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SILICEOUS CASTING CORES

Raymond Reuter, Orland Park, Ill., assignor to Nalco Chemical Company, a corporation of Delaware

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The present invention relates to improved siliceous cores useful in casting a variety of ferrous and non-ferrous metals. It is specifically concerned with new and improved binders for such cores.

A casting core is employed in the metal casting industry for the purpose of making internal or external portions of a mold. They may be either baked in their entirety, may be composed of green or dry sand or a combination of green and baked core material. To be operative as a core the aggregates of which a core is composed should possess a degree of porosity and a controlled mechanical strength which is sufficient to allow the aggregate to be assembled without breakage or crumbling. The core must possess sufficient mechanical strength to support itself or to be capable of support by an internal arbor.

A core is usually used to form internal cavities surrounded by metal, or to make it possible to draw some portion of the external surface of a casting from the sand which would not normally permit such. In some instances, cores are used to strengthen and improve a particular inner or outer surface of a casting mold because of its special properties.

To be useful, a core must possess the following properties which enable it to produce commercially acceptable castings:

(1) The core must be strong enough to retain its form without deforming in either the handling or baking processes.

(2) After being baked or dried the core must be sufficiently strong to resist erosion and deformation by the hot metal being poured into the mold.

(3) The core must have a minimum of contraction and expansion which allows the production of a true form for the casting.

(4) The core must have a low residual amount of gas-forming constituents so that the entry of excess gas into the metal is substantially reduced or eliminated.

(5) The core must remain solid during the pouring operation so that the metal will remain in a state of quietude while it solidifies.

(6) After the metal has been poured and solidifies the core must not remain in too rigid a state since such will tend to crack the casting. The core must be capable of ready removal, which is accomplished during what is known as a "shake-out" operation.

The most common type of material used in the preparation of cores is sand. Before being formed into a core it is necessary that the sand be blended and mixed with some material which causes adhesion between the sand grains and which becomes hard after some treatment. This adhesive agent is known to the art as a binder.

Binders are of various types and are used to impart some desirable properties to a core for a particular use or set of circumstances. Some of the qualifications necessary for a suitable binder are listed below:

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(1) A binder must sufficiently adhere the sand grains together so that, when the core is exposed to the pouring of molten metal, the grains will not wash from the surface.

(2) The binder should impart sufficient strength to the core so that it holds its proper shape until the metal begins to solidify and contract. After the initial contraction of the metal, the core should collapse so that strains, cracks, or fissures will not occur in the casting.

(3) The binder should not generate large quantities of gas when the core comes into contact with molten metal.

(4) The binder should impart sufficient green strength to the core so that it may be handled without fear of breakage.

(5) The binder should not cause the core to distort during baking.

(6) The binder should not deteriorate with age during storage.

(7) The binder should not be hygroscopic.

(8) The binder should be capable of uniformly admixing with the core materials so that it completely coats and bonds the individual core particles.

(9) The binder should produce a core mixture which may be formed into a core and which will not adhere to the sides of the core boxes in which such cores are usually formed.

(10) A binder should be economical to use and generally should work at relatively small dosages in relation to the entire mass of the core.

The various types of binders presently used in the casting industry conveniently may be divided into three groups, based upon their mode of setting to become firm. The first type of binders are those that become firm on freezing. This type of binder is almost exclusively limited to water and is not employed to any great extent in commercial operations. The second group of binders are those that become firm on setting at low temperatures and they consist mainly of such materials as sodium silicate, organic esters of silicic acid, Portland cement, rubber cement and chemical cements such as magnesium oxychloride. The third type of binders include such materials as oils, cereals, resins, rosins, sulfite and protein. While heat is necessary to properly develop type 3 binders, it may be said generally that some dry on heating, others harden after being heated and upon cooling, and some tend to become adhesive upon heating.

At the present time, the most popular type of binders fall within type three mentioned above. For the most part, core oils and cereal binders or mixtures of these two types are blended to form cores used in casting a wide variety of metals. While core oils are used greatly in the industry, they suffer from several disadvantages. One of the chief objections to core oils is the fact that they often tend to produce noxious vapors when contacted with hot molten metals. Another disadvantage of using core oils as binders is that unless the mixing operation is carefully conducted and the amount of oil carefully controlled the oil will tend to stick the core to the side of the core box, which means that when the core is removed after the baking, fissures or rents in the exterior surfaces of the core are formed, thus making its use in casting worthless.

