April 30, 1957 E. F. KOHL ET AL 2,790,218

SHELL MOLD STRUCTURES AND PROCESSES AND COMPOSITIONS FOR FORMING THE SAME

Filed June 29, 1954 2 Sheets-Sheet 1

FIG. 1.

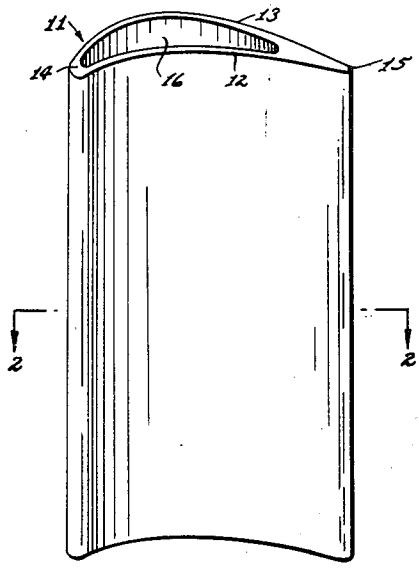
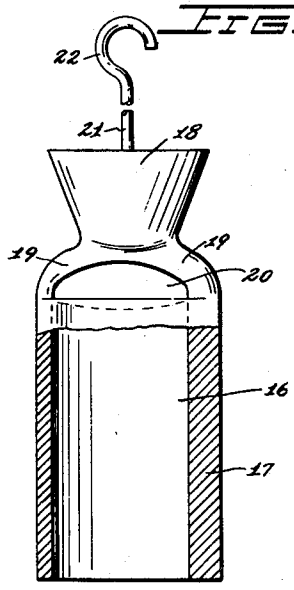


FIG. 3.



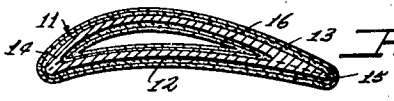


FIG. 2.

FIG. 4.

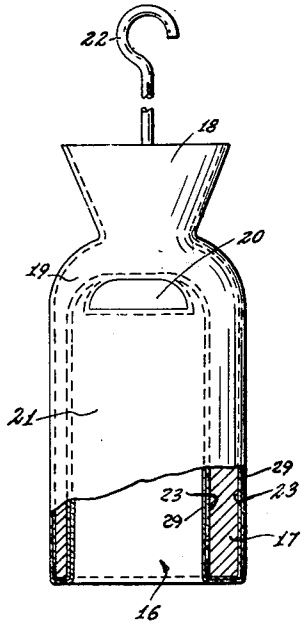
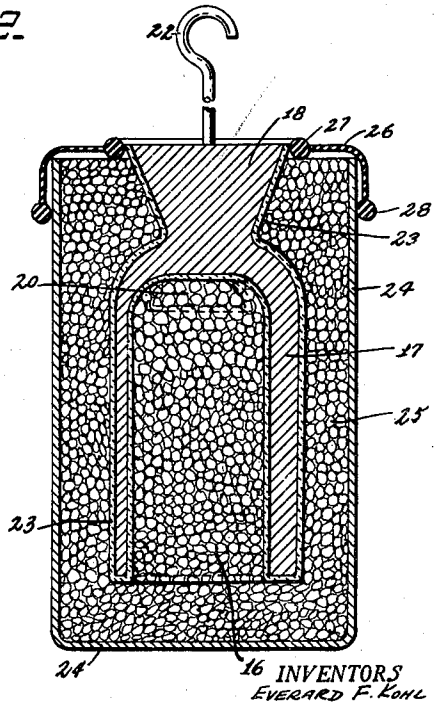


FIG. 5.



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FIG. 6.

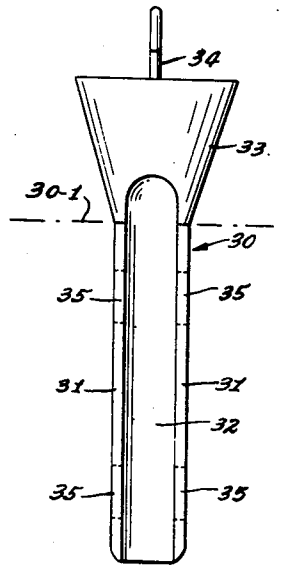


FIG. 7.

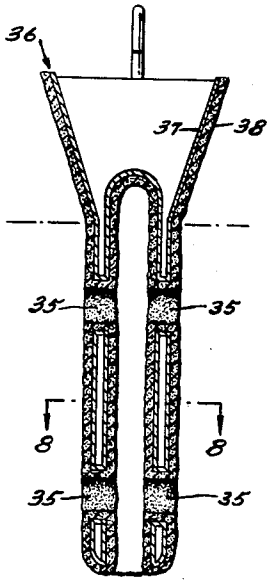


FIG. 8.

