METHOD OF MAKING CERAMIC MOLDS

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This application is a continuation-in-part of co-pending application Serial No. 20,567, filed April 7, 1960, now abandoned.

This invention relates to methods of making so-called "ceramic" molds for the precision casting of metals, alloys, plastic, glass, rubber, and the like, wherein slurries of comminuted refractory material and an organic gelling binder therefor are poured on a pattern of the article to be molded; and gelling and ultimate curing of the slurries into rigid molds and, more particularly, to techniques and compositions for providing a preliminary hardening and ageing of the gelled mold materials prior to the final curing.

As will be understood, so-called "ceramic" or precision casting molds generally of the character to which this invention relates, and the compositions and techniques for forming them, may be illustratively typified by the disclosures of such prior patents as Frangno No. 1,509,008 and Shaw et al. No. 2,795,022, etc. As noted therein, and as now well understood in this art, such ceramic molding techniques generally involve forming a slurry of finely comminuted refractory materials in an organic gelling binder, such as an alkyl silicate, and pouring on the pattern. Gelling of the silicate material occurs forming a semi-rigid mold, which is then stripped from the pattern and cured as by igniting or burning off the volatile (alcohol) material resulting from the gelation (hydrolysis) reaction.

Although the chemical reactions taking place during gelation may be quite complex and, perhaps, not thoroughly understood, it may be suggested that, immediately after gelation, the gelled mass consists of a solid phase of silicate gel (e.g., a fusible alkali silicate gel) and a liquid phase of diffusive resultant from the hydrolysis or gelling reaction (e.g., an alcohol corresponding to the alkali substituent of the silicate binder). Rapid evaporation of the liquid (alcohol) phase in normal room atmosphere may result in the unstable solid phase undergoing a reaction (perhaps, with atmospheric moisture, or otherwise) producing a different product having poor binding qualities to result in a mold of less than optimum or desired properties.

The ignition or firing of the mold immediately after gelation (as necessary with the Shaw process) avoids to a large extent such formation of unstable solid phase resultant. If this sequence of operations is to be undertaken, as required by the Shaw patents, the ignition and firing of the gelled mold as stripped from the pattern must be carried out at a place quite close to where the mold was poured, because of the close timing involved, and difficulties in actual commercial operations may be encountered in firing the mold as quickly as desired and/or even in connection with firing the mold in the particular room or location where it was poured. For example, one of the recognized concomitants of firing such molds is the production of objectionable odors and/or the necessity for definite or ventilation which may be inimical to a continuous commercial process if the firing must be undertaken at the location of pouring the mold in the first place. Even attempts to alleviate the foregoing disadvantages to one extent or another (as, perhaps, exemplified by Lubalin Patent No. 2,979,790) may not in all cases be completely satisfactory. Such attempts have included coating the outside of the mold with a wax layer (apparent to inhibit evaporation of the volatiles), but such results may give imperfect retardation, because of the practical matter of providing an absolutely impervious wax film, and may actually complicate the ultimate firing step.

If the gelling and curing reaction of the alkyl silicate binder with the comminuted refractory material (and whatever gelling accelerators may be present) be considered as involving a series of chain or polymerizing reactions taking place between the alkyl and silica groups in the gel and starting from the point of initial gelation, the various stages of reaction may be conveniently visualized as producing a solid phase arrangement which will undergo some stabilizing growth or multi-stage development enhanced by "ageing" for, for example, the first ten minutes after gelation. Such growth or hardening development or ageing may occur most rapidly during the first 10 or 15 minutes, leaving the mold in the condition of a structure which, although still partially unstable in air, is almost completely stabilized within itself and readily susceptible to the ultimate curing in whatever manner is desired.

Although the differences between an immediately fired ceramic mold of the character described and one which has been aged somewhat before ultimate curing is discernible from the finished products (and particularly with regard to the "microcrazing" taught in the various Shaw patents), the problem is much more readily visualized in terms of commercial operations on a mass production scale by noting that the semirigidity of the initially gelled mold may produce discernible sagging of the mold cavity surfaces after stripping from the pattern, whereas providing some ageing or hardening preliminary treatment prior to firing or ultimate curing (and, especially when firing is delayed for some time as with a wax coating on the mold) produces definite advantages in both the final mold structure and the ease of handling the mold during formation.