Cereal binders have many features which make them particularly adaptable to making cores. The chief disadvantage of cereal binders, however, is the fact that it is necessary to store large quantities of these binders. They are subject to attack by vermin, and hence extra precautions must be taken to prevent destruction or deterioration of the cereal binders. In some cases cereal binders will cause the core to swell or crack during the baking process, and hence care must be taken to select

a proper cereal binder as well as to make sure it is properly blended with the core materials to insure a uniform mixture therewith.

Binders which are most convenient to use in the foundry industry are the class two type binders of which sodium silicate is exemplary. Sodium silicate, however, has several disadvantages in that it does not burn out and hence affects the permeability of the core. It has also been discovered that sodium silicate tends to completely destroy the collapsible and shake-out features of the cores which are wholly bonded with this material, and therefore its use is not completely accepted by the industry. In the same fashion esters of silicic acid, such as ethyl silicate, are not entirely satisfactory for core production since the bond formed by this material when heated strongly is considerably weakened. In addition to these disadvantages, esters of silicic acid are usually supplied in alcohol solutions which present a fire hazard in most foundry set-ups.

In the production of cores it is extremely important to select proper type of sand. Several essential properties which should be considered in selecting the proper type of core sand are: grain size, shape, base permeability, distribution, sintering point, clay content and mineralogical composition. Aside from the chemical purity of the sand one of the most important characteristics of a particular sand to be used in a given operation is that of uniformity of particle size. The effect on core permeability is oftentimes directly related to the particle size distribution of the sand. As a general rule the more coarse sands tend to give greater permeability but the green strength tends to be lessened. Fine sands, such as silica flours, tend to produce cores with superior green strength but as the silica flour content increases the permeability is correspondingly reduced.

Most foundries tend to avoid the use of silica flours because of its tendency to reduce permeability, and also because of its tendency to cause silicosis. The silicosis question, for the most part, has been substantially eliminated in modern foundries due to the improved ventilating and air circulating equipment which is today prevalent and is a part of good foundry practices and operation. Another reason for avoiding the use of silica flour in present day foundry practices is that if excessive amounts are used there is tendency to form "hot tears" and "crack" defects that result because of poor collapsibility, after the metal starts to solidify.

Another interesting sidelight in the use of silica flours in the production of metal casting molds is that where high temperature metals are poured and the pressure upon the core is of substantial magnitude, the silica flour tends to stop metal penetration into the core area. These several advantages and disadvantages have thus far made the use of silica flour somewhat a subject of controversy in the industry. For purposes of this invention, silica flour may be defined as a crushed, ground, or physically acted upon sand which has a particle size, in terms of U.S. sieve size, at least 80, all particles of which after treatment will pass through U.S. standard Sieve Number 80. By indicating that the particle size is at least 80 is meant to say that 80 mesh U.S. standard sieve size silica flour would be the coarsest type of material with the sieve sizes of larger numerical order having a finer particle size.

As indicated previously, cores may be either green, that is to say in a moist condition; or they may be dry, which indicates that a core has been subjected to a baking or heating process whereby the moisture has been substantially removed from the sand. In most foundry operations it is extremely desirable to use green cores, since they are simpler to use, require less operating time, and hence enable the production of cheaper castings. There are many cases, however, where green cores are not suitable for use in certain types of operations. As a general rule, baked cores are stronger and can be more

roughly handled without breakage. A baking process will drive off volatile constituents which tend to reduce the amount of gas-forming materials present in the cores. Similarly, baked sand cores are more permeable than green sand cores made from the same mixtures and equally rammed. This higher permeability of dry cores allows easier entry and exit of gasses formed during the metal pouring operations. Oftentimes, baking is necessary because of the particular shape of the core. Under some sets of conditions shaped cores could not be used in the green state unless rods or supporting arbors were used; sometimes baking eliminates the necessities for such external or internal supports. The above indicates that there are numerous factors, conditions, and variables of all types which will influence core manufacture and the type of castings produced from such cores.

Choice of sands and binders are perhaps the most important two factors in the forming of suitable casting cores. Each foundry usually has its own sand formula, its own particular type of binder or combination of binders which it believes gives the best results. It would be extremely valuable if a binder were available for making sand cores which was a unitary material. In a similar fashion, it would be desirable to have a core-binding material which would furnish both green and dry strength to a core and would give satisfactory bonds under a variety of conditions. In a similar manner, it would be desirable to have a core-binding material which would also enable silica flours to be used in core production whereby the benefits of such materials would not be overshadowed by the deleterious side effects now experienced when silica flours are used in core production.

It, therefore, becomes an object of the invention to provide a binder for siliceous material casting cores which will be operative under a wide range of core making conditions.