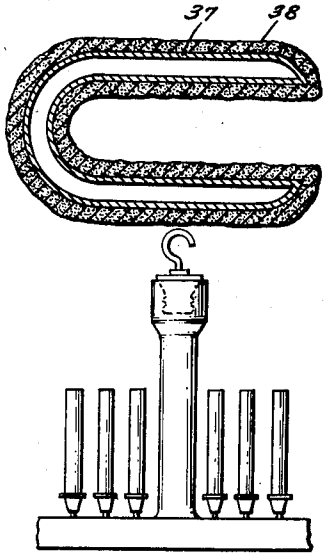


FIG. 9.

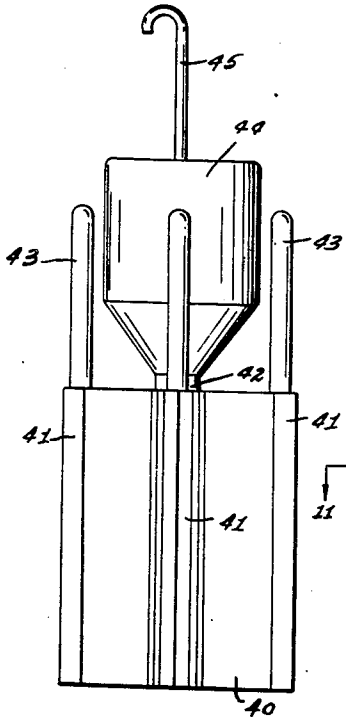


FIG. 10.

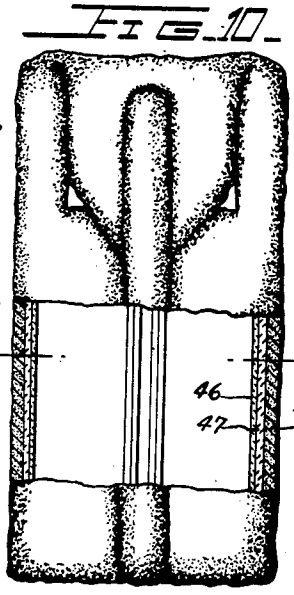


FIG. 3A

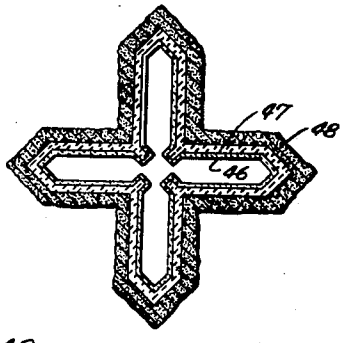


FIG. 11.

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SHELL MOLD STRUCTURES AND PROCESSES AND COMPOSITIONS FOR FORMING THE SAME

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Application June 29, 1954, Serial No. 440,056

70 Claims. (Cl. 22—193)

This application is a continuation-in-part of the co-pending applications, Serial No. 7,955, filed February 12, 1948, Serial Nos. 113,452 and 114,824, filed August 31, 1949, Serial No. 257,328, filed November 20, 1951, Serial Nos. 304,301, 304,302, 304,303, 304,304 and 304,307, filed August 14, 1952 and Serial No. 309,119, filed September 11, 1952 (all of the foregoing now abandoned), Serial Nos. 304,306 and 304,309, filed August 14, 1952, and Serial No. 309,121, filed September 11, 1952.

Application Ser. No. 309,121 is now also abandoned.

This invention relates to processes of preparing shell mold structures by means of frozen mercury patterns defining the cavity into which objects are to be cast, to mold structures produced by such processes, and to compositions utilized in preparing such mold structures.

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 shape. 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 addition it is impossible to produce with patterns of wax-like or plastic materials molds for use in casting large-size parts, because the large wax patterns tend to sag. Furthermore, if a pattern of wax-like or plastic material is used for preparing a mold for a large-size casting, the volumetric change caused by the expansion of the wax or plastic pattern material is so great that large stresses are imparted to the thick-walled mold, causing the mold to crack.

Among the objects of the present invention are thin, porous shell molds having smooth inner cavity surfaces for use in making castings of more or less complicated shape out of metals having a high melting temperature. In accordance with the invention, thin, porous shell molds are formed with a frozen mercury pattern of the object to be cast by applying to the pattern, investment compositions which comprise refractory particles as the principal solid ingredient together with an inorganic raised temperature binder, an organic resinous low temperature binder, and a liquid carrier for the ingredients of the composition, each having special characteristics which make it possible to form with such composition a self-supporting shell mold at temperatures below the freezing temperature of the pattern material, and which shell mold is thereafter heated to cause the inorganic binder to bind the refractory particles into a self-supporting shell mold and to drive off the organic binder to render the mold porous.

