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PRODUCTION OF SHELL MOLDS

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This invention relates to the production of refractory shell molds, particularly for use in precision casting of metals. The invention provides an improved method of forming such molds on an expendable pattern, and subsequently eliminating the pattern without having to reinforce the mold shell in any way. The invention further provides an improved refractory composition which is advantageously used in making shell molds by the method of the invention; and the shell mold produced by the method and with the composition of the invention is itself a part of the invention.

Refractory molds for making castings which conform accurately in dimension to the original pattern are customarily made by applying a refractory slurry composition to the outer surface of an expendable pattern, allowing such composition to harden about the pattern, and then eliminating the pattern from within the hardened refractory to form a casting mold. The simplest way of eliminating the pattern is to heat it to above its melting or decomposition temperature. However, because the thermal expansivity of the pattern material is usually much greater than that of the refractory material which forms the mold, the mold is subjected to severe stress by so doing. It has therefore been common practice heretofore to strongly reinforce the refractory mold about the pattern before eliminating the pattern by heating to above its fusion or decomposition temperature. The most common reinforcing procedure has been to place the coated pattern in a flask and then form a thick, densely packed body of refractory (termed a secondary investment) in the flask about the hardened refractory coating (the so-called primary investment) which surrounds the pattern. The resulting reinforcement of the primary investment permits heating it and the pattern material within it to a high enough temperature to melt, volatilize, or decompose and burn away the pattern material without injury to the refractory mold. It results, however, in a bulky mold which is slow to heat for pattern elimination and preparatory to casting, and which is time consuming and costly to prepare, and which is relatively difficult to break away from the completed casting.

Various procedures have been proposed heretofore to minimize or avoid the necessity for reinforcement of the primary investment preparatory to eliminating the pattern. One such procedure is to make the pattern of a material having a very low thermal coefficient of expansion. Mercury is such a material; and when a shell mold is formed by coating a frozen mercury pattern with a hardenable refractory composition, the mercury can be melted from within the hardened shell mold with but little external reinforcement of the latter. This procedure is subject to the serious disadvantage that the pattern must be made and handled at very low temperatures, far below the freezing point of water. Moreover, the corresponding low temperature at which the refractory slurry must be applied to the pattern and then hardened about it imposes severe limitations on the materials that can be used in forming the refractory investment composition.

Another procedure which has been devised to minimize the need for reinforcing the hardened primary investment once it has been formed about the pattern, is to eliminate the pattern by dissolving it in a suitable solvent. For instance, wax is readily soluble in a wide range of organic liquids, and a procedure has been devised for making shell molds by applying the primary investment to a wax pattern, and then eliminating the pattern from within the hardened investment by dissolving it in a solvent operation analogous to vapor degreasing. While this procedure eliminates the expense and difficulty incident to reinforcing the primary investment, it does so at the expense of substituting a relatively cumbersome pattern elimination procedure.

It is of course advantageous to use as the pattern material a substance which can easily be formed at moderate temperatures and which can be eliminated from the mold formed about it by heating to a modest elevated temperature. Generally speaking, the pattern materials which are most convenient and economical to employ are waxes, resinous plastic compositions, nad so-called fusible metals having a melting temperature not far above room temperature. The present invention contemplates the use of such convenient pattern materials, and makes it possible to eliminate patterns of such material from within an unreinforced shell mold by so making the shell mold as to impart to it a high degree of mechanical strength at the temperatures at which the pattern material is eliminated. This result is achieved by making the shell mold of a refractory composition in which the bonding agent is an aqueous sol containing colloidally dispersed silica, and preferably also containing a dispersed resinous polymer. (Throughout this specification the word "dispersed," as applied to resinous polymers, includes dissolved polymers as well as polymers dispersed colloidally.)

I have found that by applying a number of coats of such a composition to a pattern, allowing a sufficient time between the application of each coat for the preceding coat to harden, the resulting refractory shell is adequately strong to resist normal handling and the stresses incident to heating to the temperature necessary to eliminate the pattern without any external reinforcement. The shell thus produced resists cracking and other damage even when the pattern is a wax having a thermal coefficient of expansion much greater than that of the shell refractory and is eliminated by heating to a temperature at which the wax melts. It is necessary, in order to make the shell adequately strong, to apply a multiple number of coats of refractory to the pattern before the pattern is eliminated. At least three coats should be applied, and preferably the shell is built up of six or more successively applied coats of the refractory composition.