A further object is the provision of a metal casting core which has both green and dry strength and which may be used in the casting of a wide variety of metals.

Still another object is to provide a method for making siliceous casting cores, which method uses a single binder for the production of either green or dry molds and which is completely compatible with the siliceous materials used in the core mix.

Still another object is to provide a binder for siliceous casting cores which enables relatively large quantities of silica flour to be incorporated therewith which avoids the difficulties heretofore experienced when silica flours have been used.

A further object is to provide a siliceous casting core binder which is operative at relatively low dosages which may be conveniently applied and used by the casting industry. Other objects will be apparent hereafter.

In accordance with the invention it has been found that siliceous casting cores may be conveniently produced by blending with a foundry sand not more than 50% by weight of a silica flour and adjusting the moisture content of such mixture to not more than 10% by weight with an inorganic binder which comprises an aqueous colloidal silica sol. After the ingredients have been thoroughly blended they are then formed into a core which may be either allowed to dry at room temperature or may be placed in an oven to produce a dry core having superior qualities. In a preferred embodiment, the aqueous colloidal silica sol used as the binder in this invention is advantageously combined with a gel-accelerator which hastens the set-up of the materials which sets the core to a hard and easily handled mass. The invention also contemplates, in its preferred form, incorporation with the aqueous silica sols a compatible wetting agent which is used at not more than 2% by weight based upon the total weight of the silica sol, whereby the wetting properties of the silica sol for the siliceous materials is substantially improved, which thereby facili-

tates the mixing and uniform wetting of the individual aggregates which tend to form the core.

The use of aqueous colloidal silica sols as binders for refractory materials is well known. Its use for this purpose is described in Carter U.S. Patent 2,329,589. Several advantages are shown to be imparted to various types of ceramic bodies by incorporating therewith varying amounts of colloidal silica. While colloidal silica is used for forming ceramic materials, it will be readily apparent to one skilled in the art that the use of colloidal silica in this invention is distinct and different due to the nature of the problems involved in metal casting as well as the particular method in which the colloidal silica sols are used.

Specific application for colloidal silica in the ceramic industry is the use of silica sols in the production of investment casting molds. The use of aqueous colloidal silica sols in refractory casting molds is taught by Collins U.S. 2,380,945.

At this point it might be well to distinguish between investment casting, which is commonly referred to as casting by the lost wax method, and sand casting which is the subject of this invention. Investment casting usually uses what is commonly known as a monolithic or one-piece mold. To make the mold which is invested around the pattern material, it is the usual practice to make a thick, liquid slurry of the mold material and to admix therewith the bonding or mold-hardening ingredient. When colloidal silica sols are used for this purpose it is customary to make the slurry using dilutions of the silica sol whereby the mold-forming ingredients are rendered into a pasty or semi-fluid mass which is then poured into a structure which contains the investment. The mold material is then vibrated for a period of time sufficient to settle it around the pattern, and the result is that there is usually a substantially large quantity of water which appears on the top of the mold. Since it is one of the chief objects of investment casting to produce close tolerance, smooth metal objects it is often necessary to use very finely divided mold materials such as silica flour, zircon, alumina, magnesia, etc. After the molds have been tamped they are usually subjected to a setting up process which consists of two heating cycles. To carefully control the contours of the mold it is necessary to gradually heat the mold up to first set the material. This is usually accomplished by heating between one hundred to several hundred degrees Fahrenheit. After the mold has obtained sufficient hardness it is then again heated so that the investment material is fired out of the mold. This second firing step is usually conducted at a temperature ranging from between 1200-1800° F. If the mold is allowed to cool the investment casting is usually of inferior quality and contains many defects.

By comparison, sand casting usually pours the metal into a cold mold and there is usually no necessity to go through a bonding or hardening process of the mold materials at elevated temperatures.

Colloidal silica sols, when used in this invention, are employed at an amount substantially less than those used in precision investment casting. In effect the silica sols are used not only as bonding agents in the present invention but when so used they act as wetting agents whereby moist adhesion is given to the particles of the sand core. If such minor amounts are used in investment casting it becomes readily apparent that the quality of the investment mold would be inferior and in most instances would not be at all suitable for pouring.

One of the most important and interesting features of the present invention lies in the fact that in order to be operative it is necessary that a critical relationship exist between the types of siliceous material used in preparing the cores. It has been indicated the cores should contain not more than 50% by weight of a silica flour. As a lower limit the silica flour may be incorporated with the casting sand in an amount as little as 0.1% with

good results being obtained. In the preferred embodiment the amount of silica flour to foundry sand may vary from between 5% to 30% by weight and in a most preferred form it is desirable to maintain the amount of silica flour in relation to foundry sand at between 5% to 15% by weight.

