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**PROCESS FOR MAKING CORES AND MOLDS,
ARTICLES MADE THEREBY AND BINDER
COMPOSITIONS THEREFOR**

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The present invention relates to sand cores and other sand mold parts for metal casting and methods of making the same, and more particularly concerns a binder composition for said purposes which is essentially gasless and can be either air-dried or baked, or both.

Cores and molds, both large and small, are used in foundry practice in great numbers. One of the major problems in preparing such cores and molds involves the requirement of binding them so that they maintain their integrity during pre-heating and when fitted together prior to casting, as well as during the metal-casting operation. Various types of binder materials and binder systems have been proposed, but in general, no completely satisfactory cores and molds have heretofore been available.

Since the development of the "carbon dioxide process," alkali-metal silicate-containing mold-forming compositions have found considerable use in the foundry industry. In this process which is based on the chemical reaction between sodium silicate and carbon dioxide gas, molds and cores prepared from sand-silicate mixtures are cured or hardened in the desired casting-defining shape simply by exposing them to carbon dioxide or to carbon dioxide-containing gas. When the sand or other refractory material is mixed with the formulated binder, the individual grains of sand become coated with a film of the alkali-metal silicate. Thereafter, when the sand is compacted, thin films of the binder exist between sand grains, and reaction of CO_2 with these films causes rapid formation of a rigid silica gel, which binds the sand grains together. Despite the many advantages of such molds, certain difficulties have been encountered with prior silicate-containing mold-forming compositions, especially in the casting of high temperature melting metals such as cast iron and steels melting at temperatures of 2500° F. or higher. At these temperatures, prior silicate-containing mold-forming compositions cured with carbon dioxide generally have been characterized by excessive and sudden evolution of steam from the water released in the mold by the gassing reaction. This problem has been aggravated by the necessity of having sufficient organic additive present to provide satisfactory collapsibility after solidification of the metal in the mold. In many instances, hazardous conditions have arisen due to the sudden release of steam and combustion products from the organic material, at the moment when the molten metal is poured into the mold. The present invention comprises an improvement over prior alkali-metal silicate-containing mold-forming compositions, especially with respect to the substantially "gasless" nature of the novel binder compositions at casting temperatures.

Accordingly, it is an object of the present invention to provide a new and improved alkali-metal silicate-containing mold-forming composition which is characterized by the substantial elimination of gas evolution when the mold is fired.

A further object of the invention is to provide new

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and improved compositions for forming alkali-metal silicate-containing molds adapted to be cured by air-drying or baking or both without the necessity of reacting the mix with carbon dioxide or other gaseous curing agents.

A still further object of the invention is to provide new and improved methods of metal casting.

Broadly, the present invention provides a composition for the production of sand cores and other sand mold parts for metal casting which comprises a major proportion of a core sand and a minor proportion of a high alkaline, alkali-metal silicate sufficient to bind the core sand. Where a high degree of collapsibility is required, it has now been discovered that Al_2O_3 must be included in the mix.

As used throughout the specification and claims, the term "mold" is intended in the generic sense to mean casting forms which includes both molds and cores. Moreover, "mold" is defined to include various patterns for use in the casting art, such as hot box cores as well as shell molds including shell mold-forming elements in addition to a completed shell mold structure prepared by assembling two or more complementary thin-walled shell mold elements. Hence, it will be appreciated that the term "mold" is used to include a casting-defining surface broadly.

In a preferred embodiment, the present invention contemplates as a mold-forming composition a mixture of a major proportion of finely-divided refractory material, a minor proportion of an alkali-metal silicate solution having an alkalinity in the range of from 18-30, preferably a high alkaline sodium silicate solution, and a minor proportion of aluminum oxide, or an aluminum oxide-containing inorganic compound, preferably not in excess of about 15% by weight based upon the weight of the refractory material.

The advantages of molds fabricated in accordance with the present invention are many. Not only are aging and post-curing treatments eliminated because of the excellent green strength obtained, thus permitting rapid fabrication of molds without requiring the use of expensive equipment, but also close tolerance castings are obtainable. Moreover, the process is relatively simple and can be carried out readily on a large scale without the necessity of maintaining large tanks of carbon dioxide or carbon dioxide generating equipment.

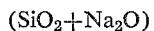
Conventional low alkalinity sodium silicate has been used for many years as a binder for sands for various industrial uses, either alone or with chemicals of an acid nature which react with the silicate. Use of conventional sodium silicate alone for foundry molds, however, has never been successful because at high temperatures the silicate simply dries to a hydrated form without any decomposition and a fluxing action occurs. This condition causes severe sintering of the sand which leads to poor collapsibility and also to core and mold distortion. By using carbon dioxide the sodium silicate is broken down by the gassing action to form colloidal silica gel which gives the required bond. When the metal is cast the elevated temperatures cause the silica gel to lose strength so that after the firing and solidification of a casting in the mold, the composition has such a low fired strength as to permit its ready removal from the casting surfaces. As has been stated above, however, a considerable quantity of free water remains in sand-mixes containing conventional silicate binders which have been cured with carbon dioxide. This water, which may be

several percent by weight of the composition, can easily lead to explosions when the mold is fired.

It has now been discovered that silicate binders can be used in the fabrication of molds and that the molds prepared can be hardened in air without gassing with carbon dioxide and without excessive amounts of free water remaining in the composition, by employing alkali-metal silicate solutions of high alkalinity, namely, in the range of from 18-30 "free alkalinity," i.e., aqueous silicate solutions containing from 18-30 percent by weight of an alkali hydroxide. That such solutions have not heretofore been employed is probably due to the fact that there was no solution known to the problem of providing adequate collapsibility of the mold after solidification of the metal therein whereby the mold-forming composition could be readily removed from the casting. In accordance with a preferred embodiment of the present invention, binder systems for sand cores and other sand mold parts are provided which have a wide range of bench life and excellent collapsibility properties, which comprise a solution of a sodium silicate having an alkalinity in the range of 20-26 and in the range of 3-100 percent of aluminum oxide, based upon the weight of sodium silicate solution utilized.

Broadly, silicates of the various alkali metals including potassium, sodium, cesium, rubidium and lithium can be employed, although sodium silicates and potassium silicates represent the more readily available silicates, while sodium silicates clearly constitute the preferred and most practicable silicates. For that reason special reference will be made herein to sodium silicates although it will be understood that the present invention is not limited thereto.

Water soluble sodium silicate glass of the composition $\text{Na}_2\text{O}-\text{SiO}_2$ is available with various proportions (ratio) of SiO_2 to Na_2O by weight. It is made by fusing high purity sodium carbonate and sand in a high temperature furnace with weight ratios of SiO_2 to Na_2O in the range of about 1.95-3.25, as desired. Higher ratios are not practicable owing to the difficulty of dissolving the silicate in water even with the application of heat and pressure. For a given ratio any number of solutions can be made by varying the concentration and ratio of solids



dissolved in water.

In accordance with the present invention the term "alkali metal silicate," preferably a sodium silicate, includes silicates having various silica to alkali metal oxide ratios, e.g., those having a silica to metal oxide ratio greater than 1:1 and desirably within the range of about 1.5-3.8 generally being suitable. The liquid silicates employed preferably have a solids $(\text{SiO}_2 + \text{Na}_2\text{O})$ concentration in the range of (percent) from 20 to 65 and are prepared using water or other suitable liquid to provide the desired silicate solution, slurry, plastic mixture or the like, depending on the application intended so that the weight percent of the free alkali hydroxide or alkali oxide therein is in the range of from 18-30, that is, having an alkalinity in the range of 18-30. The determination of alkalinity is made, for example, by neutralizing the solution with hydrochloric acid using the relationship

$$\frac{0.04 \times \text{number of ccs. of 1N HCl}}{\text{Sample weight}} \times 100 = \text{percent alkali}$$

that is, alkalinity. Such a solution can be prepared, for example, using a sodium silicate solution having SiO_2 to Na_2O ratio of 2.38, containing 47% silicate and having a specific gravity $\text{B}_\text{é}$ at 60° F. of 52.25 by adding flake caustic soda or potassium hydroxide until a total weight of the free alkali in solution is in the range of 18-30.

While the present discovery is not completely understood it is believed in the absence of CO_2 gassing the water in the composition is able to form a hydrate with the silicate. It is thereby tied up in a stable formation. In the highly alkaline solution the aluminum oxide which

is present is able to form an aluminum silicate by reacting with the ionized sodium silicate. The combination of the aluminum silicate with the sodium silicate forms a heterogeneous mixture rather than the homogeneous mixture which would be formed if only sodium silicate were present. Under these circumstances of extraordinary high alkalinity, instead of a glass-like bond being formed when the mold is fired the insoluble aluminum silicate serves to break up the binder and provides excellent collapsibility.

10 Broadly, the novel binders can be used with any finely divided refractory material such as sand, for example, Ottawa sand, finely-divided zirconia, ground silica, silica flour, ground firebrick, ground magnesia firebrick, fused magnesia, titanium oxide, beryllium oxide, mullite, as well as various mixtures thereof, as well as other materials useful as refractory substances, e.g., slags.

15 Aluminum oxide used in binder compositions of the instant invention can be pure aluminum oxide or any of the known oxide mixtures or mineral clays containing Al_2O_3 ,

20 for example, Zorb-All, a montmorillonite clay manufactured by Wyandotte Chemical Corporation, having the following composition: 15% aluminum oxide, 70% silicon dioxide, 5.4% iron oxide, 0.93% calcium oxide and 0.86% magnesium oxide with trace quantities of chromium, copper and manganese.

25 Another naturally occurring source of aluminum oxide which is suitable for the novel binder compositions is bauxite, a natural aggregate of aluminum-bearing minerals in which the aluminum occurs largely as hydrated oxides—composed of gibbsite, diasporite and other hydrous aluminum oxides.

30 Most bauxites contain from 30-75% aluminum oxide, 9-31% water, 3-25% iron oxide, 2-9% silicon dioxide, and 1-3% titanium dioxide.

35 Other Al_2O_3 -containing compounds which can be used are cement and kaolin. A suitable kaolin clay, for example, may contain about 37-40% Al_2O_3 and 2-3% mixed oxides of iron, titanium and manganese, the remainder essentially being composed of silica.

40 Where it is desired to fabricate semipermanent molds where shake-out and collapsibility is not required, excellent compositions are provided by mixing a major proportion of a core-sand with a minor proportion of an alkali-metal silicate solution having an alkalinity in the range of 18-30 and more preferably 20-26. Such compositions have high wet workability and long bench life

45 and are particularly suitable for molds of the permanent or semipermanent type.

More generally, it is desired to fabricate cores and molds having good collapsibility after firing. In accordance with the present invention a minor but collapsibility

50 imparting amount of aluminum oxide alone, or with other inorganic oxides, particularly those of di- and trivalent metals, advantageously can be used in binder compositions.

55 Preferably from 3-100% of aluminum oxide, based upon the weight of sodium silicate solution, is employed. The amount of aluminum oxide used will generally not be in excess of about 10% by weight of the sand used in the mold-forming mixture.

60 The preferable range is from 0.5 to 10%. Where oxide mixtures are used, the aluminum oxide-containing compound should contain at least 10% of Al_2O_3 .

With respect to the relative proportions of finely divided refractory, for example sand, and silicate solution, it is preferable, of course, to employ a major proportion of the sand and a minor proportion of the high alkaline

65 silicate solution as a binder. In terms of the finely divided refractory material used it is typically desirable to employ a silicate solution in an amount in the range of about 0.5-10% by weight, smaller amounts in the range of from about 1-6% by weight being preferred at present.

70 In practice the refractory material is blended with the silicate binder and then the aluminum oxide or compound containing at least 10% aluminum oxide is added. The blending may be done in any suitable manner, as by mulling or by other mixing operation. The prepared mixture is then placed in contact with a mold-defining

surface, such as a pattern. This can be, if desired, coated with a suitable parting or separating agent. When the sand-binder-aluminum oxide mixture is in contact with the mold-defining surface, it generally is desirable to compress the mixture slightly, as by compacting it against the surface.

The practice of the instant invention does not require the use of a carbonaceous material, such as has heretofore been suggested for inclusion in a mold-forming composition whereby it may be burned out during solidification of the metal, thereby to promote mold collapsibility. However, in many instances the use of an organic release agent or shake-out additive is compatible with the practice of the present invention. In this connection various polyhydroxy organic compounds such as powdered sugar, and other conventional additives may be employed, if desired. Inclusion of minor amounts of pitch or sea coal produces a controlled film of gas between the metal and the mold to assist in the parting of the mold from the metal and may be employed. The invention can be utilized in connection with the casting of all kinds of metals and alloys, such as steel, iron, copper, aluminum, lead, etc.

The invention is illustrated but not limited by the following examples. In each instance, the unfired or green strength was sufficiently high to permit handling of the mold during mold assembly and other foundry operations without injury thereto.

A simple and typical embodiment of the basic binder system is as follows:

	Wt. percent (based on sand)
Liquid binder	3
Dry activator	2

The liquid binder was prepared by mixing 7 parts by weight of NaOH (flake) with 93 parts of a 47% solution of sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.38 and a specific gravity Bé. at 60° F. of 52.25. To 93 parts by weight of this mixture was added 7 parts of water. The resulting high alkaline solution contained approximately 22 wt. percent free alkalinity.

The dry activator was prepared by mixing 82 parts by weight of montmorillonite clay containing 15% Al_2O_3 with 15 parts powdered sugar and 3 parts iron oxide.

A composition for the production of sand cores and other sand-mold parts for metal casting was prepared by adding the dry ingredients to the sand-binder mix in a muller. Where conventional release agents such as pitch and sea coal are also used, they preferably should be added with the dry powder additions. In open nullers it is usually preferable to add the basic sodium silicate solution first because the activator is a fine powder and if added to dry sand would create a dusty condition around the muller.

The above composition was a good all-purpose mix which has produced air-dried cores in excess of 300 pounds tensile and green-baked cores of slightly less than 300 pounds. It can be mulled to any desired green strength and when rammed will harden rapidly. The mix had a bench life of about one hour; scratch hardness 95-98. The cured cores were not thermoplastic and did not deform during pouring. Baked cores were not hydroscopic and could be soaked in water without softening. Air-hardened cores are waterproofed simply by applying heat, torching, light-off washes, or oven temperatures above about 425° F.

Cores made from the above mixture and air-dried were found to contain approximately 0.2% water as compared with cores made with the conventional carbon dioxide-silicate process, where 2-3% water is contained in the core. On firing, the sand-mix produced only 3 ccs. of gas per gram, compared with from 15 to 35 ccs. per gram for conventional oil binders and about 12 to 15 ccs. per gram for a conventional silicate binder, using carbon dioxide curing.

In a series of similar experiments, 35 parts of a 50-50 mixture of sea coal and pitch were added to 65 parts of the activator described above to show that large amounts of conventional organic carbonaceous materials are compatible with the novel binder system. Similarly, pure aluminum oxide, bauxite and kaolin clay and mixtures thereof, have been used as activators with and without other metal oxides and/or carbonaceous material additives to produce high quality cores having good collapsibility. For example, a mix of 3 percent of the high alkaline silicate solution described above with 2 percent pure Al_2O_3 or kaolin (40% Al_2O_3), or montmorillonite clay (15% Al_2O_3), or mixtures of these will give many hours of bench life if the sand mix is covered. These mixes give about two pounds green compression (strength) with baked tensiles of approximately 250-295 p.s.i. with AFS testing sand (50-70 grain fineness). Finer sands will increase green compression and reduce tensiles proportionately with the fineness of the sand.

From the above it is clearly seen that compositions comprising core-sand and a minor proportion of an alkali-metal silicate solution having an alkalinity in the range of 18-30 have excellent workability and bench life. Together with a minor proportion of Al_2O_3 such mixes have excellent green strength, collapsibility and water-proofing qualities. On firing the cores are essentially gasless. Accordingly, the present invention appreciably enhances the economy of core formation using silicate. Due to the high green strengths obtained it is now possible to draw the core box or pattern immediately and increase production markedly compared with the CO_2 process where sand mix must be hardened before the pattern is withdrawn. Further, the process permits the elimination of carbon dioxide gassing equipment and substantially reduces or eliminates undesirable gas formation.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited. Clearly, changes and alterations therein may be made which are within the full intended scope of this invention, as are defined in the appended claims.

What is claimed is:

1. A composition for the production of sand cores for metal casting consisting essentially of a finely-divided refractory material, a minor proportion of about 0.5 to 10% based upon the weight of said refractory material of a liquid binder composition consisting essentially of an aqueous alkali-metal silicate solution having an alkalinity calculated as weight percent of free alkali hydroxide in the range of 18 to 30, and about 3 to 100% based upon the weight of said liquid binder of a collapsibility-imparting agent consisting essentially of Al_2O_3 .
2. The composition of claim 1 wherein the alkali-metal silicate is sodium silicate.
3. A metal-casting mold comprising a casting-defining structure formed of an intimate mixture of the composition of claim 1.
4. The method of forming a sand core for foundry work which comprises placing in contact with a casting-defining surface a mixture of a finely-divided refractory material, about 0.5 to 10% based upon the weight of said refractory material of a liquid binder composition consisting essentially of an aqueous alkali-metal silicate solution having an alkalinity calculated as weight percent of free alkali hydroxide in the range of 18 to 30, and about 3 to 100% based upon the weight of said liquid binder of a collapsibility-imparting agent consisting essentially of Al_2O_3 , and thereafter drying the mixture.
5. The method in accordance with claim 4 wherein the alkali-metal silicate is sodium silicate.
6. A binder for sand cores for metal casting consisting of a liquid component consisting essentially of an aqueous solution of alkali-metal silicate having an alkalinity calculated as weight percent of free alkali hydroxide in the range of 18 to 30, and a dry component consisting essen-

tially of about 3 to 100% of Al_2O_3 based upon the weight of the alkali-metal silicate solution.

7. A binder for sand cores for metal casting consisting of a liquid component consisting essentially of an aqueous solution of alkali-metal silicate having an alkalinity calculated as weight percent of free alkali hydroxide in the range of 18 to 30, and a dry component consisting essentially of about 3 to 100% based upon the weight of said silicate solution of a collapsibility-imparting agent consisting essentially of Al_2O_3 .

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