The method of making a high-strength refractory shell mold in accordance with this invention accordingly comprises repeatedly coating an expendable pattern with a slurry of finely-divided refractory suspended in an aqueous sol containing colloidally dispersed silica, and allowing the coating to harden on the pattern, until a refractory shell of substantial thickness has been built up on the pattern. Preferably each coating is "sanded," that is it is sprinkled while still wet with relatively coarse refractory particles which embed themselves in the coaing and provide a rough surface to which the next succeeding coating can easily become bonded. After the final coating has been applied and hardened, the shell is heated without any external reinforcement to an elevated temperature high enough to eliminate the pattern. The resulting shell mold is employed in the usual manner as a mold in which to cast the molten metal.

The refractory suspended in the slurry, particularly for the second and subsequent coats, preferably is a mixture of very fine particles with relatively coarse refractory particles. Most advantageously it comprises from 30% to 70% by weight minus 270-mesh particles and the balance predominantly plus 200-mesh particles (mesh sizes stated

herein are those of the U.S. standard screen series). The aqueous sol vehicle in which the refractory is suspended contains (on a dry basis, that is by weight of the active sol ingredients, excluding water and other volatile solvents and diluents) from 60% to 80% by weight of colloidally dispersed silica, and from 8% to 35% by weight of a resinous polymer. Advantageously, the sol vehicle also includes a thickening or film-forming agent (in an amount from 0.5% to 10% on a dry basis) and a wetting agent (in an amount from 1% to 15% on a dry basis), both of which contribute to holding the finely-divided refractory solid in suspension.

Percentage composition figures given above and throughout this specification for the sol vehicle are expressed on a dry basis. That is, they state (in percent) the proportion by weight that each dispersed or dissolved active constituent of the sol bears to the total amount of all such dispersed or dissolved constituents. These percentage figures therefore are independent of the amount of volatile liquid in which the active ingredients are dispersed.

Shell molds produced in accordance with the invention, using a composition of the character described, are remarkably strong even in the "green" state (i.e., in the air dried and hardened state prior to firing to a high temperature). They are amply strong to enable a wax pattern having a thermal coefficient of expansion much higher than that of the refractory shell itself to be eliminated by fast heating of the shell without any external reinforcement to the shell. Such shells, made of the preferred composition of this invention, comprise finely-divided particles of a refractory material bonded into a unitary structure by a composition of 60% to 80% by weight silica of substantially colloidal fineness, and 8% to 35% by weight of a resinous polymer. The resinous polymer provides a low temperature bond which imparts notably high strength to the mold in the air-dried condition, enabling it to withstand the handling it is subjected to in commercial operations. Furthermore, when the mold is fired, the polymer is burned out and leaves the mold shell readily permeable by gases. The resulting finely permeable shell structure is admirably suited to making castings free from surface defects.

It has been proposed heretofore to employ silica colloidally dispersed in an aqueous sol as the bonding agent for the refractory composition in the formation of casting molds. In such prior proposals the silica sol has merely been a substitute for other available refractory bonding agents, such for example as organic silicate solutions and suspensions of finely-divided (but not colloidal) silica in phosphoric acid solution. No commercially acceptable procedure has been known for producing shell molds from such compositions which are consistently strong enough to withstand the stresses involved in eliminating a wax or similar pattern by heating to a moderately elevated temperature. Prior proposals involving the use of colloidal silica as the refractory bonding agent have therefore followed the heretofore known practices of either heavily reinforcing the primary investment formed of such material about the pattern before eliminating the pattern, or else employing some special pattern eliminating procedure such as dissolving the pattern material in a solvent. The use of aqueous silica sols as the bonding agents in refractory compositions used in making shell molds on frozen mercury patterns has of course not been proposed or used because at the low temperatures involved such sols freeze.

Following is a detailed description of a preferred embodiment of this invention, and of modifications that can be made without departing from the invention:

An accurate pattern of the article to be cast is first made by any desired procedure, preferably using wax, or a thermoplastic or thermosetting resinous polymer, or a metal having a low melting point, as the pattern material. It is characteristic of the invention that the pattern material be one which can be handled readily at ordinary room temperature. Preferably a low-shrinking wax composition is used as the pattern material.

The first step in forming the mold entails applying a number of coats of the refractory composition to the pattern. The refractory composition is a liquid suspension of finely-divided refractory particles and may be applied to the pattern by any of the methods usually employed. A particularly easy and satisfactory procedure is by dipping the pattern beneath the surface of a body of the refractory composition in a suitable container (a procedure known as "dip coating"). When the pattern is withdrawn from the body of coating material, a layer of the coating composition adheres to it. The composition may alternatively be applied by such procedures as painting it on the pattern, or spraying it thereon.