The particular silica flour used should all pass through at least U.S. sieve size of 80, preferably all through No. 325, and most preferably 400. Using the mixtures of the type described is a simple matter to select a blend of silica flour and foundry sand which will give the maximum results under a given set of foundry operating conditions. A silica flour and the foundry sand are usually blended in a mixing machine to produce a homogeneous mass or blend. After this mixture has been obtained colloidal silica sol is then added to the mix in amounts sufficient to produce a finished moisture content of the mix not greater than 10% by weight. In most casting situations it will usually be necessary to use from 2% by weight to 8% by weight of the colloidal silica sol, but in some circumstances as little as 0.5% by weight may be used. The amount necessary to produce a suitable core will in most instances be directly related to the moisture content of the particular core which is directly related to the type of metal being cast. The quantity of the aqueous colloidal silica sol is preferably sufficient to adjust the moisture content of the siliceous casting core to within the range of from 0.5% to 8% by weight. For purposes of illustration the following list of metals and the moisture contents which are normally used in making cores suitable for the casting of such metals is presented:

TABLE I

Metal	Percent Moisture-Range
Aluminum.....	6.5-8
Brass and Bronze.....	6.0-8
Copper-Nickel.....	6.0-7.5
Light Grey Iron.....	6.5-8.5
Medium Grey Iron.....	5.5-7
Heavy Grey Iron.....	4-6.5
Light Malleable Iron.....	6-8.0
Heavy Malleable Iron.....	5.5-7.5
Light Steel-Green Core.....	2-4
Steel, Dry Core.....	4-6

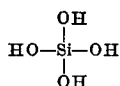
After the ingredients have been mixed as indicated above, it is only necessary to tamp the materials into the core mold to produce the particular core needed for a given operation. In most instances a satisfactory core having adequate green strength can be prepared by using this simple procedure. Where added green strength as well as hot pouring strength is needed it is oftentimes desirable to incorporate with the silica sol a gelling agent which will allow the silica sol to set up and more firmly bind the core materials. The use of the gelling agents will be described more fully hereinafter.

When it is desired to produce a dry mold having superior qualities it is necessary to take the green mold which has been treated with the colloidal aqueous silica sol and bake it at a temperature not greater than 500° F. for a period of time usually greater than one hour and not more than five hours. The baking operation, of course, is controlled primarily by the size of the mold, its moisture content and the temperature to which it is subjected. As a general rule, it is desirable to use a temperature between 350 and 480° F. and to allow the material to bake for a period of time sufficient to substantially remove all the moisture.

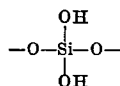
The colloidal aqueous silica sols useful in the invention may be drawn from a wide number of sources and may be produced by several well-known methods.

The silicic acid sols are generally believed to be poly-

meric derivatives of monomeric silicic acid which arbitrarily may be assigned the formula:



As this material is produced it is capable of polymerizing to form various sized polymers containing this unit:



if the mechanism is considered linear. It is known, however, if the reaction carries to completion a gel is formed which evidences a three dimensional cross-linked network formed from the starting silicic acid molecule. The polymerization mechanism thus described may begin immediately upon the formation of monomeric silicic acid and proceeds to form particles or masses of colloidal size within a very short time. The cross-linking or gelation of the sol may be inhibited by adjusting the pH of the system with acid or alkali below 4 or above 8 respectively, or adding a small amount of alkali metal oxide. Under these conditions, the sol will retain its colloidal dimensions for long periods of time. When the silicic acid reaches colloidal size and is stabilized, the particle size present is about one millimicron and possible two to three millimicrons in diameter. The exact size will depend on concentration, presence or absence of electrolytes, pH and temperature.

The silicic acid sols preferably employed in the present invention are those containing at least 3.0% SiO_2 and a pH sufficient to stabilize said sol against gelation. Silicic acid sols may be prepared by any number of well-known methods, many of which are summarized in Bechtold et al., U.S. Patent 2,574,902, and the present invention contemplates the use of any of such sols. Silica sols capable of use in the present invention may be conveniently prepared by the techniques described in Bird, U.S. Patent 2,244,325, although the well-known method of hydrolyzing sodium silicate with strong mineral acids with the subsequent removal of excess salt is equally suitable.