The various phases of the invention will be better

understood from the following description and exemplifications thereof with particular reference to the drawings, in which

Fig. 1 is an isometric view of a vane of gas turbine to be cast in accordance with the invention;

Fig. 2 is a cross-sectional view of a frozen mercury pattern of the vane;

Fig. 3 is a partial sectional view of a frozen mercury pattern used in making a shell mold of Fig. 2;

Fig. 3–A is a view of a group of frozen mercury casting patterns combined into a pattern cluster;

Fig. 4 is an elevational view, partly in cross-section of the frozen mercury pattern of Fig. 3, with one type of a shell mold of the invention formed thereon;

Fig. 5 is a vertical cross-section of the frozen mercury pattern of Fig. 3 with another type of shell mold formed thereon, as supported in a flask by a mass of loose refractory particles;

Fig. 6 is a front view of another frozen mercury pattern;

Fig. 7 is a central sectional view of a shell mold formed on the frozen mercury pattern of Fig. 6 in accordance with the invention;

Fig. 8 is an enlarged cross-sectional view on the line 8—8 of Fig. 7;

Fig. 9 is an elevational view of another frozen mercury pattern;

Fig. 10 is a similar view of a shell mold formed in accordance with the invention on the frozen mercury pattern of Fig. 9;

Fig. 11 is a cross-sectional view along line 11—11 of Fig. 10.

Referring to Figs. 1 through 4, there will now be described the phase of the invention wherein one form of a thin-walled shell mold is formed on a complex frozen mercury pattern. Figs. 1 and 2 indicate, by way of example, a gas turbine vane **11** having a hollow interior **16** and which is to be cast in accordance with the invention. The vane **11** has an air-foil contour with a generally concave thin blade section **12** and a generally convex thin blade section **13** joined along the front edge region **14** and rear edge region **15**. The vane **11** may also have an axial twist along its length.

If a frozen mercury pattern of such a turbine vane is difficult to produce from a single permanent master mold, it may be produced by making separate frozen mercury patterns of sections **12** and **13** in separate partible permanent molds. The separate sectional mercury patterns **12** and **13** may then be joined or welded at mating surfaces indicated by dashed lines in Fig. 2 to form a single, continuous integral frozen mercury pattern. The several pattern sections may be provided along their mating surfaces with suitable interfitting male and female aligning elements to facilitate ready alignment of the several pattern sections into the desired complex pattern. Such individual frozen mercury pattern sections, when brought into abutment along their mating surfaces, will become united and welded into the self-supporting complex frozen mercury pattern of the desired object which would be difficult to produce with a single permanent master mold.

Such gas turbine vanes are made of alloy metal having high hot strength and a corresponding high melting temperature. When such alloy metal is cast into the mold cavity, it will, upon solidifying, contract about the core portion of the mold which gives shape to the hollow interior of the vane. The molds for casting such parts must have mold walls which are thin enough to yield, as otherwise the thin walls of the casting may be subjected to cracks as the molten metal cools and tends to contract about the unyielding core portions of the mold structure. By making the mold structure with thin shell walls which

yield when subjected to the contracting forces of the solidifying molten metal, these difficulties are avoided.

Fig. 3 shows a cross section of the frozen mercury pattern **17** of vane **11** with a sprue **18** of frozen mercury attached thereto by means of frozen mercury arms **19** which bridge the narrow border regions of the vane-shaped frozen mercury pattern. This bridge arrangement provides passages to the inner surfaces of the hollow frozen mercury pattern **17** facing the hollow interior **16**, which inner pattern surfaces are to be coated with the shell-forming coating compositions. A strong rigid metal hook **22** having a shank which is frozen in the sprue gate portion **18** of the frozen mercury pattern, is utilized in manipulating the frozen mercury pattern while coating it with the shell mold forming compositions. Frozen mercury in the pure state is especially suitable for practicing the invention, although it is not limited thereto as long as the impurities do not affect the physical properties of mercury which render it suitable for practicing the invention.