The coating composition is formed by suspending a finely-divided refractory material in an aqueous sol containing colloidally dispersed silica. Any of the commercially available aqueous silica sols may be employed. Such sols may be prepared by separating the base ion from an alkali metal or ammonium silicate solution under conditions which retain the silica in colloidally dispersed form. As available commercially, these sols normally contain 30% or 35% by weight of colloidally dispersed silica, and no more than about 0.4% by weight NaOH or equivalent base. For purposes of this invention, however, the silica content of the sol may be as low as 10% by weight, and sols of such low concentration may be made by diluting the more concentrated sols with water The viscosity of even the more concentrated commercial sols is quite low, and their specific gravity is about 1.2.

Any desired finely-divided refractory may be suspended in the sol, including, but without limitation, zirconium silicate (zircon), zirconium oxide, aluminum oxide (especially fused alumina), silica, grog (crushed or ground fired silica-alumina clay refractories), and chromite. To form a mold having a smooth-surfaced casting cavity and thus to assure the production of castings having good surfaces, the suspended refractory should be very finely divided. For at least the coating composition applied directly in contact with the pattern, the particle size should be at least about 80% minus 270-mesh. It is particularly advantageous to employ very finely divided zircon (90% minus 325-mesh) as the refractory in the coating composition first applied to the pattern. The refractory employed in compositions used for second and subsequent coats in building up the thickness of the shell mold may be somewhat coarser. For optimum results, the refractory content of the second and subsequent coats is a mixture of very fine and relatively coarse particles. A refractory comprising 30% to 70% by weight minus 270-mesh particles and the balance predominantly plus 200-mesh particles is generally preferred. Zircon preferably is employed for the fine refractory component, and a grog for the coarse component.

Zircon is preferred as the very finely-divided refractory used in the coating composition which forms the inner surface of the mold cavity after the pattern has been eliminated, because this material imparts a particularly good surface to the metal casting. It is also advantageously used as the fine refractory component in the composition forming the second and subsequent coats, because its low thermal coefficient of expansion facilitates close control over the dimensions of the casting; and since its coefficient of expansion undergoes no substantial or abrupt change in value over a very wide temperature range, its use aids in avoiding cracking of the shell due to thermal shock. Molten metals can be poured into such molds at a temperature much higher than that of the mold without cracking of the mold. Fused alumina also may be used with notable success in the coating composition. The proportion of refractory solids to liquid sol may be varied over quite wide limits, but in general the

weight of refractory will range from ¼ to 15 times the weight of the sol vehicle.

As indicated above, the sol vehicle, in addition to containing colloidal silica, preferably also contains a dispersed resinous polymer. The presence of this agent notably increases the adhesion of the coating composition to the pattern material, greatly improves the "green" strength of the mold, and improves the water resistance and scratch hardness of the "green" mold. Any resinous polymer capable of being dispersed (colloidally, or by being dissolved) in aqueous media can be used with success, including polyvinyl acetate, the copolymer of vinyl acetate and vinyl chloride, the copolymer of a vinyl compound and an acrylic compound (e.g. vinyl chloride and acrylic acid or acrylonitrile), an acrylic polymer (e.g. polymerized acrylic acid), rubber (both natural and the various synthetics), and methyl cellulose. The resinous polymer is preferably employed in the form of an aqueous latex which can be blended with the silica sol. It is of course preferable to avoid the use of any polymer composition which causes premature gelation of the colloidal silica vehicle. The amount of resinous polymer employed generally is in the range from 8% to 35%, and in preferred compositions in the range from 12% to 25%, by weight of the active dispersed ingredients of the sol vehicle.

The polymer latex normally contains a dispersing agent; but if desired a further quantity of dispersing agent may be incorporated in the sol vehicle, to aid in maintaining the finely-divided refractory in suspension.

It is also desirable to incorporate a wetting agent in the sol vehicle. Any commercially available wetting agent may be employed, generally in an amount in the range from 1% to 15% by weight (on a dry basis), and in preferred compositions from 5% to 10% by weight, of the active ingredients contained in the sol vehicle. Typical wetting agents which can be employed with advantage are sodium lauryl sulfonate, and phosphate compounds of the type $(RO)PO(OR')_2$, in which R is a medium chain alkyl group and R' is a water solubilizing group. Inclusion of the wetting agent is particularly desirable in compositions intended to be used for coating wax patterns, but the wetting agent facilitates close conformity of the coating composition to the surface of any pattern material and thus facilitates formation of a mold which accurately reproduces all details of the pattern.

Another desirable modifying agent to incorporate in the sol vehicle is a thickening or film-forming agent. Gelatin is such an agent, and examples of others that can be used with success are ammonium alginate and carboxymethyl cellulose. Inclusion of such a film-forming agent is of value for holding the refractory solids in suspension. It also promotes the formation of a smooth, accurate mold surface, and cooperates with the resinous polymer to minimize penetration of wax from the pattern into the structure of the mold shell when the wax is heated to eliminate the pattern from the mold. The amount of such film-forming agent employed generally is in the range from 0.5% to 10% by weight (on a dry basis) of the active constituents of the sol vehicle, and in the most preferred compositions is in the range from 1% to 2%.