The Bird patent shows that alkali metal silicate solutions may be contacted with a cation exchange resin in the hydrogen form to produce a silicic acid sol of relatively high purity. After the sol is produced it may be stabilized with a small amount of alkali metal to impart to the finished sol, a high degree of stability. Silica (SiO_2) to alkali metal (calculated as Na_2O) weight ratios of 50:1 to 100:1 are preferably employed to impart such stability.

The stabilized sols produced by Bird's method are capable of use in the practice of the present invention as produced or they may be concentrated to increase the silica content thereof, several fold. While the Bird patent shows generally the method of concentrating silica sols, there are now several methods available which produce sols with a relatively high silica concentration in the form of discrete non-agglomerated particles. Such methods are shown in Bechtold et al., U.S. Patent 2,574,902, Brage et al., U.S. Patent 2,680,721 and Parma et al., U.S. Patent 2,601,235.

In concentrating colloidal silicic acid sols, the usual methods increase the size of the discrete particles present in the sol. As a general rule the more concentrated the sol, the larger will be the particle size of the silica present. In a freshly prepared batch of stabilized 3.5% by weight SiO_2 sol prepared by the Bird method the particle size is believed to be about 1 to 3 millimicrons in size. If such a sol is concentrated to about 30% SiO_2 by using the techniques of Bechtold et al., U.S. 2,574,902, the

average particle size will vary from 15 to 130 millimicrons in diameter.

Silica sols which are extremely valuable in the practice of the invention are those which have the highest conductivity and the lowest pH, when these values come from the silica only and not from impurities, and are capable of producing the highest strength gels when a suitable electrolyte has been added thereto. Sols of this type usually have a silica concentration of between about 15 and about 18% silica as SiO_2 . In general, the range of conductivity of these sols is between 1800 and 3200 micromhos and the preferred conductivity range is 2000 to 3000 micromhos. The preferred pH range is 8.5 to 9.0. The general ratio of SiO_2 to alkali metal oxide, expressed as $\text{SiO}_2:\text{Na}_2\text{O}$, is from about 160:1 to about 330:1 with the preferred range being about 170:1 to about 200:1. Generally, the specific gravities should be at least 1.047 and may be in the range of 1.047 to 1.10 at 68° F. The preferred range of specific gravities of this type of silica sol is from about 1.105 to about 1.115 at 68° F.

The SiO_2 concentration of this type of sol is extremely important in relation to the type of gels that can be produced. The sols containing from about 10 to 17.5% SiO_2 are capable of forming gels of high strength. Within this range it has been found that the higher the concentration of silica in the sol the stronger will be the gels. While the best gels are formed when the sols contain about 10 to 17.5% of SiO_2 , it is to be understood that dilutions as low as 3% SiO_2 may be used in making sand cores although they are not as strong or as useful.

As can be seen from this discussion a wide variety of colloidal silica sols are capable of being prepared. The invention will be further illustrated by the following examples in which the proportions are given by weight unless otherwise indicated. All of the colloidal silical sols described in these examples are suitable for the practice of the invention.

Example I

Commercial sodium silicate was diluted with Chicago tap water to produce a sodium silicate solution having present therein about 4.5% SiO_2 . The weight ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ was about 1:3.2, with a specific gravity of about 1.050. This diluted sodium silicate was passed through a column of a hydrogen form sulfonated polystyrene divinylbenzene copolymer cation exchanger of the type disclosed in U.S. Patent 2,366,007. The effluent contained about 3.5% SiO_2 , had a pH of 3.5 and a conductivity of about 400 to 800 micromhos. To this silicic acid sol effluent was added an amount of 26° Baumé ammonium hydroxide sufficient to adjust the pH of the acid sol to about 9.0.

Example II

The procedure used in Example I was the same except that the solution of the starting sodium silicate contained about 10% SiO_2 . The finished sol had an SiO_2 concentration of about 7% and a specific gravity of about 1.050. Ammonium hydroxide was added to the sol so that the final pH was about 10.5.

Example III

A portion of the sol of Example I was placed in an evaporating kettle and heated until ammonia and steam vapors began to come off. At this point a small amount of permanent alkali (KOH) was added and fresh ammonia stabilized sol was added to maintain the evaporating volume constant. Throughout the process the pH was never allowed to go below 8.5. This was accomplished by continually adding gaseous ammonia during the heating process. The constant evaporation was continued with constant checks being maintained to keep the pH always above 8.5, and was continued until specific gravity of the sol had reached 1.20 at 68° F. When this specific gravity had been obtained an amount of potas-

sium hydroxide was added to give the finished sol a pH of 9.0. This sol had an SiO_2 concentration of 30%.

Example IV

Another sol was produced by using the method shown in Example III. In this instance, however, the concentration process was continued until the sol had an SiO_2 concentration of about 48%.