According to this invention, by contrast, the mold as poured on the pattern (utilizing slurries of comminuted refractory materials such as alumina and silica gel) and an alkyl silicate binder which will yield volatile alcohol upon hydrolysis is subjected to immersion contact with a hardening atmosphere or bath immediately upon gelation, and with or without preliminary stripping of the gelled mold from the pattern, for an ageing period of time during which the mold becomes more or less internally stabilized sufficiently to avoid sagging or other distortions upon firing or final heat curing of the finished mold, which hardening bath or atmosphere comprises a fluid medium which is a liquid or vapor atmosphere substantially the same as or compatible with the alcohol or other volatile resultant of the hydrolysis gelling reaction in the mold or, alternatively, a surrounding aqueous or organic liquid, preferably heated, with which the volatile results of the gelation and curing reactions are miscible.

As a further feature of this invention, the particular selection of hardening bath ingredients satisfactorily includes materials substantially inert with respect to most pattern materials so that the gelled slurry poured on the pattern may be immersed in the hardening step without stripping, if desired, thus improving to an even greater extent the fidelity of pattern reproduction in the casting mold cavity; and ultimate heat curing of the resulting mold may be accelerated by having the hardening bath hot, although it is primarily desired to provide ageing of the mold between gelling and curing rather than to accelerate the curing step.

Thus, a principal object of this invention is to provide techniques and compositions for permitting the ageing or stabilization of ceramic mold materials of the character described after the gelling thereof on a pattern and
prior to the ignition or heat curing thereof into the ultimate finished casting mold as by immersing the gelled mold in a bath or atmosphere of a hardening fluid for reaction with components in the gelled mold preventing premature gelation thereof and/or initiating curing with dissolving out alcoholic hydrolysis products without exposing the mold directly to reaction with atmospheric constituents between gelling and final curing thereof.

Another object of this invention is to provide techniques and compositions for use in the manufacture of ceramic casting molds of the character described which permit a substantial ageing time between gelation and ultimate curing for convenience in handling the molds in commercial installations so that the ultimate heat curing or firing thereof may conveniently occur at a point remote from the pouring thereof without sacrifice of mold quality from either considerations of time delay or undesired reaction between the atmosphere and constituents of the gelled mold.

A further object of this invention is to provide an immersion bath or atmosphere reactant or protective ingredients in which the gelled molds may be conveniently maintained without deterioration thereof between gelling and final curing and, indeed, productive of ageing characteristics of the mold reactants to provide an ultimately cured mold of greater fidelity to the pattern and other enhanced structural characteristics.

Still another object of this invention is to provide techniques and compositions for a preliminary hardening step, intermediate gelation and final curing to avoid, with or without stripping the gelled mold from the pattern, enhanced ageing and internal stabilization of the mold materials, as protected from the ambient atmosphere for enhanced rigidity even prior to curing and to produce enhanced preliminary internal structure or ultimate curing into the finished casting mold.

Other objects and advantages hereof will be apparent from the following description and the appended claims.

As is now well understood in connection with the manufacture of ceramic molds of the character to which this invention relates, a slurry or semi-fluid paste is formed by admixing a comminuted refractory material (such as silica, alumina, or other suitable refractory oxides or silicates) with a binder and gelling accelerator. The binder is satisfactorily an organic silicate, such as ethyl orthosilicate, or any other low alkyl-substituted silicate which readily yields a volatile alcohol upon hydrolysis in a manner such that the volatile alcohol may be eliminated from the gelled mold by heat curing, igniting, etc. The accelerator, as noted in the patents mentioned above, may be of either acid or basic origin, as conventional in this art, with the preferred employment of a material which permits gelation to occur on the acid side of neutral pH.

After pouring such slurry on the pattern of the casting to be made, the mold material is allowed to gel into a semi-rigid form, which may then be stripped from the pattern for hardening in accordance herewith and ultimate curing. Alternatively, as may be preferred with certain pattern configurations and particularly involving mold cavities with extremely thin sections, the mold in accordance herewith may be treated with the hardening environment without stripping from the pattern because the hardening materials hereof are generally inert to virtually all materials from which such mold patterns would conveniently be formed.