Still another modifying agent that may be added, if desired, is any conventional anti-foaming agent, such as a dimethylpolysiloxane. An anti-foaming agent is not necessary, but it may be advantageous to minimize any tendency of the composition to foam when subjected to agitation during dip coating operations, and so to avoid inclusion of bubbles in the completed shell mold.

The coating composition is conveniently prepared by mixing suitable quantities of an aqueous silica sol and an aqueous latex or other dispersion of the resinous polymer, and adding to the resulting liquor the desired amounts of thickening or film-forming agent, wetting agent, and anti-foaming agent. These latter modifying agents may also be employed in liquid form (e.g. as aqueous solutions) and in such case are merely stirred into the sol. If added in their normal solid or liquid form, they should of course be water-soluble and agitated in the sol long enough to dissolve therein.

To complete the coating composition, an appropriate amount of the finely-divided solid refractory is stirred into the sol vehicle to form an aqueous suspension. The viscosity of the resulting composition can be varied substantially, as desired. To a considerable extent viscosity of the suspension is determined by the proportion of finely-divided refractory suspended in the sol. It can be modified further by appropriate selection of the resinous polymer, and by the concentration of colloidal solids (particularly the resinous polymer) and the gelatinous film-forming agent in the sol. It is even possible, if desired, to incorporate a thickening agent in the sol vehicle to increase its viscosity, but generally the inclusion of such an agent is unnecessary. As ready for use, the composition is composed of an aqueous liquid vehicle in which the colloidally dispersed silica and the other agents are dissolved or dispersed, with the finely-divided solid refractory suspended in the vehicle. The resulting slurry, as previously indicated, generally will contain from ¼ to 15 parts by weight of finely-divided refractory particles suspended in one part by weight of the sol vehicle. Preferably, and especially in the compositions used to form the second and subsequent coats on the pattern, the refractory is employed in the proportions of 5 to 8 parts by weight per part by weight of sol vehicle. The sol vehicle itself contains (on a dry basis), as colloidally dispersed or dissolved active constituents, from 60% to 80% (and preferably from 65% to 75%) by weight of silica, from 8% to 35% (and preferably from 12% to 25%) by weight of resinous polymer, from 0.5% to 10% (and preferably from 1% to 2%) by weight of film-forming agent, and from 1% to 15% (and preferably from 5% to 10%) by weight of wetting agent.

It is to be noted that the composition of the slurry as a whole is expressed in terms of parts by weight of the suspended refractory particles per part by weight of the liquid sol; whereas the composition of the sol itself, insofar as the active ingredients dispersed in it are concerned, is expressed on a dry basis. (i.e., by excluding the water or other volatile liquid in which the active ingredients are dispersed). Thus the weight of active ingredients plus liquid in which they are dispersed are included in the total weight of the slurry for the purpose of expressing the proportion by weight of the slurry that is vehicle and the proportion by weight that is suspended refractory solids; but for the purpose of expressing the proportion by weight of the dissolved or colloidally dispersed substances in the sol vehicle considered by itself, the weight of the water or other volatile liquid in the sol is deducted from its total weight and the proportions expressed as percentages of the remaining weight of active ingredients.

Viscosity of the coating composition should of course be adjusted to the value best suited for the mode in which it is to be applied to the pattern. If the composition is to be sprayed on the pattern, its viscosity should be quite low; but it may be of substantially greater viscosity if it is to be painted or applied by dip coating the pattern. The greater the viscosity, the thicker will be the coat of composition which adheres to the pattern.

If, as is generally preferred, the refractory composition is applied by dip coating, the pattern is immersed in a vessel containing an adequate depth of the coating composition and then is lifted out and held for a brief time over the vessel while excess composition drains off. The coated pattern is then set aside until the coating has hardened. Hardening occurs in consequence of evaporation of water from the sol vehicle, with the result that the dispersed colloidal constiutents of the sol coagulate and bond the finely-divided refractory particles together. Hardening proceeds reasonably rapidly at room tempera-

ture (about 70° C.), but the coated pattern may be held at a somewhat higher temperature to accelerate the hardening process if desired. Relative humidity of the atmosphere also affects the rate of hardening—a high humidity tends to retard it, while a low humidity tends to increase it. In a typical case, the coatnig will harden quite completely in a period of 1 to 2 hours at a temperature of 70° F., and a relative humidity of 50%.

It is desirable to "sand" the coating on the pattern while the coating is still wet. "Sanding" involves sprinkling the surface of the coating with relatively coarse particles of refractory. These particles penetrate partially below the surface of the still-wet coating, and promote bonding of the first-applied coating to the next coating applied thereover.