Example V

This silica sol is a high conductivity, high gel strength type and was prepared by passing an aqueous sodium silicate solution having a specific gravity of 1.045 at 68° F. and containing 4% SiO_2 through a column of polystyrene divinylbenzene sulfonic acid cationic exchange resin (Nalcite HCR) with the effluent having a specific gravity of 1.026 at 68° F. and an SiO_2 concentration of 4.5%, a pH of 3.7, and a conductivity of 800 micromhos. Ammonium hydroxide was added until the pH was adjusted to 9.1. Eighty-five gallons of ammonium hydroxide adjusted silica sol produced from this ion exchange operation were placed in a 150-gallon steam kettle and the temperature was raised until the liquid began to boil. At this point additional ammonium hydroxide adjusted ion exchange or effluent sol was added to maintain the volume in the kettle constant and enough potassium hydroxide was added, as was indicated from previous experience, to adjust the pH to 8.5 at the end of concentration. The evaporation concentration process continued for eight hours. During the first few hours it was necessary to add ammonium hydroxide to the boiling sol to maintain the pH at 9. Near the end of the process the pH was gradually allowed to fall to about 8.5. The total amount of potassium hydroxide added during the process was equal to 9.0 grams per gallon of produced sol. Throughout the process described, specific gravities were constantly checked and the highest point ever reached was 1.115. After the concentration had stopped, 10% by volume of Chicago tap water was added to adjust the gravity to 1.111.

The finished sol had the following properties:

Conductivity in micromhos	2200
pH	8.5
Percent SiO_2	16.5
Specific gravity	1.111
Relative viscosity at 77° F. (centipoises)	2.0
Methylorange alkalinity	2.0

In general, the silicic acid sols are preferably used in their more concentrated form. Sols containing about 30% SiO_2 have given superior results, yet sols having an SiO_2 content as low as 3% have shown effectiveness when used in the practice of the invention.

These aqueous sols are sensitive to low temperatures but they may be treated by two methods whereby the effects of lower temperatures are avoided. The first method is to incorporate therewith an antifreeze such as methyl alcohol or ethylene glycol. This can be easily done by adjusting the pH of the sol to about 2.5. The second method is to treat the sol with an alkylamine so that if the sol is frozen it may be redispersed in a colloidal state. This latter mode of treatment is shown in Horning, U.S. Patent 2,601,91.

In order to facilitate application of the sols to the various sand mixtures used in producing cores, it is desirable to add to the sols minor amounts of compatible wetting agents. The only requirement of such agent is that it be compatible with the sol insofar as it is soluble and does not cause precipitation or gelation. Anionic synthetic detergents of the alkali metal alkyl (e.g., octyl or nonyl) benzene sulfonic acid type are admirably suited for the purpose of the invention. Any compatible anionic or non-ionic wetting agent can be employed; for example, those listed in the article "Synthetic Detergents—To Date, II," by John W. McCutcheon, appearing in Soap and

Sanitary Chemicals, July, August, September and October issues, 1952. Cationic wetting agents tend to form gels or precipitates when added to these sols and should be avoided. The wetting agents cause the sols to more uniformly wet the aggregate surfaces, thus enabling a firmer bond to be formed as well as giving a more uniform moisture control to the core ingredients.

To improve the strength of the core after it has been treated with the silica sol binder, it is usually preferable to allow the core to stand for a period of time ranging from several minutes to several hours at room temperature or at a temperature not greater than 110° F. to allow the silica sol to set up. The formation of gels is dependent upon numerous factors which must be taken into consideration if proper controllable gels are to be formed. As a general rule the gels will form more rapidly at elevated temperatures.

To improve the gelation rate of the silica sol as well as to improve the strength of the bond it is preferable to incorporate with the silica sol a gel accelerator. These accelerators may be chosen from a large number of electrolytes. As a general rule, strong electrolytes should be used in smaller amounts than weak electrolytes. If excess accelerator is used, the gelation will occur too rapidly and as a result the gels formed are not as strong as those formed under more favorable conditions. In the practice of this invention, it has been found that excellent results have been obtained by using such electrolytes as epsom salts, which is known commercially as magnesium sulfate, citric acid, magnesium silico fluoride, and disodium pyrophosphate.

In order to illustrate the controllability of the gels formed from sols made in accordance with the present invention, various mixtures of the sol disclosed in Example I were made with two different electrolytes and the gelation time was measured with the results being shown in Table II.