Also, as will be understood, the immersion of the gelled mold in a bath or atmosphere in accordance herewith is preferably actual immersion of the entire mold in a liquid bath, although the foregoing expressions are to be understood herein as including applying the hardening liquid to the outside of the mold as a continuously wet and heavy layer and/or placing the gelled mold into a cabinet or other enclosure in which the atmosphere is substantially entirely that of vapors of the particular hardening fluid involved for surrounding and contacting all internal and external surfaces of the gelled mold substantially immediately with an atmosphere or bath of hardening fluid such as prior to gelation for reaction with the silicate binder, exclusive of the ambient room atmosphere and any reaction therewith, and/or removal and solution of volatile reactants of the gelling or hydrolysis reaction from the mold—all to produce the desired ageing and internal stabilization of the mold material immediately after gelation thereof and prior to the final heat curing or firing of the mold and in the absence of both prolonged contact with the normal ambient room atmosphere and pronounced evolution of noxious volatile reactants of the gelling or curing reactions into the work space where the molds must be poured and handled.

Although satisfactory results are achieved with the hardening medium referred to above being either a liquid bath or vapor atmosphere, a liquid bath is preferred for most applications with most sizes of molds, as well as being preferred for reasons of operational practicality. Preferably also, and especially when the mold is completely immersed in a reservoir of hardening medium, a highly volatile or even flammable medium is preferred for the ready removal thereof during heat curing of the mold, especially in instances when such heat curing is desired to be accomplished by a heat oven or similar step instead of by actual firing or ignition.

Although a variety of materials are available with which satisfactory results have been achieved in accordance herewith for the hardening fluid, preferred results in accordance herewith are achieved if the hardening medium fluid is either substantially the same as the volatile reactant of the hydrolysis reaction, i.e., the lower alcohol when the mold binder is ethyl silicate evolving ethyl alcohol as a result of the hydrolysis reaction) or a bath of liquid with which such volatile resultant of the hydrolysis reaction is readily miscible. As will be understood, the former category includes any of the lower aliphatic alcohols (commercial ethyl alcohol being preferred when ethyl silicate is the binder) while the latter category includes such materials as conventional organic solvents (e.g., acetone, kerosene, benzene, other hydrocarbons, etc.), water, etc. Of course, the particular selection of the hardening medium fluid, especially in the latter category, is dependent on the type of final curing step. For example, if final curing of the mold and removal of the hardening medium clinging to the outside thereof is to be accomplished by ignition or firing, a readily flammable medium will be selected (yet not one such as benzene which produces inordinate amounts of soot upon ignition). Also, if the ultimate curing of the mold is to be accomplished by heating other than ignition, the hardening medium bath is preferably elevated to a temperature substantially above the boiling point of the volatile resultant of the hydrolysis reaction.

Although the exact explanation for the hardening step or contribution in accordance with this invention may not be thoroughly understood with certainty, useful hypothesis may be made from the results actually observed in the practicing of this invention. For example, ageing is definitely effected to an enhanced degree, as compared with immediate contact from the pattern the reaction in the medium, utilizing the same alcohol for the hardening medium as is produced by the hydrolysis reaction of the binder, and in a manner which suggests and is believed to be distinct from merely isolating the mold in its entirety from direct contact with the ambient room atmosphere (as might be done temporarily by covering the mold; or by wrapping the mold in a plastic sheet). Thus, assuming an actual reaction at some point in the process and/or, at least, a distinction between merely isolating the mold from air and maintaining the mold entirely in an atmosphere (liquid or vaporous) substantially identical with the volatile resultant of the binder hydrolysis reaction. Alternatively,
since it is believed that the transition from internally un-stable and semi-rigid gelled structure to the ultimately desired strong finished mold is accelerated by heating (albeit preferably deferred during ageing), the utilization of a hot bath also produces enhanced results even if the bath liquid is not identical with the volatile resultant of the hydrolysis reaction, providing that it is miscible with such volatile resultant. Thus, immersing the gelled mold in boiling water produces the ageing and protective effect desired while also accelerating the ultimate heat curing step, and the temperature of the hot water tends to drive the volatiles out of the mold (where they are dissolved in the water bath) in a manner so that, when the hardened mold is removed from the hot water (or hot hydrocarbons, as the case may be), there are substantially no volatile materials in or on the mold requiring special attention or handling in the heat curing step or other special considerations regarding flammable products in a commercial installation.

Also, as will be apparent from the foregoing, the hardening bath or medium may satisfactorily comprise a mixture of liquids for the purpose of controlling the ultimate volatility thereof, as well as, as noted, a chamber or other enclosure wherein an atmosphere of hardening fluid (e.g., air) or a continuous spray or shower of hardening liquid is maintained. The degree of volatility or flammability of the hardening medium, of course, is selected in accordance with the type of final curing step desired. In many instances, an actual ignition or firing is not to be preferred in some commercial operations, in which event satisfactory results are achieved by removing volatiles and alcohol hardening medium by baking or heating, although this may require special equipment for accommodating and exhausting the volatiles. Using a relatively non-volatile hardening bath (e.g., water or heavier hydrocarbons), it is especially if the bath be heated sufficiently to permit the curing as desired in accordance herewith while also driving most of the volatiles out of the mold for solution in the hardening bath, thus to leave after hardening and ageing a mold which is merely coated on the outside with water in a manner readily and economically to be removed.

As will be understood from the foregoing, the duration of immersion or other enveloping contact of the mold with the hardening medium may not, in all instances, be considered particularly critical in accordance herewith. That is, generally, 10 or 15 minutes of ageing of the gelled mold in a hardening bath produces the noted enhanced results in the ultimate mold structure, although maintaining the gelled mold in overall contact with the hardening medium for a longer time has not been found to be detrimental, either because some additional ageing occurs and/or because the mold is still maintained out of direct and reacting contact with the ambient atmosphere to avoid degradation of the gelled bond even after an enhanced internal stability is achieved. As a matter of operating practicality in commercial installations, of course, the features of this invention permitting an accumulation of a plurality of molds in hardening baths for simultaneous heat curing of all the molds achieve a certain advantage, especially if the ultimate curing step is an oven heating operation, rather than individual firing of the molds. Particularly in the latter instance it is preferred in connection herewith to utilize a heated and relatively non-volatile hardening medium liquid miscible with the volatiles of the hydrolysis reaction to produce a mold which is merely covered on the outside with a layer of water readily to be dried and from which the flammable volatiles have been safely removed in the hardening bath so as to require no ignition or firing. Nevertheless, whether or not the volatiles are actually removed from the mold by solution in the hardening bath or the hardening step be directed merely to maintaining a stable and compatible atmosphere in and around the mold for the ageing thereof, it is primarily an ageing effect for establishing an enhanced internal stabilization of the mold which is of interest here, and not merely isolation of the mold products from the ambient atmosphere, whether this hardening step be accomplished by maintaining the mold completely in a liquid or vaporous atmosphere identical or compatible with the volatile resultant of the hydrolysis reaction or, alternatively, maintaining the mold as actually immersed in a different liquid hardening medium with which evolving volatile materials are readily miscible for the ultimate removal thereof from the mold structure.

It has also been discovered, particularly from observation of actual commercial utilization of this invention, that the desired internal stabilization of the mold resulting in an enhanced ultimate set or cured structure, may be further improved when the pH of the hardening medium bath or atmosphere is maintained at a level somewhat higher than that of the mold and, preferably, on the alkaline side of neutral pH. Especially is this true when the binder component (such as a liquid alkyl silicate) is intentionally maintained on the acid side of neutral pH for purposes of its own stability (as generally taught in this art). Decreasing such acidity (such as by raising the pH of the hardening bath or atmosphere) tends to accelerate the setting and gelation into the desired final form. Therefore the optional addition of an alkaline material to the hardening bath may definitely be preferred in accordance herewith in a variety of applications of this invention. When water is the hardening bath, of course, a variety of alkaline materials are available for such pH control, and, especially when an organic liquid or fluid makes up the hardening bath, liquid "alkaline" materials may advantageously be added to the bath—such as, for example, organic amines or other generally alkaline ammonium compounds. Satisfactory results have been achieved in accordance with this feature of this invention, for example, by the addition of monothanolamine as a pH-controlling material which is readily miscible with virtually all of the liquids or fluids which are useful as the hardening medium in accordance herewith, and when added to the hardening bath sufficiently to raise the pH thereof above at least about 8 for accelerating the rate of setting and curing. Conversely, it is desired to delay the ultimate stabilizing reaction in the mold between gelation and final curing, maintaining the hardening bath at a lower pH satisfactorily produces such desired effect.

As will be apparent from all the foregoing, there are provided in accordance herewith a variety of techniques and compositions for treating ceramic molds of the character here described after the gelation thereof and prior to achieving the final cured condition by maintaining the gelled mold (with or without stripping from the pattern) in an enveloping bath or atmosphere of hardening medium fluid to produce quite important operational latitudes in the commercial production of such ceramic molds, while also enhancing the final structure or internal characteristics of the cured molds. In accordance herewith, such techniques and compositions not only permit varying the time for actual curing after gelation without degrading the final cured bond achieved within the mold (as by isolating the mold from reacting contact with the ambient atmosphere), but there are also provided actual reactive hardening atmospheres for enhancing the rate of ultimate setting as by pH control or maintaining the atmosphere with respect to the volatile materials being evolved within the mold as a result of the hydrolysis or gelling or curing reaction. Similarly, such ageing of the preliminary reactions is achieved in accordance herewith while also removing in a safe or nonhazardous manner the volatile resultant of reactants in the mold and in a manner which may actually remove the necessity for firing the mold at any point during the production thereof.
While the techniques and compositions described herein preferred embodiments of this invention, this invention is not limited to these precise techniques and compositions, and modifications may be made therein without departing from the scope of this invention which is defined in the appended claims.

What is claimed is:

1. In a method for making refractory ceramic casting molds from a slurry of comminuted refractory material and a gelling alkyl silicate binder therefor in which said slurry is poured on a pattern and gelled thereon into semi-rigid form by hydrolysis reaction of said binder forming an alcohol as a resultant of said hydrolysis reaction, the steps which comprise enveloping said mold as poured on said pattern and after at least partial gelation of said binder with a hardening medium fluid in which said alcohol is miscible, retaining said mold enveloped in and surrounded by said hardening medium fluid for a time sufficient to produce internal stabilization and aging of the product structure of said hydrolysis reaction of said binder with said comminuted refractory material for achieving an internal stabilization of said binder and said refractory material into a stable form more rigid than said semi-rigid form achieved on gelation of said binder, and heat-curing said mold to final rigid form thereof with removal from said mold of said hydrolysis reaction product and said hardening medium materials.

2. A method as recited in claim 1 in which said hardening medium fluid comprises an alcohol.

3. A method as recited in claim 1 in which said hardening medium fluid comprises the same alcohol as results from said hydrolysis reaction.

4. A method as recited in claim 1 in which said enveloping of said mold in said hardening medium fluid is effected by immersing said mold in a bath of liquid different from but miscible with said alcohol resultant of said hydrolysis reaction.

5. A method as recited in claim 1 in which said bath is heated to a temperature substantially above the boiling point of said alcohol resultant of said hydrolysis reaction for driving said alcohol resultant out of said mold and into solution in said liquid bath.

6. A method as recited in claim 1 in which said enveloping of said mold with said hardening medium fluid is effected by immersing said mold in a liquid bath of said hardening medium fluid.

7. A method as recited in claim 1 in which said gelled mold is stripped from said pattern prior to said immersion in said bath.

8. A method as recited in claim 1 in which said enveloping of said mold with said hardening medium fluid is effected by placing said gelled mold in an enclosure in which there is maintained an atmosphere of said hardening medium fluid in vaporized form.

9. A method as recited in claim 1 in which said enveloping of said mold with said hardening medium fluid is
effected by placing said mold in an enclosure in which there is maintained an atmosphere of sprayed droplets of said hardening medium fluid.

10. A method as recited in claim 1 in which said heat-curing of said mold is effected by igniting and firing flammable or volatile materials thereon including said alcohol resultant of said hydrolysis reaction and remnants of said hardening medium fluid.

11. A method as recited in claim 1 in which said heat-curing of said mold is effected by heating said mold after removal from said hardening medium fluid for eliminating from said mold said alcohol resultant of said hydrolysis reaction and remnants of said hardening medium fluid.

12. A method as recited in claim 1 in which said mold is maintained as enveloped and surrounded by said hardening medium fluid for at least 10–15 minutes after said gelation of said binder in said mold and prior to said heat-curing thereof.

13. A method as recited in claim 1 in which said hardening medium fluid consists essentially of a material selected from the group consisting of alcohol, aromatic and aliphatic hydrocarbons, acetone, water, and mixtures thereof.

14. A method as recited in claim 1 in which said hardening medium fluid also contains admixed therein a material for providing a pH different from that of said hydrolysis reaction in said mold.

15. A method as recited in claim 1 in which said hardening medium fluid also contains admixed therein a material for providing a pH substantially greater than that of said hydrolysis reaction in said mold.

16. A method as recited in claim 1 in which said hardening medium fluid also contains admixed therein an organic amine as a material providing a pH substantially greater than that of said hydrolysis reaction in said mold.

17. A ceramic casting mold of the character described and formed of the reaction product of comminuted refractory material and a gelled and heat-cured alkyl silicate binder material, said mold being further characterized as produced in accordance with a method as recited in claim 1.

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