The first coating composition applied to the pattern is preferably one in which the suspended refractory is very finely-divided zircon, advantageously 90% or more minus 325-mesh. This refractory forms an exceptionally fine mold surface and has a very low coefficient of thermal expansion. It therefore aids in forming a mold shell in which castings of very accurate dimensions can be made. However, it is not necessary that the refractory of even the first coat be zircon. Satisfactory results have been obtained using other finely-divided refractories, e.g. fused alumina the particles of which are 80% or more minus 270-mesh; and even silica having particles 75% or more minus 270-mesh may be used when the metal to be cast does not have a very high melting point. Blended refractories, such as a blend of zircon and silica, may be used in place of a single refractory compound.

After the first coating on the pattern has hardened, a second coat of the refractory composition is appplied. As in the case of the first coating, the second coating may be applied by spraying, painting or dipping, though generally dip coating is most convenient and is preferred. This second coating, like the first, is advantageously sanded while still wet, and the pattern which it covers is then set aside while it hardens. After it has hardened, a third coating is applied, and the sequence of operations is repeated until a sufficient number of coats of refractory composition have been applied to build up a shell of desired thickness.

The second and subsequent coating compositions may with advantage contain suspended refractory of somewhat greater particle size than is optimum for the first coating. For example, the refractory employed in the second and subsequent coating compositions may be a fused alumina, or a grog, or preferably a mixture of a very fine refractory such as zircon with a relatively coarse grog. In some cases ground flint or other form of silica may be used.

The refractory with which each coating (except the last) is "sanded" should of course be considerably coarser than the refractory suspended in the coating composition. Particularly advantageous sanding refractories are fused alumina and grog ground fine enough to pass a 60-mesh screen, but preferably not over about 20% minus 200-mesh. The thermal expansivity of the sanding material of course affects the expansion characteristics of the shell, and it is desirable to select as sanding material a refractory having a coefficient of thermal expansion which is not too dissimilar from that of the refractory suspended in the coating composition.

In order to build up a refractory shell of maximum strength, it is desirable (though not necessary) to wet each coating on the pattern, after it has hardened and immediately prior to applying the next coating, with an aqueous sol of substantially the composition of the vehicle used in making the refractory composition, but containing no suspended non-colloidal refractory particles. Wetting the hardened coating with the thin (non-viscous) sol notably improves the adhesion of the succeeding coating to the previous already hardened coating, and it helps to eliminate air pockets between successively applied coatings. In both of these ways such wetting contributes to formation of a strong refractory shell.

Generally speaking, at least three successive coats of the refractory composition are required to build up a shell of adequate mechanical strength. Preferably, six or more coats of refractory are applied successively to the pattern, each coat being allowed to harden quite completely before the succeeding coat is applied. The thickness of the shell is about ⅛ inch or more after the final coat of refractory composition has been applied.

After the final refractory coating has been applied and allowed to harden, the pattern is eliminated from within the resulting shell. This is accomplished in accordance with the invention without having to reinforce the shell externally in any way. The shell formed by application to a pattern of a multiple number of coats of refractory composition bonded with colloidal silica, with hardening of each coat before the next is applied, has proved to be adequately strong to resist cracking and other injuries even when a wax pattern is eliminated from within it by heating to a temperature at which the wax fuses. Since elimination of the pattern by heating to a moderately elevated temperature is the most convenient procedure, it is the procedure which is preferably followed in accordance with the invention. If the pattern is of wax, as it preferably is, the pattern with the hardened refractory thereon is placed in an oven or in other apparatus in which it is heated to a temperature high enough for the wax to liquefy and drain from within the refractory shell. If the pattern is of a resinous thermoplastic composition, it is similarly heated. If the pattern is of fusible metal, it is heated to above the melting temperature of the metal.

While it is preferred to eliminate the pattern by heating the pattern material to above the fusion temperature, other pattern elimination procedures may if desired be employed (for example, the pattern may be extracted by a liquid or vapor solvent). However, these alternative pattern elimination procedures generally have disadvantages which make them less desirable to employ than is simple fusion of the pattern material, and some of the advantages of the invention may be lost by adopting them.

In the case of fusible metal patterns, the gating should be adequate for complete drainage of the metal from within the shell. If the pattern is of wax or of a resinous plastic material, a residue of pattern material may remain in the shell and must be eliminated by heating to a high enough temperature to volatilize or decompose it. Moreover, even when the pattern is of fusible metal, the hardened shell contains organic constituents which must be eliminated before the shell is used as a casting mold. In any case, therefore, after so much as possible of the pattern material has been eliminated by melting and draining, the shell with such residue of pattern material as still clings to it is heated to a high enough temperature to volatilize or decompose both the residue of pattern material and the organic constituents of the shell itself, i.e. the resinous polymer, the film-forming agent, the wetting agent, the anti-foaming agent, and any other organic agents present. For this purpose the shell is brought to a temperature upwards of 1000° F. or 1200° F. The furnace atmosphere during such heating may with advantage be oxidizing to facilitate complete burning of the last traces of the organics. Elimination of the resin (and other organic agents) from the body of the shell renders the shell structure very finely porous. This is an advantage in that it facilitates escape of gases and vapors during the casting operation and so aids in formation of a casting free from surface blemishes. At the relatively high temperature to which the shell is heated to assure substantially complete elimination of the organics, a strong bond between the particles of refractory material with the siliceous residue of the sol vehicle is achieved.

After the shell has been completely freed from residues of pattern material and from the organic materials originally present in the coating composition, it is mounted in position to receive molten metal and is heated to the proper temperature for casting. Molten metal is poured into the shell, and then is allowed to solidify, in accordance with conventional precision casting practice. Very satisfactory castings of high melting point metals, such as stainless steels, high cobalt alloys, refractory alloys of nickel and chromium, etc., have been made in shell molds made as described above. Excellent castings also have been made of lower melting point alloys, such as brasses, bronzes and aluminum. After the casting has solidified in the shell, the latter is broken away. An advantage of some consequence obtained when using shell molds according to the invention is that the mold material breaks readily and cleanly away from the casting, making final cleaning of the casting remarkably easy.

Following are specific examples of the invention herein described:

Example 1.—A vehicle for a coating composition was prepared by mixing 11,250 parts by volume of a silica sol (specific gravity 1.20) containing 30% by weight of colloidally dispersed silica with 1688 parts by volume of an aqueous latex-like dispersion of polyvinyl acetate (specific gravity 1.09) containing 55% by weight of the polymer. A 6.8% aqueous solution of ammonium alginate (specific gravity 1.00), in the amount of 1406 parts by volume, together with 450 parts by volume of an undiluted liquid phosphate type wetting agent (specific gravity 1.10) and 88 parts by volume of a 6% solution (specific gravity 1.00) of dimethylpolysiloxane (an anti-foaming agent) were added to the silica-polymer sol. The resulting aqueous vehicle was of quite low viscosity and contained (on a dry basis) approximately 71.6% by weight of silica, 17.8% by weight of polyvinyl acetate, 1.6% by weight of ammonium alginate, 8.6% by weight of the wetting agent, and approximately 0.9% by weight of dimethylpolysiloxane was also added as an anti-foaming agent. (The "dry basis" composition of the sol vehicle is determined as follows: The silica sol, being 30% by weight silica and having a specific gravity of 1.20, contains $0.3\times1.20\times11{,}250=4{,}050$ parts by weight silica. The polyvinyl acetate dispersion contains $0.55\times1.09\times1688=1{,}012$ parts by weight of polymer. The ammonium alginate solution contains $0.068\times1.00\times1406=95.6$ parts by weight of dispersed ammonium alginate. The wetting agent amounted to $1.10\times450=495$ parts by weight, and the anti-foaming agent amounted to $0.06\times1.00\times88=5.3$ parts by weight of dimethylpolysiloxane. Thus the total quantity of solids, on a dry basis, in the vehicle, was $4050+1012+95.6+495+5.2=5657.9$ parts by weight. The amount of silica in the sol vehicle, expressed on a dry basis, therefore, was $4050\div5657.9\times100=71.6\%$, and the other percentage figures, expressed on a dry basis, were similarly computed.)

A first dipcoat composition was prepared by suspending ½ part by weight of finely milled zircon (90% minus 325-mesh) in one part by weight of the above-described vehicle. A second dipcoat composition was prepared by suspending 3 parts by weight of finely milled zircon (90% minus 325-mesh) and 3 parts by weight of grog (99% minus 60-mesh, 20% minus 200-mesh) in one part by weight of sol in the above-described sol vehicle.

A wax pattern was given an initial refractory coating dipping it beneath the surface of a body of the above-described first dipcoat composition. The pattern was then removed from the solution, allowed to drain, and "sanded" by sprinkling with fused alumina having a screen analysis showing 95% minus 100-mesh, 93% plus 200-mesh. The sanded coating was allowed to harden by standing in air at room temperature and about 50% relative humidity for an hour. After hardening, the coating was wetted with the above-described vehicle, and while thus wetted a second coat of refractory composition was applied by dipping beneath the surface of a body of the second dipcoat composition described above. After removal of the pattern, and while the second coat was still wet, it was "sanded" by sprinkling with a fire clay grog having a screen analysis of 90% minus 60-mesh, 20% plus 200-mesh. The second dipcoat composition was then allowed to harden at room temperature and about 50% relative humidity for an hour. A third coat of refractory was then applied by repeating the procedure for the second coat, and fourth, fifth and sixth coats of refractory were similarly applied, except that the sixth coat was not sanded.