TABLE II

Time to Gel in Min.	Grams $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per 100 ml. of Sol				Grams of $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ per liter of Sol	
	At 80° F.	At 68° F.	Diluted 1/2 Vol. with Chicago Tap Water at 68° F.	Diluted with 60% by Vol. Chicago Tap Water at 80° F.	At 80° F.	At 68° F.
15	1.75					
20	1.35					
30	1.03	1.85				
40	.7	1.35				
50		1.15		6.5		
60		1.02	2.0	3.5		
70		.95	1.6	2.0		
80		.70	1.4	1.3		
90			1.28	.8	1.75	
100			1.18		1.98	
120			1.05			
140			.97			1.4
160			.7			
180			.5			1.6
200						1.8

From Table II it becomes evident that the gelation of the sols at various temperatures may be controlled by the amount of the electrolyte used as well as the particular type of electrolyte shown. This particular feature enables the operator to choose a gelation or setting time sufficiently compatible with his operating schedules so as to make the aqueous colloidal silica sols thoroughly practicable from an operational standpoint.

In order to further illustrate the invention the following additional examples are presented:

Example VI

To present the results of several series of tests using various types of mold mixtures, silica sols, and different

types of metals the following table is presented to illustrate the several advantages of the invention:

sol used or the percentage of silica flour in relation to foundry sand used in a given core material.

TABLE III

Core No.	Foundry Sand		Silica Flour		Sol. No.	Per-cent Moisture	(2) Gel Accelerator, Percent	Green	Baked, F. °	(1) Permeability	Green Compression, Lbs.	Deformation, Inches	Metal	Casting Condition	Remarks
	Parts	U.S. Sieve	Parts	U.S. Sieve											
1-----	1,400	60	-----	-----	III	6	-----	Yes-----	No	-----	-----	-----	Steel-----	-----	Core Chip- page. 1½ min. Collapse. Poor Core Quality.
2-----	1,400	60	320	325	III	4	-----	No-----	420	160	7.9	.036	do-----	Good-----	
3-----	1,200	40	-----	-----	III	6.4	.6	Yes-----	-----	-----	-----	-----	Cu-Ni Alloy.	-----	
4-----	1,200	40	320	200	IV	6.3	.6	Yes-----	-----	43	8.6	.016	do-----	Excel- lent.	Core Col- lapsed on Pouring.
5-----	1,200	40	320	200	IV	6.3	.6	No-----	500	45	8.6	.014	do-----	do-----	
6-----	60	40	40	325	V	7.5	.5	No-----	400	16	8.2	.015	Brass	do-----	
7-----	920	40	-----	-----	V	6.8	-----	No-----	400	8	6.2	.025	do-----	Poor-----	
8-----	920	200	400	400	V	5.3	.3	-----	400	15	7.5	.016	do-----	Good-----	
9-----	100	85	-----	-----	V	7.2	1.2	-----	425	7.5	6.7	.018	Alumi- num.	-----	Passible.
10-----	100	85	20	320	V	7.2	1.2	-----	425	13	8.2	.014	do-----	Excel- lent.	

(1)=A.F.A. No.

(2)=MgSO₄.

Test No. 1 shows that when the silica sols are used as a binder for conventional foundry sand, the casting does not have sufficient green strength and is not considered suitable for use as a core. Test No. 2 illustrates that when a small amount of a silica flour is combined with the foundry sand and the silica sol is used as a binder, a superior casting is produced. Test No. 3 illustrates the same effect as Test No. 1 when a copper-nickel alloy is cast. Test No. 4 shows improved results are obtained on the same alloy with a silica sol plus a silica flour combined with the foundry sand. Test No. 5 demonstrates that when the core is baked an improved result is obtained over a similar core in a green condition. Test No. 6 shows the utility of the invention when practiced in the casting of brass. Test No. 7 points out that when the silica flour is omitted from the formulation a poor quality casting is produced since the core collapsed at the time the metal was poured. Test No. 8 shows the same formula to which 40 parts of a 400 mesh silica flour was added. As a result the improvements in the casting were superior. Test No. 9 shows that the silica sol binder produced a fair casting using commercial 85 mesh foundry sand and casting aluminum. A substantial improvement was obtained when only 20 parts of a silica flour was added to the initial sand mixture, the amount of silica sol being kept constant.

When the amount of silica flour is relatively high, e.g. greater than 30% by weight, there is sometimes a tendency for the collapsibility of the core to be unduly prolonged. This usually can be corrected by controlling tamping or packing operations so that not as much pressure is used in forming the core. The added strength is then imparted to the core mixture by using a greater amount of silica sol and/or gel accelerator to give a sufficient green strength to permit handling of such cores.

