont de Nemours & Co., Inc. No. 22 sodium silicate solution was used to prepare the silicate binding solution employed. It contained 1 part of Na_2O to 2.3–2.6 parts of SiO_2. The compositions were then formed into standard size figure 8 briquette sand cores by exerting about 80 p.s.i. pressure on the wet sand mixture which had been mulled in a conventional manner in order to intimately and uniformly blend the additive-containing sodium silicate solution with the sand. The briquettes were cured according to the CO_2 process by passing carbon dioxide gas through them under about 15 pounds pressure for periods of time ranging from 10 to 20 seconds but mostly about 15. Unwashed Vassar Bank Sand (AFS 95–100) was employed in the preparation of all of the compositions. The combined total content of clay and alkali material in the sand was found, upon analysis, to vary from about 1.1 to 1.4 percent by weight. The results are set forth in the following tabulation, wherein additive "S–1" indicates a 45 percent by weight xylene solution of a siloxane copolymer composed of 75 mole percent of monomethylsiloxane, 24 mole per-

cent of dimethylsiloxane and 1 mole percent of trimethylsiloxane, which copolymer contained about 6 percent by weight of silicon-bonded isopropoxy groups; additive "S–2" indicates a monopropylsiloxane containing from 15 to 25 percent by weight of silicon-bonded ethoxyl groups; and additive "S–3" indicates an 85 weight percent xylene solution of a mixture of 85 percent by weight of a partial hydrolyzate of a methoxylated mixture of by-produced chlorosilicon compounds obtained from the reaction of methyl chloride and silicon and 15 percent by weight of a methylsiloxane resin (being a material of the type described in U.S. Patent No. 2,706,723, particularly as Fluid "D" of Example 3 thereof). In the table, the term "bonded strength" refers to the maximum tensile stress necessary to rupture a test briquette of standard dimensions. It is measured in pounds per square inch (p.s.i.) and is also representative of the maximum tensile stress which a sand mixture is capable of developing. "Surface hardness" is measured on the smooth side of the briquette specimen with a Dietert No. 673 Dry Hardness Tester. In this test the instrument is pressed down on the specimen. The maximum hardness reading on a hard surface would be 100 units. "Collapsibility" or "shake-out" is a term used with regard to the disintegratability of the sand mold after solidification of the molten metal therein. The collapsibility test consists of determining the tensile strength of a specimen which has been heated without access to air for one hour at 650° F. A "hot strength" test is similarly performed. From practice, one can determine the proper hot strength that will present hot cracking of castings due to weak cores at 650° F., 1000° F., and so on up to 2500° F.

bond the same unwashed Vassar Bank Sand as described above and using a 30 second gassing time with the CO_2. Compositions containing about 6 percent of the aqueous dispersion of the sodium otho silicate binder and about 0.375 percent of the additive secure excellent bond strength, are not objectionably friable and have suitable collapsibility.

In contrast with the foregoing, dissatisfactory or inoperative results were experienced when other varieties of organosilicon compounds were attempted to be employed as additives in a similar manner in the same types of compositions. Thus, a monoamylsiloxane resin actually decreased the bonded strength of the cured compositions from the control. An organosilicone compound composed of a water solution of a mixture of 75 percent by weight of $CH_3Si(OCH_2CH_2OCH_3)_3$ and 25 percent by weight of propyltriacetoxysilane was completely incompatible with the sodium silicate solution. Likewise found to be incompatible and responsible for dissatisfactory results was a compound composed of a liquid copolymer of dimethylsiloxane and trimethylsiloxane as well as one which was a resinous copolymer of 85 mole percent of monomethylsiloxane and 15 mole percent of dimethyl siloxane.

Results similar to the foregoing may be obtained when organosilicon additives of the indicated variety are utilized in the above indicated manner for other alkali metal silicates, including potassium and lithium silicates, wherein the ratio of SiO_2 to alkali oxide is at least about 0.5 part by weight to 1, respectively, and, more advantageously, at least about 2 to 1, particularly when potassium silicates are utilized.

TABLE

Effect of additives on foundry core compositions [f]

Sample	Percent by wt. 50° Bé. Sodium Silicate	Additive	Percent by wt. Additive in Sodium Silicate Solution	Percent by wt. Additive in Total Mix	Percent by wt. Sand in Total Mix	Average Tensile Strength: Bond Strength 24 Hours after Gassing	Average Tensile Strength: Collapsibility Test [a]	Average Tensile Strength: Percent Increase in p.s.i. over Control Sample [b]	Percent Collapsibility [c]	Surface Hardness Test Average	Compatibility of Additive with Sodium Silicate Solution	Shelf Life of Additive-containing Sodium Silicate Solution
"A" [d]	6.00	None	0.0	0.0	94.0	202	150	----------	25.7	94	----------	
"B"	5.91	"S–1"	1.52	0.09	94.0	225	110	11.4	51.2	90	Excellent.	Indefinite.
"C"	5.82	"S–1"	3.09	0.18	94.0	297	55	47	81.5	94	---do-------	Do.
"D"	5.61	"S–1"	6.95	0.39	94.0	212	180	10.7	15.1	97	---do-------	Do.
"E"	5.40	"S–1"	11.10	0.60	94.0	262	57	29.7	78.2	93	---do-------	Do.
"F"	5.91	"S–2"	1.52	0.09	94.0	225	120	11.4	55.5	89	---do-------	Do.
"G"	5.82	"S–2"	3.09	0.18	94.0	286	60	41.5	79.2	94	---do-------	Do.
"H"	5.61	"S–2"	6.95	0.39	94.0	212	190	10.5	5.66	92	---do-------	Do.
"J"	5.40	"S–2"	11.10	0.60	94.0	206	50	ca 2	75.6	95	---do-------	Do.
"K"	6.00	"S–3"	3.50	0.21	93.79	242	(e)	19.2	(e)	94	---do-------	Do.

[a] Collapsibility tests—p.s.i. after specimens were exposed to 650° F. for 1 hour without air.
[b] Percent increase in p.s.i.—average p.s.i. increase divided by p.s.i. of control×100.
[c] Percent collapsibility—average p.s.i. decrease divided by original p.s.i.×100.
[d] Designates blank or control sample.
[e] Actual value not determined although appreciably reduced from "bonded strength."
[f] All data represent average values of three identical test specimens.

As is apparent from the foregoing, the samples prepared from the compositions of the present invention showed an improvement in bond or tensile strength of up to about 70 percent and an increased collapsibility of 5, and usually much greater, to more than 80 percent over the control sample formulated identically excepting for the additive. None of them exhibited excessive or objectionable friability characteristics.

Similar excellent results were obtained when compositions of the demonstrated types were essentially duplicated and fabricated into briquettes excepting to cure the briquettes by heating them in an oven after their formation for about 25 minutes at a temperature of 325° F.

By way of still further illustration, good results are also had when additional sodium silicate bonded sand mixtures are prepared following the foregoing general procedure using minor proportions of the same operable organosilicone additives, but employing an aqueous dispersion of sodium ortho silicate (one part Na_2O to 0.5 part Si_2O) having a specific gravity of about 1.60 in order to

Cores and molds prepared from the sand compositions of the present invention (similar to those illustrated in the foregoing) which are cured by either heating at elevated temperatures or by practice of the CO_2 process are well adapted and can advantageously be used successfully to cast grey iron according to conventional techniques and to provide excellent results in the finished castings. The castings obtained are precisely formed and have good surface finishes. After the casting, the collapsibility and shake-out characteristics of the forms (especially cores) are found to be excellent. A foundry sand core fabricated from a sand composition in accordance with the present invention is illustrated in the sole figure of the hereto annexed drawing.

What is claimed is:

1. Composition for the fabrication of foundry cores and molds which comprises (1) a preponderant proportion of sand; (2) a binding quantity up to about 10 percent by weight, based on the weight of the composition, of an aqueous solution of an alkali metal silicate having

a silicate concentration of at least about 10 percent by weight and a silica to alkali metal oxide ratio of at least 0.5 to 1; and (3) a small quantity of an organosilicone additive which is compatible with the aqueous silicate solution and which has an average of from about 0.9 to 1.7 monovalent aliphatic hydrocarbon radicals per silicon atom in the polymer molecule and wherein therein is contained at least about 3 percent by weight of organic substituents consisting of alkoxy radicals of from 1 to about 6 carbon atoms; said organosilicone additive being present in said composition in an amount between about 1 and 15 percent by weight, based on the weight of the aqueous silicate solution in the composition.

2. The composition of claim 1 containing between about 4 and 6 percent by weight of said aqueous solution of alkali metal silicate, based on the weight of the composition, and from about 0.1 to about 0.6 percent by weight of said organosilicone additive, based on the total weight of the composition.

3. A composition in accordance with the composition set forth in claim 2, wherein said aqueous solution of alkali metal silicate is an aqueous solution of sodium silicate having a concentration of from about 30 to 50° Bé. and a SiO_2 to Na_2O ratio of at least 2:1.

4. The composition of claim 1, wherein said organosilicone additive is composed of a copolymer of about 75 mole percent of monomethylsiloxane, about 24 mole percent of dimethylsiloxane and 1 mole percent of trimethylsiloxane with about 6 percent by weight of silicon-bonded isopropoxy groups being contained in the polymer molecule.

5. The composition of claim 1, wherein said organosilicone additive is composed of monopropylsiloxane containing from 15 to 25 percent by weight of silicon bonded ethoxy groups.

6. The composition of claim 1, wherein said organosilicone additive is composed of about 85 percent by weight of a methoxylated partial hydrolyzate of a methoxylated mixture of by-produced chlorosilicon compounds obtained from the reaction of methyl chloride and silicon and about 15 percent by weight of a methylsiloxane resin.

7. Method for improving sand compositions containing aqueous solutions of an alkali metal silicate as a binder and adapted to be fabricated into foundry cores and molds which method comprises uniformly incorporating in said composition between about 1 and 15 percent by weight, based on the weight of the aqueous silicate solution in said wet sand composition of an organosilicon additive which is compatible with the aqueous silicate solution and which has at least about 1 percent by weight of silicon-bonded groups therein and an average of from about 0.9 to 1.7 monovalent aliphatic hydrocarbon radicals per silicon atom in the polymer molecule and wherein there is contained at least about 3 percent by weight of organic substituents consisting of alkoxy radicals of from 1 to about 6 carbon atoms.

8. The method of claim 7, wherein said aqueous solution of alkali metal silicate is an aqueous solution of sodium silicate having a concentration between about 30 and 50° Bé. and a SiO_2 to Na_2O ratio of at least 2:1.

9. In the method of fabricating foundry molds and cores from sand compositions containing an aqueous solution of an alkali metal silicate as a binder, wherein said sand is mixed with up to about 10 percent by weight, based on the weight of the composition, of the aqueous silicate solution having a silicate concentration of at least about 10 percent by weight and a silica to alkali metal oxide ratio of at least 0.5:1 and said composition is fabricated and subsequently cured, the improvement which comprises uniformly incorporating in said sand composition prior to its fabrication and curing, a minor proportion, in an amount between about 1 and 15 percent by weight, based on the weight of the aqueous silicate solution in said wet sand composition of an organosilicone additive which is compatible with the aqueous siilcate solution and which has at least about 1 percent by weight of silicon-bonded groups therein and an average of from about 0.9 to 1.7 monovalent aliphatic hydrocarbon radicals per silicon atom in the polymer molecule and wherein there is contained at least about 3 percent by weight of organic subtituents consisting of alkoxy radicals of from 1 to about 6 carbon atoms.

10. The method of claim 9, wherein said aqueous solution of alkali metal silicate is an aqueous solution of sodium silicate having a concentration between about 30 and 50° Bé. and a SiO_2 to Na_2O ratio of at least 2:1.

11. The method of claim 9, wherein said organosilicon additive is composed of a copolymer of about 75 mole percent of monomethylsiloxane, about 24 mole percent of dimethylsiloxane and 1 mole percent of trimethylsiloxane with about 6 percent by weight of silicon-bonded isopropoxy groups being contained in the polymer molecule.

12. The method of claim 9, wherein said organosilicone additive is composed of monopropylsilioxane containing from 15 to 25 percent by weight of silicon bonded ethoxy groups.

13. The method of claim 9, wherein said organosilicone additive is composed of about 85 percent by weight of a methoxylated partial hydrolyzate of a methoxylated mixture of by-produced chlorosilicon compounds obtained from the reaction of methyl chloride and silicon and about 15 percent by weight of a methylsiloxane resin.

14. A shaped article for molding metals in casting processes, said article being fabricated from a composition in accordance with the composition set forth in claim 1.

15. A shaped article for molding metals in casting processes, said article being fabricated from a composition in accordance with the composition set forth in claim 3.

16. The method of casting metals which comprises mixing sand with a minor proportion of up to about 10 percent by weight, based on the weight of the resulting composition, of an aqueous solution of an alkali metal silicate having a silicate concentration of at least about 10 percent by weight and a silica to alkali metal ratio of at least 0.5:1, said composition containing a minor proportion of between about 0.001 and 0.1 percent by weight, based on the weight of the aqueous solution of alkali metal silicate in the wet sand composition, of an organosilicone additive which is compatible with the aqueous silicate solution and which has at least about 1 percent by weight of silicon-bonded groups therein and an average of from about 0.9 to 1.7 monovalent aliphatic hydrocarbon radicals per silicon atom in the polymer molecule and wherein there is contained at least about 3 percent by weight of organic substituents consisting of alkoxy radicals of from 1 to about 6 carbon atoms; forming a mold of the resulting sand composition; and casting the metal in the resulting mold.

17. The method of claim 16, wherein said aqueous solution of alkali metal silicate in an aqueous solution of sodium silicate having a concentration between about 30 and 50° Bé. and a SiO_2 to Na_2O ratio of at least 2:1.

18. The method of claim 16, wherein said metal that is cast is a ferrous metal.

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