After the final coat of refractory composition had hardened, the shell on the wax pattern was approximately ⅛ inch thick, and remarkably hard and scratch-resistant. At the same time, it possessed a notable degree of toughness and a measure of elasticity. The shell-covered pattern was heated in an oven to a temperature of about 250° F., at which temperature the wax pattern melted and ran easily from within the refractory shell. The refractory withstood the stresses due to thermal expansion of the wax without cracking or showing any other sign of damage or deformation. After as much wax had been removed as would flow out in liquid form, the shell was heated to a temperature of about 1200° F. in an oxidizing furnace atmosphere. As a result of such heating, the last traces of wax pattern material, and the resin, the ammonium alginate, the wetting agent, and the anti-foaming agent were all completely vaporized or decomposed and thus eliminated from the residual refractory shell.

The shell was then heated to a temperature of approximately 1800° F., and a casting was made by pouring a molten stainless steel (18% chromium, 8% nickel, balance iron) into the shell cavity. The metal and the shell mold containing it were then cooled to near room temperature, and the shell was removed by breaking it from the solidified metal casting. The shell broke readily and separated cleanly from the metal, and the metal casting was found to have a fine, smooth surface, free from blemishes.

Example 2.—Castings were made by the procedure described in Example 1, but using dipcoat compositions prepared with a vehicle made by mixing 76 parts by volume of a silica sol containing 30% by weight of colloidal silica with 12 parts by volume of an acrylic polymer latex containing approximately 47% by weight of the polymer. To the resulting sol 10 parts by volume of 5% ammonium alginate solution and 2 parts by volume of a phosphate type of wetting agent were added. A dipcoat composition was prepared by suspending 450 parts by weight of finely milled zircon in 130 parts by weight of the liquid vehicle (a ratio of about 3.5 parts by weight of suspended refractory per part by weight of vehicle).

Example 3.—Castings were prepared in the manner described in Example 1, in shell molds made by applying to a wax pattern a multiple number of coats of a refractory coating composition of the character described in Example 2, except that the polymer used was an aqueous latex containing 43% by weight of a vinyl chloride-acrylic acid copolymer.

Example 4.—A dipcoat composition similar to that described in Example 3, but made using 12 parts by volume of a rubber latex containing 60% by weight of rubber instead of the acrylic polymer latex, was used to make shell molds as described in Example 1.

Example 5.—A dipcoat vehicle was prepared by mixing 1940 parts by volume of a silica sol containing 13% by weight of colloidal silica with 50 parts by volume of an aqueous solution containing 7½% by weight of sodium lauryl sulfonate (a wetting agent). Finely ground flint, 99% minus 200-mesh, was suspended in the above-described vehicle in the proportions of about 2 parts by weight of flint per part by weight of vehicle. A shell mold was formed by applying six successive coats of this refractory composition about a wax pattern. Each coat

was applied by dipping the pattern beneath the surface of the body of the composition, and then allowing the adhering coating to harden at atmospheric temperature. Each coat was "sanded" immediately after its application about the pattern with a fire clay grog ground to minus 60-mesh. After the final coat had been applied, the pattern was eliminated and a casting made in the manner described in Example 1. The shell mold prepared in accordance with this example was hard and scratch resistant, and although perhaps somewhat less resilient and tough than shell molds made from the compositions of the other examples, it proved adequately strong to resist damage during handling or elimination of the pattern.

We claim:

1. A composition for making a high-strength refractory shell mold by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ to 15 parts by weight of finely-divided solid refractory material suspended in 1 part by weight of an aqueous sol, said sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer.

2. A composition for making a high-strength refractory shell mold by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ part to 15 parts by weight of finely-divided refractory material suspended in 1 part by weight of an aqueous sol, said aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica, from 8% to 35% by weight of a resinous polymer, and from 0.5% to 10% by weight of a film-forming agent.

3. A composition for making a high-strength refractory shell mold by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ part to 15 parts by weight of finely-divided refractory material suspended in 1 part by weight of an aqueous sol, said aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica, from 8% to 35% by weight of a resinous polymer, from 0.5% to 10% by weight of a film-forming agent, and from 1% to 15% by weight of a wetting agent.

4. A composition for making a high-strength refractory shell mold by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ part to 15 parts by weight of finely-divided refractory material suspended in 1 part by weight of an aqueous sol, said aqueous sol containing (on a dry basis) from 65% to 75% by weight of colloidally dispersed silica, from 12% to 25% by weight of a resinous polymer, from 1% to 2% by weight of a gelatinous film-forming agent, and from 5 to 10% by weight of a wetting agent.

5. A composition for making a high-strength fine-surfaced refractory shell mold for precision casting by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ part to 15 parts by weight of finely-divided zircon suspended in 1 part by weight of a aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer.

6. A composition for making a high-strength refractory shell mold by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ to 15 parts by weight of finely-divided solid refractory suspended in 1 part by weight of an aqueous sol, said refractory comprising from 30% to 70% by weight minus 270-mesh particles and the balance predominantly plus 200-mesh particles, and said sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer.

7. A composition for making a high-strength refractory shell mold by coating on an expendable pattern, said composition being a fluid slurry consisting essentially of from ¼ to 15 parts by weight of finely-divided refractory suspended in 1 part by weight of an aqueous sol, said refractory comprising from 30% to 70% by weight of minus 325-mesh zircon particles and the balance predominantly plus 200-mesh grog particles, and said sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer.

8. The method of making a high-strength refractory shell mold which comprises coating an expendable pattern with a fluid slurry of finely-divided refractory suspended in an aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer, allowing the coating to harden on the pattern, wetting the hardened coating with an aqueous sol containing colloidal silica and substantially free of suspended non-colloidal refractory, then further roating the resulting wetted surface with a slurry of finely-divided refractory suspended in an aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer, allowing said further coating to harden, and thereafter eliminating the pattern from within the resulting hardened refractory shell.

9. The method of making a high-strength refractory shell mold which comprises coating an expendable pattern with a fluid slurry of finely-divided refractory suspended in an aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer, applying relatively coarse grains of refractory to the surface of the coating while it is still wet and soft, allowing the coating to harden on the pattern, wetting the hardened coating with an aqueous sol containing colloidal silica and substantially free of suspended non-colloidal refractory, then further coating the resulting wetted surface with a slurry of finely-divided refractory suspended in an aqueoust sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer, allowing said further coating to harden, and thereafter eliminating the pattern from within the resulting hardened refractory shell.

10. The method of making a high-strength smooth-surfaced refractory shell mold for precision casting which comprises coating an expendable pattern with a fluid slurry of very finely-divided zircon suspended in an aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica, and from 8% to 35% by weight of a resinous polymer allowing the coating to harden on the pattern, then applying a further coating of a slurry of finely-divided refractory comprising from 30% to 70% by weight minus 325-mesh zircon particles and the balance predominantly plus 200-mesh grog particles suspended in an aqueous sol containing (on a dry basis) from 60% to 80% by weight of colloidally dispersed silica and from 8% to 35% by weight of a resinous polymer, allowing such further coating to harden to form a shell of substantial thickness about the pattern, and then heating the resulting hardened shell without external reinforcement to an elevated temperature high enough to eliminate the pattern and to drive off the resinous polymer.

11. A shell mold having sufficiently high green strength to enable a wax pattern to be eliminated from within it by melting without external reinforcement, comprising from ¼ to 15 parts by weight of a refractory bonded by 1 part by weight of a composition (on a dry basis) of 60% to 80% by weight of silica of colloidal fineness and 8% to 35% by weight of a resinous polymer.

12. A shell mold having sufficiently high green strength to enable a wax pattern to be eliminated from within it by melting without external reinforcement, and adapted upon elimination of the pattern to be left with a fine-surfaced mold cavity for forming a precise cast of the pattern, comprising from ¼ to 15 parts by weight of

finely-divided zircon bonded by 1 part by weight of a composition (on a dry basis) of 60% to 80% by weight of silica of colloidal fineness and 8% to 35% by weight of a resinous polymer.

13. A shell mold having sufficiently high green strength to enable a wax pattern to be eliminated from within it by melting without external reinforcement, and adapted upon elimination of the pattern to be left with a fine-surfaced mold cavity for forming a precise cast of the pattern, comprising from ¼ to 15 parts by weight of a refractory comprising finely divided zircon intermixed with relatively less finely divided alumina, said refractory being bonded by 1 part by weight of a composition (on a dry basis) of 60% to 80% by weight of silica of colloidal finess, 8% to 35% by weight of a resinous polymer, and 0.5% to 10% by weight of a film-forming agent.

14. A shell mold having sufficiently high green strength to enable a wax pattern to be eliminated from within it by melting without external reinforcement, comprising from ¼ to 15 parts by weight of a refractory of which from 30% to 70% is minus 325-mesh particles and the

balance is predominantly plus 200-mesh particles, said refractory particles being bonded by 1 part by weight of a composition (on a dry basis) of 60% to 80% by weight of silica of colloidal fineness and 8% to 35% by weight of a resinous polymer.

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