By using silica flour in making the molds of the invention, an additional advantage is obtained since the penetration of large, dense castings into the mold surfaces is substantially reduced. It is also to be noted that when the cores which are treated with colloidal silica sols and silica flour have been fairly dried so as to remove substantial quantities of the moisture therefrom, that the gas content is practically at a minimum and, therefore, bad effects from this source are practically non-existent in castings made using this process. There is no odor nor disagreeable chemicals used in the present invention as practised in foundries. The invention also simplifies the problem of formulating one or more binders to produce a given effect. If a concentrated silica sol is used variations in bond may be accomplished by varying either the gel accelerator, baking time, concentration of the silica

The invention is primarily directed to the production of siliceous cores for use in sand casting. It is to be understood that the teachings for the invention are equally applicable to the production of sand molds. During the course of this disclosure, discussion has been made dealing with foundry sand. Foundry sand is intended to cover a siliceous material which is composed primarily of silica which may have a particle size in terms of U.S. sieve number ranging from No. 4 up to and including 200 mesh. It will be understood that, while the sieve numbers of the silica flours and the foundry sands may overlap, the silica flours usually have a certain percentage of fine materials which have particle sizes within the range of just a few microns. It is believed, since the silica flours are crushed sand and that they contain a certain percentage of extremely fine materials, that such aids in the bonding effects are achieved when silica sols are used as binders. This is, of course, a theory and is not intended to be a limitation of this invention.

Having thus described my invention it is claimed as follows:

1. The process of producing a siliceous casting core which comprises the steps of blending a foundry sand with from 0.1% to 50% by weight of a silica flour having a U.S. sieve size of at least 80, adjusting the moisture content of such mixture to from 0.5% to 8% by weight by the addition thereto of at least 0.5% by weight of an aqueous colloidal silica sol which has a silica content of from 15% to 18.5% silica as SiO₂, a conductivity of at least 1800 micromhos, a pH of from 8.4 to 10 and a specific gravity of at least 1.047 at 68° F., and then forming these ingredients into a core.

2. The process of claim 1 where the aqueous silica sol has a conductivity of from 2000 to 3000 micromhos, a pH of from 8.5 to 9.0 and a specific gravity of from 1.105 to 1.115 at 68° F.

3. The process of claim 1 where the silica flour has a sieve size of at least 325.

4. The process of claim 1 where the aqueous silica sol contains an electrolyte from the group consisting of magnesium sulfate, magnesium silicofluoride, disodium pyrophosphate and citric acid.

5. The process of producing a siliceous casting core which comprises the steps of blending a foundry sand with from 0.1% to 50% by weight of a silica flour having a U.S. sieve size of at least 80, adjusting the moisture content of such mixture to not more than 10% by weight by the addition thereto of at least 0.5% by weight of an aqueous colloidal silica sol which contains at least 3%

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by weight of silica as SiO_2 , and has a conductivity of at least 1800 micromhos, a pH of from 8.4 to 10, and a specific gravity of at least 1.047 at 68° F., forming these ingredients to a core and then firing said core at a temperature not greater than 500° F. for a period of time sufficient to uniformly dry said core.

6. The process of claim 5 where the aqueous silica sol has a conductivity of from 2000 to 3000 micromhos, a pH of from 8.5 to 9.0, and a specific gravity of from 1.105 to 1.115 at 68° F.

7. The process of claim 5 where the silica flour has a U.S. sieve size of at least 325.

8. The process of claim 5 where the aqueous silica sol contains an electrolyte in an amount sufficient to cause a uniform and controlled gelation of said silica sol, and the electrolyte gelling agent is from the group consisting of magnesium sulfate, magnesium silicofluoride, disodium pyrophosphate and citric acid.

9. A process of producing a siliceous casting core which comprises the steps of blending a foundry sand with from 0.1% to 50% by weight of a silica flour having a U.S. sieve size of at least 80, adjusting the moisture content of such mixture to not more than 10% by weight

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with at least 0.5% by weight of an aqueous colloidal sol which contains at least 2% by weight of SiO_2 and not more than 2% by weight of a wetting agent from the group consisting of nonionic and anionic wetting agents, said aqueous colloidal silica sol having a conductivity of at least 1800 micromhos, a pH of from 8.4 to 10 and a specific gravity of at least 1.047 at 58° F., and then forming these ingredients into a core.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,949,375

August 16, 1960

Raymond Reuter

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 23, for "entirely" read -- entirety --;
column 9, line 63, for "2,601,91" read 2,601,291 --.

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents