Jan. 21, 1958 E. F. KOHL 2,820,268

METHOD OF MAKING SHELL MOLDS WITH THIN CORE

Filed Sept. 16, 1955 3 Sheets-Sheet 1

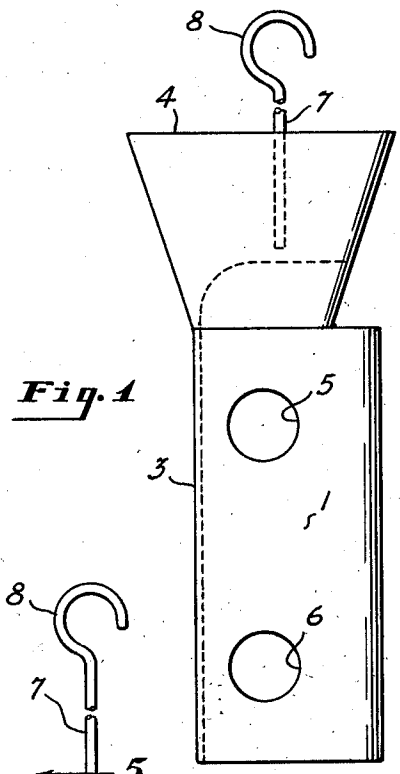


Fig. 1

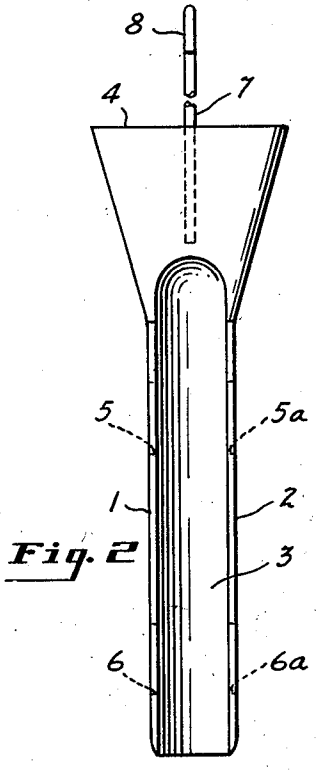


Fig. 2

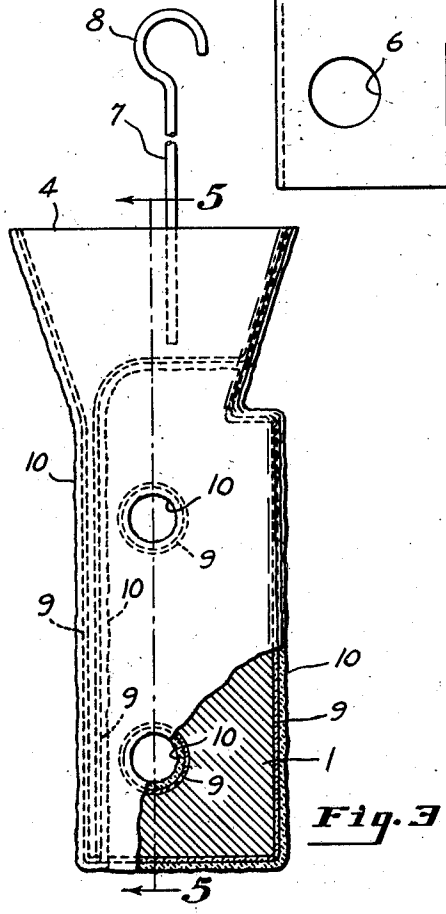


Fig. 3

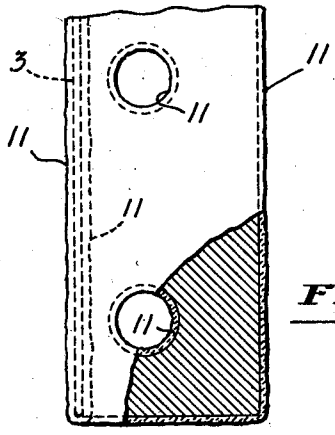


Fig. 4

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METHOD OF MAKING SHELL MOLDS WITH THIN CORE

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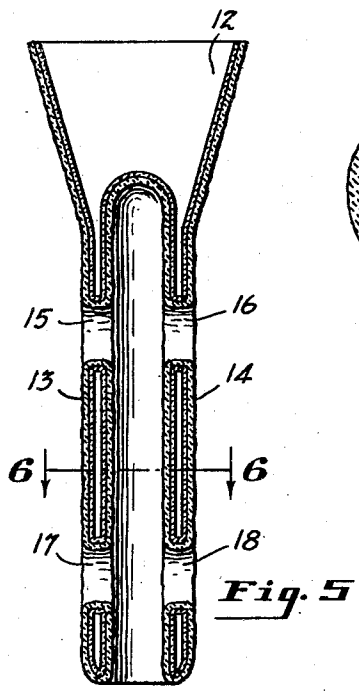


Fig. 5

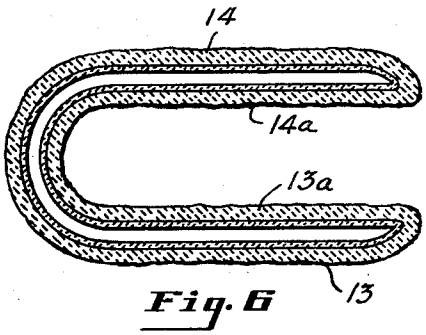


Fig. 6

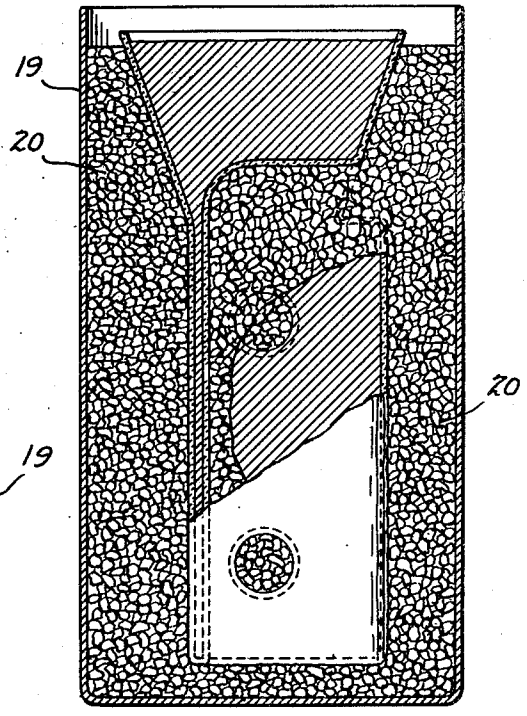


Fig. 8

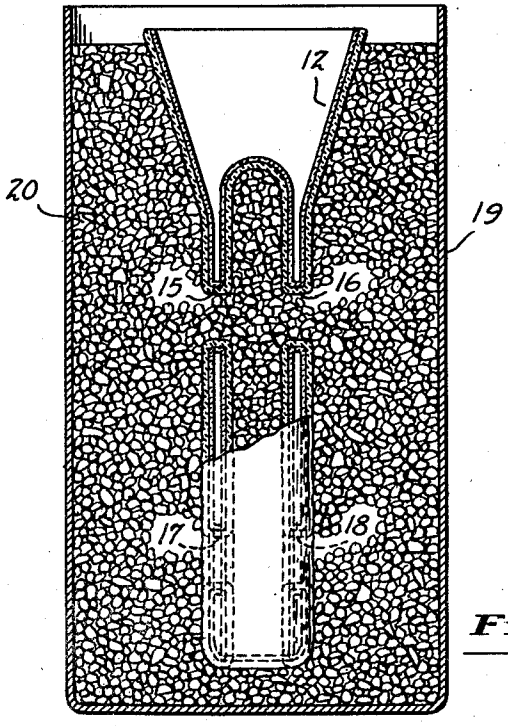


Fig. 7

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METHOD OF MAKING SHELL MOLDS WITH THIN CORE

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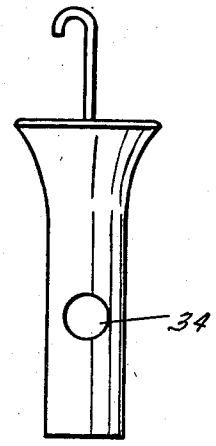


FIG. 9

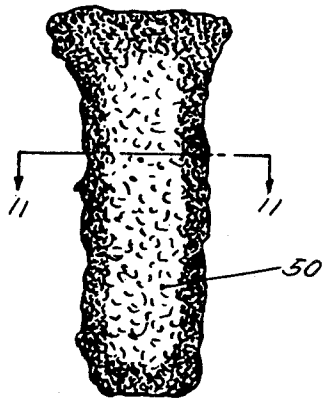


FIG. 10

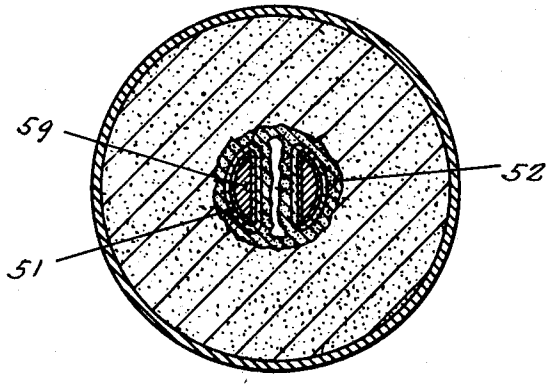


FIG. 11

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2,820,268

METHOD OF MAKING SHELL MOLDS WITH THIN CORE

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Application September 16, 1955, Serial No. 534,667

4 Claims. (Cl. 22—193)

This application is a continuation-in-part of my applications Serial No. 7,953, filed February 12, 1948, and Serial No. 192,002, filed October 25, 1950 both now abandoned.

This invention relates to shell molds and to an improved process of preparing same by means of a frozen mercury pattern of the object to be cast.

As a result of past efforts, there has been developed a commercial method of preparing precision castings by molds made with what is known as the "lost-wax" method. However, the "lost-wax" method of precision casting has many serious limitations. With the "lost-wax" method it is impossible to produce thin-walled porous shell molds with mold cavities of fine surface finish for use in casting metal parts having intricate shapes. Because of the relatively great expansion coefficient of wax-like or plastic patterns, molds formed over such patterns must be of relatively great thickness to resist the large expansion forces of such pattern when the mold and pattern are heated to melting or burning-out temperature of the pattern for removing the pattern from the mold cavity.

In the past, it has been practically impossible to produce metal castings having thin cast-metal walls spaced from each other by a hollow space, such as hollow gas turbine vanes, hollow rifle receiver bodies, or other like metal castings. Thus, when hot metal is cast into a mold cavity having the shape of the desired thin hollow metal body, the molten metal will upon solidifying, contract about the mold core and develop enormous forces. Prior to the invention, the forces developed by the contracting, solidifying molten metal poured into such mold cavities of prior-art thick molds, resulted in most cases in cracking of the casting.

Among objects of the invention is a method of preparing shell molds which make it possible to cast hollow metal articles having thin walls. In accordance with the invention, shell molds suitable for casting thin-walled, hollow metal articles are formed over a frozen mercury pattern of the object to be cast, by applying thereto a liquid slurry of refractory particles with an admixture of a small content of a raised-temperature binder and a low-temperature binder, until there is formed a shell mold wherein—after the raised-temperature binder has been rendered effective—the mold walls around which the cast solidifying metal contracts, will resist the impact of the molten metal cast into it, but will be thin enough to yield when the cast metal contracts about them during cooling.

In the accompanying drawings which are illustrative of specific embodiments of the present invention,

Fig. 1 is a side elevational view of a frozen mercury pattern;

Fig. 2 is a front elevational view of the pattern shown in Fig. 1;

Fig. 3 is an elevational view of the pattern shown in Fig. 1 having a thin inner coating and an outer supporting coating applied thereto;

Fig. 4 is a fragmentary portion of the pattern shown in Fig. 3 having a coating of a refractory material applied thereto of sufficient thickness to provide a shell mold;

Fig. 5 is a cross sectional view of the shell mold formed from the coated pattern shown in Fig. 3 taken on a plane passing through the line 5—5 of Fig. 3 with the pattern material removed;

Fig. 6 is a cross sectional view on an enlarged scale of the shell mold shown in Fig. 5 when taken on a plane passing through the line 6—6 of Fig. 5, looking in the direction of the arrows;

Fig. 7 is a vertical sectional view of a flask having a shell mold suspended therein and showing a refractory material for supporting the shell mold while metal is being cast into the cavity of the mold; and

Fig. 8 is a view similar to that shown in Fig. 7 with metal cast into the mold.

In preparing a shell mold by the present process a frozen mercury pattern of the object to be cast is utilized which may be formed in a permanent partible mold. Frozen mercury in a comparatively pure state is especially suitable although the invention is not to be limited in this respect.

The frozen mercury pattern may, for instance, be of the type shown in Figs. 1 and 2 having portions corresponding to the receiver of a gun. As shown the pattern has side walls 1 and 2 joined together by an arcuate-shaped portion 3, and an upwardly extending sprue 4 for providing a gate. The side wall 1 of the frozen mercury pattern is provided with spaced openings 5 and 6 and the side wall 2 is provided with spaced openings 5*a* and 6*a*, one of which is in alignment with opening 5 and the other of which is in alignment with opening 6. A rod 7 may be embedded in the mercury during the freezing process which is provided with a handle or hook 8 by means of which the frozen mercury pattern may be manipulated during the coating process.

When molten metal of high melting temperature, such as stainless steel alloy, is poured into a mold cavity having the shape of the pattern of Figs. 1 and 2, the metal filling the mold cavity tends to shrink when it cools and solidifies, and the solidifying cast metal contracts around the hollow mold core portions which correspond to the openings 5 and 6 of the pattern.

According to the invention, the difficulties caused by the contraction of the solidifying cast metal around hollow core portions of thin shell molds of the type described above are eliminated by making the thin hollow shell mold core portions thick enough to resist the impact of the cast molten metal while keeping the shell walls of the hollow core mold portions thin enough so that they yield when molten metal contracts about them as the metal solidifies.

To form the thin self-supporting shell molds over frozen mercury patterns of the type shown in Figs. 1 and 2, a slurry-like composition containing refractory particles in a finely divided state is applied to the frozen mercury pattern in the form of one or more films or layers or strata to build up a shell mold, or the inner layer of a shell mold consisting of an inner shaped layer and an outer supporting layer, and if the shell mold is composed of an inner shaped layer and an outer supporting layer, a composition containing refractory particles which are partly in the finely divided state and partly in the form of coarse particles is applied over the inner layer to build up the outer supporting layer.

According to the present invention, the composition that is utilized in preparing the shell mold is in the form of a slurry at temperatures below —40° centigrade, which is the freezing point of mercury, and contains a predominant amount of refractory material in the form of small particles, which may constitute approximately 90% or

more of the solid ingredients of the slurry. The composition must also contain a low temperature binder for the refractory particles which is adherent to the frozen mercury pattern and is effective in binding and is present in an amount sufficient to bind the refractory particles together and to the frozen mercury pattern. The low temperature binder must also be effective in binding and must be present in an amount sufficient to bind the refractory particles together at normal temperatures and to bind the refractory particles and the raised temperature binder to the frozen mercury pattern and the refractory particles and the raised temperature binder together at temperatures ranging from below —40° centigrade up to the temperature at which the raised temperature binder becomes effective in binding the refractory particles together. When a raised temperature binder is present, it is desirable to utilize a low temperature binder that is capable of at least partially volatilizing, decomposing and volatilizing, or becoming otherwise modified to provide a vapor for producing a porous mold when the shell mold is heated to a temperature above that at which the raised temperature binder becomes effective in binding the refractory particles together, such as at temperatures ranging from approximately 590° to 1250° centigrade.

As the refractory material, any suitable material that is capable of resisting high temperatures which may be prepared in the form of small particles may be utilized, such as silica, zirconia, zirconium silicate, magnesium oxide, chromite, alumina, ground quartz, graphite, flint, silicon carbide, an aluminum silicate, such as sillimanite, or a mixture of two or more of such materials, or a mixture of magnesium oxide and calcium oxide, may be employed. In preparing most shell molds, a silicious material, such as silica or zirconium silicate, or a combination of silica and zirconium silicate, is desirable.

In preparing the slurry for forming the inner layer of a shell mold, the refractory material should be of a sufficiently fine texture so that when metal is cast into the shell mold, a casting having a smooth surface will be obtained. The particular size of the refractory material, however, may be widely varied and will depend upon the size and intricacy of the castings to be produced and the requirements with respect to surface. For instance, —60 mesh particles size may be utilized. Extremely fine particles, such as —1000 mesh size, however, adversely affect the porosity of the mold. A comparatively smooth cavity surface will be obtained even with refractory particles of —140 mesh to —325 mesh.

As the low temperature binder, an organic material consisting predominantly of carbon and hydrogen but which contains some oxygen atoms may be utilized, such as polymerized n-butyl-methacrylate, high or low viscosity polymerized isobutylmethacrylate, polymerized vinyl acetate, or ethyl cellulose that has been ethylated to an extent of 46.5% or more. For instance, an ethyl cellulose that has been ethylated to an extent of 46.5% to 48.5% may be employed. An organic material consisting predominantly of carbon and hydrogen but which contains some nitrogen atoms is also effective, such as the copolymers of acrylonitrile and butadiene ranging in proportions from approximately 33% acrylonitrile and 67% butadiene to 40% acrylonitrile and 60% butadiene. A mixture of two or more of the binders may also be utilized. When polymerized isobutylmethacrylate is employed as the binder, the high viscosity type has proven particularly effective.

When any one of the low temperature binders mentioned, or a combination of two or more of them, is present in the coating composition in an amount ranging from .25% to 5% of the weight of the normally solid ingredients in the slurry which form the applied coating after the liquid carrier volatilizes, the low temperature binder should be present in an amount sufficient to bind the refractory particles to the frozen mercury pattern, and if a raised temperature binder is present, the low temperature binder should be present in an amount sufficient to bind the refractory particles and the raised temperature binder to the frozen mercury pattern and to bind the refractory particles and the raised temperature binder together up to the temperature at which the raised temperature binder becomes effective as a binder for the refractory particles.

Certain of the binders mentioned, however, have particular properties which render them especially desirable in certain applications. In this connection, it may be stated that in subjecting patterns that have been coated with the slurry at low temperatures to the air at normal temperature or in melting frozen mercury patterns from shell molds formed by applying the slurry to a frozen mercury pattern to provide or build up the shell mold, moisture in the air condenses on the cold shell mold which tends to soften it. When ethyl cellulose is utilized alone as the binder for the refractory material or in combination with one or more of the other binders in proportions of 50% or more, however, the shell mold is not affected by the condensed moisture.

When it is desired to impregnate the shell mold with a binder that becomes effective at intermediately high temperatures in the form of an aqueous solution, polymerized vinyl acetate or the copolymers of acrylonitrile and butadiene are especially suitable as a binder for the refractory material because they permit the shell mold to take up the solution to a greater extent than the other binders. The copolymers of acrylonitrile and butadiene also have the distinct advantage that they volatilize, decompose and volatilize, or become otherwise modified to provide vapors for producing a porous mold, at higher temperatures than the other binders mentioned and consequently molds in which the copolymers of acrylonitrile and butadiene are utilized as a binder for the refractory material are strong throughout the entire baking or firing range when the raised temperature binder becomes effective as a binder for the refractory particles below or at approximately 595° centigrade.

In preparing the slurry, a liquid is utilized which acts as a carrier for the refractory material and the binder, or mixture of binders, which liquid may be a solvent or a partial solvent for the low temperature binder. A liquid having a comparatively low boiling point which volatilizes at low temperatures is desirable. For instance, the carrier may be in the liquid state at temperatures below —40° centigrade and have a boiling point below 20° centigrade. A liquid which is a gas at normal room temperature and has a boiling point below 0° centigrade is especially suitable because such liquids volatilize at normal atmospheric pressure at temperatures below —40° centigrade in a short period of time. Liquefied monochlorodifluoromethane, liquefied methyl chloride, liquefied dimethyl ether, dichloromonofluormethane, trichloromonofluormethane, or a mixture of two or more of such liquids may be employed. Liquefied monochlorodifluoromethane, liquefied methyl chloride, and dichloromonofluoromethane, or a mixture of two or more of such liquids in any desired proportion, are solvents for all the low temperature binders mentioned, and polymerized n-butylmethacrylate, polymerized isobutylmethacrylate and polymerized vinyl acetate, are soluble in dimethyl ether. All of the liquids mentioned have boiling points below 0° centigrade with the exception of dichloromonofluoromethane and trichloromonofluoromethane which boil at approximately normal room temperature at normal atmospheric pressure and consequently the drying of a layer or film of the coating composition on a frozen mercury pattern will be slower when dichloromonofluoromethane or trichloromonofluoromethane is utilized than liquids which have a boiling point below 0° centigrade. When dichloromonofluoromethane and trichloromonofluoromethane are utilized, it is therefore desirable to mix one or both of them with a liquid having a lower boiling point, such as liquefied monochloro-

difluoromethane. As the carrier, liquefied monochlorodifluoromethane has been found to be particularly suitable. Certain of the liquids mentioned are also solvents for some of the binders. For instance, polymerized isobutylmethacrylate is soluble in a mixture consisting of 90% liquefied dichloromonofluoromethane and 10% dichloromonofluoromethane, and ethyl cellulose and polymerized vinyl acetate are soluble in dichlorodifluoromethane when mixed with 30% or more of liquefied dichloromonofluoromethane.

A sufficient amount of the liquid carrier should be present to provide a slurry of the desired viscosity which viscosity may of course be varied over a considerable range, such as from approximately 100 to 1600 centipoises at —60° centigrade. For coating intricate patterns, the viscosity of the slurry for preparing the shell mold or the inner shape-controlling layer of a shell mold composed of two layers, must be low, such as from 100 to 150 centipoises at —60° centigrade, so that the slurry when applied will penetrate into small openings or indentations and will form a thin film or layer on blades or fins arranged in close proximity to each other, whereas for less intricate patterns, the slurry for preparing the inner coating may be higher, such as 150 to 250 centipoises at —60° centigrade. In applying the outer coating layer when two coatings are applied, the viscosity of the slurry may be still higher. For instance, it may range from 400 to 1600 centipoises at —60° centigrade.

The raised-temperature binder for the refractory material is so chosen as to become effective in binding the refractory particles together at temperatures ranging from 315° C. to 1250° C., and that after becoming effective it shall bind the refractory particles together up to the temperature at which molten metal is cast into the mold, such as at temperatures ranging up to approximately 1650° centigrade or higher.

Various compounds may be used as a raised-temperature binder for the refractory particles of the shell mold, such as primary, secondary or tertiary ammonium phosphate having a particle size ranging from 150 to 325 mesh or less, the alkali metal phosphates, or a mixture of an alkali metal and an ammonium phosphate, such as microcosmic salt, the alkali metal fluorides, such as sodium, potassium or lithium fluoride, compounds containing an alkali metal fluoride, such as cryolite, barium nitrite, boron nitride, the alkali metal silicates which contain water of crystallization, such as sodium or potassium metasilicate or a mixture of two or more of such compounds. An alkali metal borate or an alkali metal tetraborate, such as a borate or tetraborate of sodium, potassium, or lithium, or a mixture of an alkali metal borate or an alkali metal tetraborate and an alkali metal fluoride, such as sodium, potassium, or lithium fluoride, or a mixture of compounds which react on heating to form an alkali metal borate or an alkali metal tetraborate and an alkali metal fluoride, may be utilized. For instance, a mixture of sodium or lithium fluoride and a boron compound, such as boric acid or boric oxide, has been found to be satisfactory. The amount of boric acid or boric oxide which is added to a slurry containing an alkali metal fluoride to provide a raised temperature binder for the refractory material may range from more than incidental impurities up to an amount sufficient to react with all of the alkali metal fluoride. For instance, when sodium fluoride and boric acid are utilized, the boric acid may be present in amounts greater than incidental impurities up to approximately three parts by weight of the boric acid to one part by weight of the sodium fluoride. When a shell mold containing sodium fluoride and boric acid or boric oxide is heated to approximately a red heat, the sodium fluoride and boron compound react to form molten borax which envelopes the grains of the refractory material to provide a binder therefor. When utilizing an alkali metal fluoride and a boron compound, such as boric acid or boric oxide, it is desirable, however, to mix the compounds together in such proportions that some of the alkali metal fluoride will be present after the reaction takes place. For instance, approximately three parts by weight of the sodium fluoride may be utilized to one part by weight of the boric acid in which case the raised temperature binder for the refractory material which becomes effective at intermediately high temperatures consists of a mixture of sodium borate and the reaction product of the sodium fluoride and the refractory material.

An ammonium phosphate, such as primary ammonium phosphate, has the particular advantage as a raised-temperature binder for the refractory particles from below —40° C. up to intermediately high temperatures, because it decomposes at temperatures ranging from 150° to 430° centigrade to form a phosphoric acid which becomes effective as a binder for the refractory particles before the heating modifies the low temperature binder to provide vapors for producing a porous mold. Consequently a shell mold in which an ammonium phosphate is utilized as the raised temperature binder, has good strength throughout its entire baking range. In this connection, it may be stated that the low-temperature binders which are effective in binding the refractory particles together from below —40° centigrade up to intermediately high temperatures gradually lose their binding properties at temperatures ranging from approximately 150° to 540° centigrade, depending upon the particular binder, or mixture of binders, although they may possess some binding properties up to a temperature of approximately 595° centigrade depending upon the rate of temperature rise.

When an ammonium phosphate is utilized to provide a potential binder that becomes effective at raised temperatures, it is essential that it shall be of small particle size. Particles or crystals of ammonium phosphate of minus 150 to 325 mesh have proven satisfactory.

In providing a shell mold having a thin inner shaped layer and an outer supporting layer, the inner shaped layer should be thin and hard. It has been found that when an alkali metal fluoride or an alkali metal boron compound, or a mixture thereof or compounds which react to form such compounds or mixtures, are utilized as the raised temperature binder for the refractory particles, a shell mold having a harder inner cavity surface is provided than that produced when the reaction product of phosphoric acid and the refractory material constitutes the binder for the refractory particles. By varying the proportion of such compound or mixtures of compounds, the hardness of the inner cavity surface of the shell mold may also be more accurately regulated than when ammonium phosphate particles are utilized to provide a phosphoric acid which reacts with the refractory particles to provide the binder which becomes effective at raised temperatures. For instance, the hardness of the inner shaped layer may be increased by increasing the amount of the raised temperature binder that is utilized.

When an alkali metal fluoride, an alkali metal boron compound, or mixtures thereof, or compounds which react at intermediately high temperatures to form such compounds or mixtures, are present as the raised temperature binder for the refractory particles, however, the binder does not become effective at as low a temperature as the phosphoric acid which is formed by the decomposition of ammonium phosphate particles and consequently when such binders are utilized in both the inner and outer coating layers, the shell mold which is formed has the tendency to sag a slight amount when heated to a high temperature. This is due to the fact that a considerable portion of the low temperature binder volatilizes, or decomposes and volatilizes, or is otherwise modified before the alkali metal fluoride, the alkali metal borate, or the alkali metal tetraborate, which is present or which is formed by the reaction of an alkali metal fluoride and

boric acid or boric oxide, becomes effective as a binder for the refractory material. In the outer supporting layer, however, the phosphoric acid which is finally formed by the decomposition of the ammonium phosphate under the influence of heat reacts with the refractory particles and becomes effective as a binder for the refractory particles at lower temperatures than an alkali metal fluoride or alkali metal boron compounds or their mixtures. A shell mold having an inner layer formed of refractory particles bound together by the reaction product of an alkali metal fluoride and the refractory material, an alkali metal boron compound, or the combination of an alkali metal boron compound and the reaction product of an alkali metal fluoride and the refractory material, and an outer supporting layer in which the refractory particles are bound together by the reaction product of a phosphoric acid and the refractory material, will therefore have an inner surface of the desired hardness and the shell mold will retain its shape during the firing operation. Such a mold has a region at the junction of the inner shaped layer and the outer supporting layer in which the refractory particles are bound together by a small amount of an alkali metal phosphate, such as sodium phosphate, which, while possessing some binding power after it becomes effective as a binder for the refractory particles, nevertheless provides an intermediate region where the binding action is weak enough to provide a buffer layer between the inner shaped layer and the outer supporting layer which intermediate region is capable of yielding when molten metal is cast into the cavity of the shell mold which in turn permits the thin inner shaped layer to yield and thus prevents cracking of the inner shaped layer. It also permits the inner shaped layer to yield or collapse when molten metal cast around cores or inserts in the cavity of the mold contracts about such inserts or cores during cooling, although according to the present invention, the entire shell mold may be made thin enough to yield or collapse when metal which is cast about parts of the shell mold contracts during cooling.

The amount of the raised temperature binder which becomes effective at intermediately high temperatures in the layer or films of the applied coating must be sufficient to bind the refractory particles together after the shell mold has been heated to a temperature sufficient to modify the low temperature binder to provide vapors for forming a porous mold and also during the casting of metal into the shell mold. Amounts ranging from approximately .1% to 5% of the total amount of solids in the applied layer or films which remains after the liquid carrier vaporizes, depending upon the particular binder that is utilized, have proven satisfactory. In compositions for preparing the inner shaped layer of a shell mold consisting of an inner shaped layer and an outer supporting layer, the amount of the binder which becomes effective at intermediately high temperatures may be somewhat higher. For instance, it may be present in amounts ranging from .2% to 5% of the total amount of solids in the applied layer or films which remain after the liquid carrier vaporizes. When primary ammonium phosphate is utilized as the binder which becomes effective at intermediately high temperatures, approximately 2% to 4% of the binder, based on the total amount of solids in the applied layer or films remaining after the liquid vaporizes, has been found to be especially suitable.

To provide a composition for producing the outer supporting layer of a shell mold consisting of an inner shape-controlling layer and an outer supporting layer, the ingredients of the composition may be the same as that utilized to provide the inner layer. When it is desired to build up the outer supporting layer quickly, however, or when it is desired to provide considerable strength for the inner layer, it is formed of a mixture of coarse and fine refractory particles. The fine refractory particles may be of the same material as that utilized in the inner shape-controlling layer. For the coarse particles, any suitable refractory material may be utilized that is capable of resisting high temperature, such as prefired brick particles, prefired silica sand, zirconia, and aluminum silicate, such as sillimanite or mullite, a micaceous material, such as vermiculite, or a mixture of two or more of such materials. The size of the coarse refractory particles and the proportions utilized may be widely varied, for instance, they may have minus 12 mesh to plus 60 mesh particle size, and may be present in proportions ranging from a substantial amount up to a major proportion of the refractory particles utilized. A sufficient amount of the finely divided refractory particles should be present, however, to prevent the coarse particles from settling from the slurry.

The following are specific examples of compositions for application to a frozen mercury pattern, to form a shell mold consisting of an inner shell-like layer and an outer supporting layer.

Example 1.—Composition for inner shell-like shaping layer

	Grams
Liquefied monochlorodifluoromethane	10,500.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° centigrade with molar solution in benzene	81.0
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	94.5
Sodium fluoride	54.8
Boric acid	18.2
Zirconium silicate, —325 mesh	35,928.0

Example 2.—Composition for outer supporting shell-like layer

	Grams
Liquefied monochloromethane	28,200.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° centigrade with molar solution in benzene	798.0
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	222.0
Primary ammonium phosphate	1,200.0
Zirconium silicate, —325 mesh	33,228.0
Mullite (aluminum silicate), —14 mesh +35 mesh	21,952.0

In the foregoing examples, the phenol-formaldehyde condensation product which has been condensed to its intermediate or "B" state in which it is soluble in ordinary solvents, such as acetone, is utilized to improve the adherent properties of the composition when it is applied in the form of a layer or film to a frozen mercury pattern or the coherent properties of the composition when it is applied over a dried or partially dried previously applied layer or film, and may be present in proportions ranging from .3% to 3% of the total solids in the films or layers of the applied coating after the liquid carrier vaporizes. Its presence, however, is not essential, and if desired, it may be omitted or other resinous material, such as the polymerization product of indene and coumarone, may be substituted therefor. When a phenol-formaldehyde condensation product is utilized, it also acts as a binder for the refractory material and improves the strength of the shell mold at temperatures ranging from approximately 150° centigrade up to approximately 495° to 530° centigrade. When the shell mold is heated to higher temperatures, however, the phenol-formaldehyde condensation product volatilizes, or decomposes and volatilizes, and has little or no binding properties beyond 530° centigrade. The vapors produced during the volatilization of the phenol-formaldehyde condensation product aid in providing a porous shell mold.

In preparing a slurry from the composition disclosed in Example 1, the solid ingredients of the composition including the polymerized vinyl acetate, the phenol-formaldehyde condensation product, the sodium fluoride, and the zirconium silicate, are pre-cooled to a temperature below —40° centigrade and are then mixed with the liquefied monochlorodifluoromethane and the slurry thus

obtained is maintained below —40° centigrade and is applied to the frozen mercury pattern at temperatures below —40° centigrade by any desirable method, such as by dipping, pouring, brushing, or spraying. For instance, in building up the inner shell-like shaped coating layer, the composition may be applied to the frozen mercury pattern, including the wall openings, by dipping the pattern in the slurry while the slurry is maintained below the freezing point of the frozen mercury pattern to provide films or layers which must be dried, or at least partially dried, below —40° centigrade. It is also essential that the drying, or partial drying, shall take place below the boiling point of the liquid carrier utilized in forming the slurry, otherwise, a smooth film or layer will not be obtained. The coated frozen mercury pattern may then be again dipped into the slurry while the slurry is maintained below the freezing point of mercury and at least partially dried at temperatures below the freezing point of the mercury and below the boiling point of the liquid utilized in forming the slurry, which process may be repeated a sufficient number of times to build up the inner shell-like shaped coating layer.

The composition as disclosed in Example 2 is then applied over the inner shell-like shaped layer to form the outer supporting coating layer.

In preparing a slurry from the composition disclosed in Example 2, a mixture of the normally solid ingredients of the composition, namely, the polymerized vinyl acetate, the phenol-formaldehyde condensation product, the primary ammonium phosphate, the zirconium silicate, and the mullite, is precooled below the freezing point of mercury and is then mixed with the liquefied monochlorodifluoromethane, and is applied over the inner layer in any convenient manner, such as by dipping, at temperatures below the freezing point of the frozen mercury, each film or layer when applied being at least partially dried below the freezing point of the mercury and below the boiling point of the monochlorodifluoromethane, a sufficient number of layers or films being applied to build up the outer supporting coating layer.

Instead of coating the frozen mercury pattern with an inner shaped layer and applying over the inner layer an outer supporting coating layer, a single coating layer may be applied to the frozen mercury pattern. For instance, a slurry prepared from the composition disclosed in Example 1 may be applied by any convenient means, such as by dipping, pouring, brushing, or spraying, to the frozen mercury pattern while the slurry and the frozen mercury pattern are maintained below the freezing point of the frozen mercury pattern and below the boiling point of the liquid utilized to form the slurry until a coating layer of the desired thickness is built up, or if desired, the coating layer may be prepared from a slurry as disclosed in Example 2, with the exception that the coarse refractory particles may be omitted. The following composition, for example, may be utilized:

Example 3.—Composition for preparing a shell mold

	Grams
Liquefied monochlorodifluoromethane	10,500.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° centigrade with molar solution in benzene	189.0
Phenol-formaldehyde condensation product condensed to intermediate soluble stage	94.5
Primary ammonium phosphate, —325 mesh	661.5
Zirconium silicate, —325 mesh	17,935.0

The slurry disclosed in Example 3 may be prepared by precooling a mixture composed of the polymerized vinyl acetate, the phenol-formaldehyde condensation product, the primary ammonium phosphate, and the zirconium silicate to a temperature below —40° centigrade and mixing it with the liquefied monochlorodifluoromethane, and the slurry thus provided may be applied to the frozen mercury pattern including wall openings by dipping, pouring, spraying, or brushing while the frozen mercury pattern and the slurry are maintained below —40° centigrade, each film or layer being at least partially dried below —40° centigrade and the boiling point of the liquid utilized in the slurry, the process being repeated until a coating layer of the desired thickness is obtained. The phenol-formaldehyde condensation product is utilized primarily to improve the adherent properties of an applied film or layer of the composition to the frozen mercury pattern and the coherent properties of an applied film or layer to a previously applied and at least partially dried film or layer, but as previously stated it possesses some binding properties at temperatures ranging from approximately 150° to 530° centigrade. Its presence in the slurry, however, is not essential and if desired, it may be omitted.

When the slurry is applied to the frozen mercury pattern, the binder which is effective at low temperatures binds the refractory particles and the raised temperature binder together and to the frozen mercury pattern and a new article of manufacture is thus provided that may be stored at temperatures below the freezing point of mercury until ready for use in preparing the shell mold or it may be transported while being maintained below —40° centigrade to any convenient location for preparing the shell mold and the precision casting. To expedite the drying of the applied coating, reduced pressure may be provided or air maintained at temperatures below the freezing temperature of the mercury may be circulated around the coated pattern, or the coated pattern may be rotated in air maintained —40° centigrade.

Thin self-supporting shell molds of the invention may be formed around the frozen mercury pattern of Figs. 1 and 2 with the compositions of Examples 1 and 2 or of Examples 1 and 3. The composition of Example 1 is applied to the frozen mercury pattern of Figs. 1 and 2 by any desirable method, such as by dipping, pouring, brushing or spraying. The composition of Example 1 is applied in the form of thin coating strata as layers to all exposed surfaces of the frozen mercury pattern of Figs. 1 and 2, including the hollow wall opening portions 5 and 6 so as to form over these exposed pattern surfaces a thin inner shell layer as indicated at 9 in Figs. 3 and 4. The composition is applied to the frozen mercury pattern while the pattern and the composition are maintained below the freezing point of the frozen mercury pattern. The applied coating layers of the composition are dried or at least partially dried below the freezing temperature of the mercury pattern. It is also essential that the drying or partial drying of the investment coating composition shall take place below the boiling point of the liquid carrier utilized in forming this slurry-like investment composition as otherwise the thin shell mold layer will not provide a smooth inner cavity surface and it will be impossible to form with the composition a smooth shell layer or film. The coating composition is applied to the frozen mercury pattern a sufficient number of times, each followed by partial drying of the previous coating stratum, until an inner shell layer of desired thickness, such as 1/30 inch has been formed.

After thus forming the inner shell mold layer 9 over the frozen mercury pattern, the composition of the type given by Examples 2 or 3 is applied over the exterior of the inner shell layer 9 to form thereover the outer backing or supporting shell layer 10. The outer shell layer composition of Examples 2 or 3 are likewise applied either by dipping, pouring, brushing or spraying and each applied coating stratum of such composition is dried or partially dried before applying thereover the next stratum of the composition, the process being continued until the outer shell layer of desired thickness is formed.

The frozen mercury pattern may then be liquefied and poured from the applied coating layers to form a shell mold in any desirable manner. For good results the frozen mercury pattern is liquefied by passing it with the mold

through a high frequency induction field. The removal of the frozen mercury pattern may be effected by immersing the coated pattern in a bath of liquid mercury at room temperature, or liquid mercury at normal or raised temperatures may be sprayed into the mold cavity. Because of the thermal conductivity of mercury, the frozen mercury pattern is rapidly liquefied by this process.

The shell mold as shown in Figs. 5 and 6 is formed to provide a gate 12 and a pair of spaced side walls 13 and 14 united together by an arcuate-shaped portion, wall 13 being provided with an opening 15 in alignment with an opening 16 in wall 14 and an opening 17 which is in alignment with an opening 18 in wall 14. A shell mold formed of a single shell-like layer may of course be provided by liquefying and removing the mercury from the coated pattern shown in Fig. 4.

Because of the low thermal coefficient of expansion of frozen mercury which approximates zero at its melting point, the frozen mercury may be liquefied and removed from the dried coating layer or coating layers to provide a shell mold in which the thickness of the shell mold is extremely thin. It is therefore only necessary to provide a shell mold of sufficient thickness to resist the impact of molten metal cast into its cavity. For instance, when the thickness of the frozen mercury pattern of the object to be cast varies from approximately 1/16 to 1/8 of an inch, a coating layer, or combined coating layers, having a thickness varying from 1/16 to 1/8 of an inch depending upon the thickness of the frozen mercury pattern, is sufficient to provide a shell mold that will resist the impact of molten metal cast into its cavity and a shell mold having such thickness is capable of yielding when molten metal which is cast into the cavity of the shell mold contracts about portions of the shell mold upon cooling. When two coating layers are provided, the inner coating layer is thin. It may, for instance, vary from 1/64 to 1/32 of an inch in thickness and the outer supporting coating layer is thick enough to provide, together with the inner coating, a thickness ranging from 1/16 to 1/8 of an inch. In the shell mold shown in Figs. 5 and 6, metal cast into the mold contracts during cooling about the inner portions 13*a* and 14*a* of the side walls as shown in Fig. 6 and also about the hollow mold wall portions forming openings 15, 16, 17 and 18, and consequently the side walls 13 and 14 of the shell mold must be thin enough to yield slightly to prevent cracks from forming in the comparatively thin side walls of the casting and in those portions of the casting which contract about the hollow mold core portions.

It will of course be understood that as the thickness of the frozen mercury pattern of the object to be cast in increased, the thickness of the coating layer, or the combined thickness of the two coating layers, which is applied to the pattern must also be increased to provide upon the liquefaction and removal of the mercury a shell mold of sufficient thickness to resist the impact of the molten metal cast into the shell mold which in such cases will be larger in amount than when a thin casting cavity is provided and consequently the casting which is formed will exert a greater force upon those portions of the shell mold about which it contracts during cooling than when thin castings are formed. In such cases, the portions of the shell mold about which the cast metal contracts during cooling must of course be thin enough to yield during the contraction of the metal to prevent cracks from forming in the casting. When the thickness of the frozen mercury pattern is large, it is not necessary, however, to increase the thickness of the applied coating layer or coating layers in the same ration because in such cases only a slight increase in the thickness of the coating layer, or combined coating layers, will provide ample strength in the shell mold which is finally formed to resist the impact of the larger amount of molten metal which is cast into the shell mold, and even when the pattern of the object to be cast is comparatively large, it is not necessary to provide a shell mold having a thickness greater than approximately 1/8 to 1/4 of an inch because mold shells having such thickness will resist the impact of a large amount of molten metal cast into the shell mold and will be thin enough to yield when metal which is cast into the cavity of the shell mold contracts about portions of the shell mold during cooling. When a shell mold having a thickness of from 1/8 to 1/4 of an inch is provided, the thickness of the inner layer when two coatings are provided may vary from approximately 1/32 of an inch to 1/16 of an inch in thickness.

After the liquefied pattern material has been removed from the shell mold, metals having a fusion point below that at which the low temperature binder is modified, or plastic material, such as resins or ester gums, may be cast into the shell mold shown in Figs. 5 and 6 without further treatment of the shell mold, and in such cases it is not necessary to utilize a raised temperature binder.

To provide a shell mold in which metals having a high fusion point are to be cast, such as stainless steel, it is necessary to subject the shell mold to a baking or firing operation at temperatures which may vary from 540° to 1250° centigrade. During the firing operation, the low temperature binder for the refractory particles in each coating is modified by a change in its chemical or physical state and provides vapors for forming a porous shell mold and the raised temperature binder becomes effective in binding the refractory particles together. For instance, when an ammonium phosphate is utilized in the investment composition to prepare the inner and outer layer structures as illustrated in Examples 1 and 2, it is decomposed during the firing operation before the low temperature binder is modified to form a vapor, and a phosphoric acid is formed which reacts with the refractory particles to bind them together after the shell mold is heated to a temperature sufficient to cause a reaction between the phosphoric acid which is finally formed and the refractory particles. When an alkali metal fluoride is utilized as the raised temperature binder, as disclosed in Example 1, it reacts with the refractory particles at raised temperatures to bind the refractory particles together. When a mixture of an alkali metal fluoride and boric acid is utilized, the alkali metal fluoride and boric acid react at elevated temperatures to form an alkali metal borate or an alkali metal tetraborate which envelops the grains of the refractory material to form a binder therefor, and if any excess alkali metal fluoride is present, it of course reacts with the refractory particles to provide an additional binding action. When an alkali metal borate or an alkali metal tetraborate is utilized, it envelops the grains of the refractory material at raised temperatures and provides a binder therefor.

In preparing shell molds consisting of a single shell-like layer from a coated frozen mercury pattern as shown in Fig. 4, the binder which becomes effective at raised temperature may be omitted when the coating compositions are applied to the frozen mercury pattern. For instance, the coating layer in Fig. 4 may be applied from the composition disclosed in Example 1 with the sodium fluoride omitted, or from the composition disclosed in Example 2 in which the primary ammonium phosphate is omitted, or a different low temperature binder may be utilized in the compositions for preparing the coatings. For instance, the inner shaped coating layer and the outer supporting coating layer may be formed from the compositions disclosed in the following examples:

Example 4.—Composition for preparing inner shaped coating

	Grams
Liquefied monochlorodifluoromethane	3,200
Copolymers of 40% acrylonitrile and 60% butadiene	54
Zirconium silicate, 325 mesh	5,345

Example 5.—Composition for preparing outer supporting coating

	Grams
Liquefied monochlorodifluoromethane	3,600
Polymerized isobutylmethacrylate, high viscosity	120
Zirconium silicate, 325 mesh	2,365
Fire brick particles which pass through 15 mesh screen and are retained on 40 mesh screen	3,515

The composition or compositions may be prepared and applied to the frozen mercury pattern in the manner previously specified while maintaining the composition below the freezing point of the mercury pattern prior to and during application and after the coating or coatings are dried which drying must take place below —40° Centigrade and below the boiling point of the liquid carrier, a new article of manufacture is provided that may be stored at temperatures below the freezing point of mercury until ready for use in preparing a shell mold or transported while being maintained below the freezing point of mercury to any desirable location for preparing the shell mold.

After the coating or coatings have dried, the frozen mercury pattern is liquefied and removed from the coatings. The shell mold thus formed may then be impregnated with a binder that becomes effective in binding the refractory particles together at raised temperatures. For instance, such shell molds may be impregnated with an aqueous solution of phosphoric acid of a strength varying from 10% to 85%, or an aqueous solution of ethyl silicate. Aqueous solutions of sodium silicate, sodium metasilicate, or of zirconium oxychloride may also be utilized. In impregnating the shell mold with such solution, a small amount of a wetting agent, such as approximately 1% of dioctyl sodium sulfosuccinate may be added.

In introducing the raised temperature binder by such method, a shell mold, such as shown in Figs. 5 and 6, may be immersed into the composition for sufficient time to permit the solution to completely penetrate the shell mold, or to a desired depth into the inner and outer portions of the shell mold without penetrating into the intermediate portion. The time a shell mold is exposed to the solution depends upon the thickness of the shell mold and the depth of penetration that is desired which will vary depending upon the particular metal that is to be cast into the shell mold. For small shell molds, less than a a minute may be required whereas several minutes may be required when the shell mold is comparatively thick, such as approximately ¼ of an inch in thickness.

The following specific examples illustrate solutions which have been utilized to impregnate shell molds formed of a refractory material and a low temperature binder:

Example 6.—Raised temperature binder impregnating composition

	Grams
Sodium metasilicate	482
Dioctyl sodium sulfoscuccinate	10
Water	1,000

Example 7.—Raised temperature binder impregnating composition

	Grams
Phosphoric acid, 85% solution	50
Dioctyl sodium sulfosuccinate	1
Water	50

After the shell mold is impregnated with the raised temperature binder, it is of course necessary to bake or fire the shell mold at a sufficient temperature, such as at temperatures ranging from approximately 540° to 1250° centigrade, to cause a modification of the low temperature binder to provide a porous shell mold and to cause the raised temperature binder to become effective in binding the refractory particles together.

In preparing castings, the shell mold as thus prepared may be supported in a flask, such as flask **19** as shown in Fig. 7 and a refractory material **20** may be poured in the flask around the shell mold to form a backing or a support therefor. Any suitable refractory material of small particle size may be used for this purpose, such as sand. Sand, however, has the tendency to flow when pressure is applied thereto. It is therefore more desirable to utilize an inorganic aggregate having irregular surfaces and a low specific gravity which is capable of yielding without flowing, such as ground fused quartz, ground cinders, ground titanium, or vermiculite that has been coated with a material capable of resisting high temperatures. The refractory particles may also be coated with water glass, such as an aqueous solution of sodium or potassium silicate having a specific gravity ranging from 30° to 42° Baumé, in any suitable manner. For instance, the refractory particles may be submerged in the water glass and then spread on a screen, the excess water glass passing through the screen. They may then be heated to a temperature of 535° to 1100° centigrade.

The refractory particles may vary in size from those which pass through a 4 mesh screen to those which pass through a 16 mesh screen. For supporting shell molds having a complicated configuration or small holes or indentations, a refractory material of comparatively small size is utilized while the coarser refractory particles can be utilized to support larger sized shell molds or even small shell molds of simple shape. While refractory particles that are in a more finely divided state that that specified may be employed as the supporting material, particles small enough to pass through a 32 mesh screen are not usually required unless the shell mold is very small.

In cases where high temperature metal is to be cast into the shell mold or when it is desired to form coatings having thin wall sections, the flask containing the supporting material and shell mold may be heated to the desired temperature, such as to temperatures ranging from 500° to 1200° centigrade before the metal is cast. When casting metal having a low melting point, it is also desirable to heat the shell mold before casting the metal to prevent solidification of the metal before it completely fills the shell mold.

In retrieving the casting, a large proportion of the shell mold may be easily removed from the casting. If the metal casting may be quenched with liquids, such as oil or water, without adversely affecting its physical or metallurgical properties, or if quenching is desirable to improve its physical properties, the casting may be quenched and a considerable portion of the investment composition will fall off during the quenching operation. The remainder may be removed by blasting, such as sand blasting. In the blasting operation, it is sometimes desirable to utilize shell particles, such as pecan shells, instead of sand, or the shell particles may be mixed with the sand.

Instead of forming the investment composition with a liquid carrier consisting of an aliphatic chloro-fluoro compound and known as Freon, the composition may be formed with a liquid carrier consisting of methyl chloride having a freezing point of —97.7° C. and a boiling point of —24.2° C., or methylene chloride having a freezing point of —96.7° C. and a boiling point of 40° C. may be used or a mixture of these carriers, although shell molds formed with investment compositions embodying such carriers dry slower, but in such cases the drying may be speeded up by circulating around the dried shell mold a drying atmosphere maintained below the freezing point of the casting pattern from which the vapors of the carrier liquid have been removed. It is accordingly desired that the present invention shall not be limited to the specific exemplifications thereof described herein.

I claim:

1. The method of preparing a porous self-supporting

shell mold in the form of a porous thin shell layer formed over the exposed surfaces of a frozen mercury pattern of an object to be cast with metal of high melting temperature, which method comprises the procedure of providing a frozen mercury casting pattern having spaced pattern wall portions united by an intermediate pattern wall portion, preparing a liquid slurry-like investment composition which will adhere to said pattern surfaces when applied thereto as a coating stratum at very low temperatures below the freezing temperature of said pattern material which investment composition comprises refractory particle material constituting a predominant amount of the normally solid composition ingredients applied to form said shell layer, a low temperature synthetic organic resinous binder for the refractory material that is adherent to said pattern and which is effective in binding and is present in an amount sufficient to bind the refractory material together at temperatures ranging from said very low temperatures up to at least about 110° C., and a liquid carrier for the binder and the refractory material that is in the liquid state at said very low temperatures and has a boiling point below 20° C. and which is present in the composition in an amount to provide a slurry of sufficiently low viscosity to enable the composition to be applied to said pattern in the form of a shell layer, thereafter applying said composition to said pattern at said very low temperatures until there is formed a shell layer which adheres to said pattern and has a thickness of at most about ¼ inch, and is self-supporting after removing therefrom the liquefied mercury thereafter drying the shell layer adhering to said frozen pattern at said very low temperatures and below the boiling point of the liquid carrier to solidify said shell layer, thereafter liquefying the material of the pattern and removing the liquefied pattern material from the solidified shell layer to provide the shell mold, said procedure including also embodying in the solid ingredients forming the shell layer a raised temperature binder which constitutes about 0.1% to 5% by weight of said solid composition ingredients and which, after becoming effective, binds the refractory particles at temperatures in the range from said very low temperatures up to the high casting temperature of metals having a melting temperature of at least about 700° C., said procedure also further comprising heating the shell layer so formed and embodying said raised temperature binder to a high temperature to cause the raised temperature binder to become effective as a binder for the refractory particles and to modify said resinous binder to provide vapors which leave the shell layer and render it porous, at least the inner stratum of said shell layer being formed with an investment composition containing refractory particles of sufficiently fine size to give the inner cavity of the shell layer a relatively smooth cavity surface, the step of applying said composition over said intermediate pattern portions being carried on until the shell layer facing said intermediate pattern wall portions has a thickness which after making the raised temperature binder effective is great enough to resist the impact of molten metal cast into the mold cavity but thin enough to yield when the cast metal contracts about such portions of said shell layer during cooling.

2. The method of producing a porous self-supporting shell mold as claimed in claim 1 wherein said shell layer is formed on said frozen pattern at said very low temperature with a coating composition containing said raised temperature binder.

3. The method of producing a porous self-supporting shell mold as claimed in claim 1, wherein the prepared frozen pattern has an opening extending through a body portion of said pattern and wherein said composition is applied to said pattern including the pattern surfaces surrounding said pattern opening to form a shell layer having a core-like shell layer portion projecting into the mold cavity until there is formed a shell layer having a wall thickness which after making the raised temperature binder effective is at least in the region of the core-like shell layer portion sufficiently thin to yield when molten metal cast into the mold cavity contracts around the core-like portion while cooling.

4. The method of producing a porous self-supporting shell mold as claimed in claim 3, wherein said shell layer is formed on said frozen pattern at said very low temperature with a coating composition containing said raised temperature binder.

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