The frozen mercury pattern **17** is now ready for coating with the mold forming composition. This is accomplished by repeatedly immersing the frozen mercury pattern in, or pouring over its surface a slurry of the coating composition while the pattern and the slurry are maintained at a temperature below the freezing point of mercury. The coating slurry comprises a liquid carrier, fine particles of refractory material, a raised temperature binder for the refractory particles which is ineffective at the freezing temperature of mercury but which becomes effective as a binder for the refractory particles at raised temperatures and an organic resinous binder that has the physical property of being adherent to the frozen mercury pattern at temperatures below the freezing point of the pattern and which is effective as a binder for the refractory particles and the raised temperature binder at temperatures from below the freezing point of mercury up to the raised temperature at which the raised temperature binder becomes effective as binder for the refractory particles and of causing the bound particles to adhere to the frozen mercury pattern at such very low temperatures. The raised temperature binder is so chosen that it becomes effective as a binder for the refractory particles at raised temperatures below that at which the resinous binder ceases to have the required properties of holding the refractory particles bound in the desired shell mold. The liquid carrier is chosen to have a low boiling point and to volatilize in a short period of time at temperatures from below the freezing temperature of mercury, i. e. below −40° C. up to about normal temperatures, such as up to 0° C.

The viscosity of the refractory slurry depends upon the size and complexity of the frozen mercury pattern to be coated. For example, the slurry must be thin enough to readily penetrate all narrow openings or slits and all narrow corners. Between each successive coating, by immersion or dipping of the pattern in the slurry, or by spraying the slurry on the pattern, a period of time is allowed to at least partially dry the applied coating stratum or film. The successive coating and drying operations are carried on until a shell layer of the desired thickness has been formed around the surfaces of the frozen mercury pattern. After applying the last coating stratum, the shell layer or mold is dried.

Both the coating and drying of each shell layer stratum should be carried on in an atmosphere refrigerated to well below the freezing point of the mercury pattern material. In particular, the drying of the shell mold layer should be effected at temperatures below the boiling point of the carrier so as to provide a smooth film or shell layer. The drying may be expedited by circulating through the drying space where intermittent drying takes place an atmosphere of air refrigerated to below the freezing temperature of the mercury pattern material and below the boiling point of the carrier. The vapor of the liquid carrier absorbed into the refrigerated atmosphere may be recovered by conventional compression techniques or the like, whereby the liquid carrier may be used again to form the coating composition. The continuous circulation of the refrigerated atmosphere from which the carrier vapors have been removed, also reduces the vapor pressure of the liquid carrier, thereby expediting the volatilization of the liquid carrier from the coating layers. A suitable degree of vacuum may be applied to the drying space for expediting the volatilization of the carrier.

Fig. 4 shows a substantially self-supporting mold structure with thin shell walls consisting of the shell layers formed in accordance with the invention over the frozen mercury pattern of the vane of Fig. 3. The thin shell mold generally designated **21** (Fig. 4) has an inner thin shell layer **23** and an overlying supporting or backing shell layer **29** forming with the inner shell layer **23** a self-supporting shell mold structure from which the frozen mercury pattern **17** may be readily removed, as by heating to above the melting point of mercury and pouring it out of the mold cavity. The two layer shell mold **21** so formed is sufficiently thin to yield when molten metal cast into the mold cavity contracts about parts of the shell mold such as the inner hollow shell core of the shell mold **21**, thereby preventing formation of cracks in the casting. When the frozen mercury pattern of the object to be cast is comparatively thin, as in the case of the thin wall gas turbine vane, the walls of the shell mold of the type shown in Fig. 4 may have an overall thickness from about 1/16 to about 3/16 inch.

The inner shell layer **23** is first formed over the exposed surfaces of the frozen mercury pattern **17** by applying thereto several strata of the slurry-like shell-forming coating composition, each coating stratum being at least partially dried before applying thereover the next stratum of the coating composition in the manner explained hereinabove.

After drying the exterior stratum of the inner shell layer **23**, the outer supporting backing shell layer **29** is formed thereover with a modified shell-forming coating composition having characteristics similar to that used for forming the inner shell layer **23**. In order to give the outer backing shell layer **29** relatively great strength, the refractory particle material of the backing layer coating composition is chosen so that it contains partly coarse size particles and partly fine size particles. Such double shell layer mold may be made with a very thin inner shell layer of fine refractory particles, the outer backing shell layer **29** with its coarser refractory particles providing the required strength, while the combined overall thickness of the two shell layers **23**, **29** is small enough to permit wall portions of the shell mold to yield when the molten metal which is cast into the mold solidifies and contracts about the core portions of the mold which it partially or wholly surrounds. By way of example, for cast objects of the type described such as the gas turbine vanes or gas turbine buckets, good results are obtained with the inner shell layer **23** made with a wall thickness of about 1/64 to 1/32 inch, and the overall thickness of the two shell layers **23**, **29**, about 1/16 to 3/16 or 1/4 inch.

According to a phase of the invention, explained in connection with Fig. 5, frozen mercury patterns may also be used to form thereon thin single-layer shell molds, the walls of which are backed in a special way by a mass of relatively loose refractory particles. Fig. 5 shows the same frozen mercury pattern **17** of the hollow vane Fig. 3 having formed thereon only a single-layer shell mold **23** corresponding to the inner shell layer **23** of the two-layer mold of Figs. 2, 4. The thin shell mold **23** of Fig. 5 is formed over the frozen mercury pattern **17** in the same way as the inner shell layer **23** of the two-layer shell mold **21** shown in Figs. 2, 4. The walls of the thin shell mold **23** of Fig. 5 are made sufficiently thin to yield when molten metal contracts about parts of the shell mold in cooling, thus preventing damage to the cast-

ing and cracking thereof. In case of frozen mercury patterns for thin castings, such as the vane of Figs. 1 and 2, the walls of the shell mold **23** may have an overall thickness from about 1/32 to about 1/8 inch. This phase of the invention constitutes the subject matter of application Ser. No. 192,001, filed October 25, 1950, now Patent No. 2,682,692, and need not be more fully explained herein.

After forming on the frozen mercury pattern the thin shell mold **21** (Fig. 4) and drying the applied coating composition layers by driving off the liquid carrier, the mercury of the pattern is liquefied and removed, as by pouring from the cavity of the self-supporting shell mold. The frozen mercury may be melted by bringing liquid mercury into contact with the mercury in the mold cavity. Another and effective method of liquefying the frozen mercury pattern is to place or pass the shell mold containing the frozen mercury pattern through a high-frequency induction field.

After the mercury pattern has been liquefied, the mercury is poured from the shell mold by inverting the flask. The frozen mercury pattern may also be provided with a narrow sprue outlet portion at its bottom, in which case the liquid mercury may be drained from the bottom of the mold. The small aperture remaining in the bottom portion of the mold may be plugged with refractory material prior to casting the molten metal into the mold cavity.

To harden the shell mold **21** and render it resistant to molten metal having a high melting point, the flask **24** with the shell mold **23** and backing mass **25** held therein is now heated in a furnace to a sufficiently high temperature to cause the raised temperature binder to become effective as a binder for the refractory particles in the shell mold and to modify the organic resinous binder as by driving it off, or vaporizing it, to thereby impart porosity to the shell mold. The baking or firing temperature, which may be up to 1250° C., as well as the time required for baking depend upon several factors such as the size and thickness of the shell mold, the temperature of the molten metal to be cast, and the hardness of the mold surface required. Good results are obtained with a baking temperature of red heat or about 1000° C.

When the shell mold has been properly hardened, the mold is removed from the furnace and the mold is ready for casting. When high melting temperature metal is to be cast, or where thin sections are involved, the metal is cast into the shell mold while the mold is still hot. In casting metal having a low fusion point, it is also desirable to cast the metal into a hot mold in order to prevent solidification of the metal before it completely fills the mold.

After the cast metal has been cooled and solidified, the casting may be retrieved by removing the thin shell mold from the casting. A large portion of the shell mold may be easily broken away from the casting and the remainder of the refractory mold may be removed by blasting, such as with sand.

According to a phase of the invention, the molten metal is cast into a shell mold of the type described above while the latter is maintained at temperatures below 0° centigrade, in which case the shell mold may be made without the raised temperature binder. An auxiliary freezing liquid having a higher freezing point than mercury, such as water or a mixture of water and alcohol, may be poured into the mass of loose refractory particles **25** within the flask **24**. This phase of the invention constitutes the subject matter of the copending application Ser. No. 381,723, filed September 22, 1953, and need not be explained herein.

Figs. 7 and 8 show a thin two-layer shell mold of receiver part of a rifle shown in Fig. 6. The receiver pattern **30** of Fig. 6 is used to cast the receiver part of a rifle, indicated below the dash-dot line **30—1**. Such rifle receiver has very thin side walls, only one thirty-second (1/32) of an inch thick, and the inner surface has special guide ways, which heretofore had to be produced by accurate machining operations. The frozen mercury pattern **30** has a gate portion **33** forming a pattern for the mold gate into which the shank of a rigid metal hook **34** is embedded during the freezing of the mercury. Each of the two side walls **31** of the pattern has two spaced openings **35**.

Figs. 7 and 8 show the shell mold **36** of the invention which has an inner thin shell layer **37** and an outer supporting shell layer **38** which were formed on the surfaces of the frozen mercury pattern shown in Fig. 6, including its aligned openings **35** in the manner explained in connection with Figs. 2, 4. The inner shell layer **37** is made very thin, and the outer shell layer **38** provides the required strength, while the combined thickness of the two shell layers **37** and **38** is small enough to permit wall portions of the shell mold to yield when molten metal cast into the mold cools and contracts about portions of the mold which it surrounds. By way of example, for cast objects which are similar to the pattern shown in Fig. 6, having a wall thickness of about 1/16 to 1/4 inch, the inner shell layer may have a thickness of 1/64 to 1/16 of an inch, and the overall thickness of the two shell layers **37** and **38** of the completed shell mold may be 1/16 to 1/4 of an inch thick.

As the thickness of the frozen mercury pattern of the object to be cast is increased, the thickness of the shell layer 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 case will be larger in amount than when a thin casting cavity is provided. When the thickness of the frozen mercury pattern is large, it is not necessary, however, to increase the thickness of the applied shell layer, or shell layers, in the same ratio as the thickness of the pattern is increased because in such cases only a slight increase in the thickness of the shell layer, or combined shell layers, will provide ample strength in the finally formed shell mold. Even when the pattern of the object to be cast is comparatively large, it is not necessary to provide a shell mold having an average thickness greater than approximately 1/4 to 3/8 of an inch because shell molds 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 an average thickness of 1/4 to 3/8 of an inch is provided, the average thickness of the inner shell layer may vary from approximately 1/32 to 1/16 of an inch in thickness.

When molten metal of high temperature is cast into the mold cavity, such as shown in Figs. 7 and 8, to form concave or hollow metal articles, the molten metal contracts upon cooling about portions of the shell mold which it partly or wholly surrounds and these shell mold portions must be thin enough to yield to prevent the formation of cracks in the casting. The solidifying cast molten metal also contracts about convex portions of the shell mold which define the concave inner surfaces of the cast metal article, such as shown in Fig. 8, and these convex mold portions must also be thin enough to yield to prevent formation of cracks in the thin casting portions. The portion of the shell mold structures where the highest contraction of the cast metal takes place, such as the slot sections **35** of Figs. 7, 8, may be made in the form of a thin single shell layer, while other portions of the mold may consist of two shell layers, suitable masks or removable blocking elements being applied to the slot sections **35** when the second shell layer is formed on other parts. The outer shell layer is formed of a coating composition similar to that used in making the inner layer, except that the refractory material consists partly of fine particle size and partly of coarse particle size.

According to a phase of the invention, in cases re-

quiring still larger self-supporting mold structures, the shell molds of the invention may be made out of three shell layers, as shown by way of example in Figs. 9, 10 and 11. A frozen mercury pattern 40 (Fig. 9) of the object to be cast has four wings 41 extending from a central body part 42. The several elements of the structure are of relatively intricate designs. The four wings 41 of the pattern have sprue pattern 43, and at the center there is a gate pattern 44. A metal hook 45 is frozen into the mercury pattern for handling it.

Figs. 10 and 11 show a three-layer shell mold formed with the frozen mercury pattern of Fig. 9. It comprises a thin inner shell layer 46, a thin intermediate buffer layer 47, and an outer shell layer 48. The buffer layer 47 is formed of relatively movable or loose refractory particles which while resisting lateral displacement of the inner shell layer 46 permits it to yield slightly when hot molten metal is cast into the shell mold. The inner shell layer 46 is of sufficient thickness to permit it to yield when cast molten metal contracts on cooling about mold portions or about cores or mold inserts. The outer shell layer 48 serves as a backing support for the inner and buffer shell layers 46, 47 and prevents lateral displacement of the inner shell layer portions 46 under the impact of cast molten metal.

The thickness of the inner shell layer 46 may vary in thickness from about 1/50 to 1/20 of an inch. The outer shell layer may be of sufficient thickness to provide an overall mold thickness of about 1/8 to 3/8 of an inch. In general, the overall thickness of the shell mold structure, whether consisting of two or three shell layers, need not be greater than about 1/8 to 3/8 of an inch. Such thin shell molds may be placed in a mass of loose freely flowing sand within a surrounding flask and the thin shell walls have the desired strength to prevent lateral deformation of the shape-defining inner shell layer by the impact of cast molten metal.

According to a phase of the invention, the shell-forming investment coating compositions which are used to prepare the inner shell layer comprise refractory particles constituting a predominant amount of the solid ingredients of the composition, a raised temperature binder that is ineffective as a binder for the refractory particles at the freezing temperature of mercury but which becomes effective at a raised temperature and which after becoming effective binds the refractory particles together up to the casting temperature of substantially all metals and alloys as well as at low temperatures, and an organic resinous binder having the properties of being adherent to a frozen mercury pattern at temperatures below the freezing point of the pattern and being coherent to previously applied layers or films of the same or a similar composition at temperatures below the freezing point of mercury. The organic resinous binder must also be capable of binding the refractory particles and the raised temperature binder together at temperatures from below the freezing point of mercury up to the raised temperature at which the raised temperature binder becomes effective in binding the refractory particles. It is also desirable that the organic resinous binder shall have the property of becoming modified on heating, as by decomposition or vaporization, to provide vapors which exude through the shell walls and render them porous. In practice, this is achieved by baking the shell mold at a raised temperature, usually about 1000° C., for causing the raised temperature binder to become effective as a binder for the refractory particles. However, it is not essential that the raised temperature binder shall form part of the coating composition because after the mercury has been liquefied and removed from the mold cavity, the shell mold may be impregnated with a binder that becomes effective as a binder for the refractory particles at raised temperatures.

To enable the composition to be applied in the form of a slurry to the frozen mercury pattern, there is provided a liquid carrier for the solid composition ingredients. The carrier must remain liquid at least at temperatures as low as the frozen mercury pattern and must have a boiling point below normal temperatures so that it will volatilize in a short period of time at temperatures below the freezing point of the pattern.

Any suitable refractory material that may be formed into fine particles and which is resistant to high temperatures may be used in shell-forming coating compositions for preparing the shell molds of the invention. Among desirable refractory materials are zirconium silicate and zirconia (zirconium oxide). Also beryllium oxide, aluminum oxide and silicon oxide. Also silica, chromite, magnesium oxide, aluminum silicate, such as sillimanite or mullite, alumina, ground quartz, flint, silicon carbide. Also, a mixture of two or more of such materials, or a mixture of magnesium oxide and calcium oxide. As an example, in commercial practice, very good results are obtained by using zirconium silicate as the refractory particle material. Good results are obtained with the refractory particles forming about 85% to 95% or more of the normally solid ingredients of the composition.

In the investment coating composition for forming the inner shell layer 23, 37 or 46 of a shell mold structure consisting of two or more shell layers, such as shown in Figs. 4, 7 and 10, or a thin single layer shell mold, such as shown at 23 in Fig. 5, the refractory particles should be sufficiently fine to provide a smooth hard mold cavity surface so as to yield a metal casting having a smooth surface. In practice, excellent results are obtained with refractory particles of —325 mesh particle size. In general, particles of an average size from minus 60 mesh to minus 1000 mesh are suitbale. A comparatively smooth mold surface will be obtained with the refractory particles minus 150 mesh to about minus 350 mesh in size. Extremely fine refractory material are less desirable as the resulting shell mold is of lesser porosity. When extremely fine particles are used, it is desirable to mix them with 80 to 90% coarser particles.

The low temperature binder for the refractory particles of the investment composition must be effective as a binder at temperatures from very low temperatures below the freezing temperature of the frozen mercury pattern up to at least normal temperatures and must have the physical properties of being adherent to a frozen mercury pattern and coherent to additional layers or films of the same or an equivalent composition at said very low temperatures. Certain synthetic organic resinous compounds meet these requirements.

Very good results are obtained with investment compositions containing as low temperature binder a mixture of polyvinyl acetate and ethyl cellulose. Ethyl cellulose that has been ethylated to a material extent, such as to an extent of 46.5 or more, for example 49%, is particularly effective in such binder mixture. Polymerized vinyl acetate retains its binding properties to a greater degree at temperatures ranging from 425° to 540° C. and higher than ethyl cellulose. When a coating composition containing polymerized vinyl acetate is applied to a frozen mercury pattern to form a layer or film, the applied layer or film is also more adherent to the frozen mercury pattern and is more coherent to a previously applied layer or film of the same or similar compositions than layers or films which contain ethyl cellulose as the organic resinous binder. On the other hand, when ethyl cellulose is utilized as a binder for the refractory material, or in combination with one of the other binders, the shell layer is more resistant to moisture than a shell layer in which it is not present.

In utilizing—as an organic resinous binder—a mixture of polymerized vinyl acetate and ethyl cellulose that has been materially ethylated such as to an extent of at least 46.5%, their relative proportions may be varied. For instance, a resinous binder consisting principally of polymerized vinyl acetate and a small but substantial amount of the ethyl cellulose will bind more effectively than

polymerized vinyl acetate alone. Likewise, a resinous binder consisting principally of ethyl cellulose and a small but substantial amount of polymerized vinyl acetate will bind more effectively than ethyl cellulose alone. In general, the resinous binder may consist of from about 3 to 6 parts of polymerized vinyl acetate and 1 part of ethyl cellulose to from 3 to 6 parts of ethyl cellulose and 1 part of polymerized vinyl acetate. Investment compositions in which the polymerized vinyl acetate and ethyl cellulose are present in equal proportions are satisfactory. It has been found to be desirable, however, and particularly when the investment composition is applied to the frozen mercury pattern by dipping it, to have an excess of the polymerized vinyl acetate, such as 3 to 6 parts thereof and 1 part ethyl cellulose. (Throughout the specification and claims all proportions are given by weight unless otherwise specifically indicated in each specific instance.)

Other organic resinous binders suitable for such investment coating compositions are the copolymers of acrylonitrile and butadiene ranging in proportions from approximately 33% acrylonitrile and 67% butadiene to 40% acrylonitrile and 60% butadiene. The copolymers of acrylonitrile and butadiene when utilized in coating compositions as the organic resinous binder for the refractory material, have greater strength over a temperature ranging from approximately 425° to 450° C. than the other binders mentioned. Other suitable resinous binders are polymer compounds such as polymerized n-butylmethacrylate, high or low viscosity polymerized isobutylmethacrylate.

The amount of such resinous binder that is present in the investment coating composition may vary from about .25 to 7% of the solid ingredients of the investment composition remaining therein after evaporation of the liquid carrier. Good results are obtained with the low temperature binder forming from approximately .5% to 2% of the solid investment ingredients.

It is also desirable to embody in the investment coating composition a thermosetting resinous material, such as a coumarone-indene resin or a phenol-formaldehyde condensation product in its intermediate soluble stage, in an amount ranging from .25% to 3% of the solid investment ingredients. The phenol-formaldehyde condensation product in its intermediate soluble stage, when dispersed or partially dissolved in the liquid carrier is not adherent to a frozen mercury pattern and has no binding properties at or below the freezing temperature of mercury. It does, however, have the property of giving a smoother surface to the coating strata applied to the frozen mercury pattern. Its presence in the composition, however, is not essential.

The shell-forming slurry-like coating composition to be applied to the frozen mercury pattern also contains a liquid carrier which is capable of holding the refractory particles, the raised temperature binder and the organic resinous binder in a dispersed state or in colloidal solution, at least, if the liquid is stirred or otherwise agitated. It is desirable to provide the resinous binder in the form of small particles so that the resinous binder particles may be held uniformly dispersed or in colloidal solution in the liquid carrier and to have a carrier, which at least partially dissolves the phenol-formaldehyde condensation product. The liquid carrier should be present in an amount sufficient to provide with the normally solid ingredients of the composition a slurry of sufficiently low viscosity to enable the composition to be applied to the frozen mercury pattern in the form of a stratum or film by dipping the frozen mercury pattern in the slurry although it is within the scope of the present invention to apply the composition in any suitable way, such as by pouring, brushing, pumping or spraying on the frozen mercury pattern.

A suitable liquid carrier is one which is liquid when applied to the frozen mercury pattern substantially below its freezing temperatures, such as −60° C. and has a boiling point below normal atmospheric temperatures, such as 15° to 25° C. or within a temperature range of 55° C. or 65° C. higher than the freezing temperature −40° C. of mercury at atmospheric pressure, and particularly an organic liquid which has a boiling point between about −40° and 0° C. at atmospheric pressure. Suitable liquid carriers are aliphatic chloro-fluoro compounds such as liquefied monochlorodifluoromethane (Freon 22) or dichlorodifluoromethane (Freon 12), liquefied methyl chloride, or of two or more mixtures of these liquid carriers are satisfactory. Polymerized n-butylmethacrylate, polymerized isobutylmethacrylate, and polymerized vinyl acetate can be used with liquefied dimethyl ether either alone or mixed with one of the two other carriers or solvents. All of the organic resinous binders given above are suitable for use with a liquid carrier of dichloromonofluoromethane (Freon 21) having a boiling point of 8.9° C. or about 48.9° C. above the freezing temperature of mercury, or trichloromonofluoromethane (Freon 113) having a boiling point of 47.6° C. or about 87° C. higher than the freezing temperature of mercury at atmospheric pressure. Dichloromonofluoromethane and trichloromonofluoromethane, however, boil at temperatures considerably above −18° C. and consequently, the drying of the coating composition on a frozen mercury pattern will be slower when one of these carriers is utilized than lower boiling point carriers. Similar conditions apply to other liquid carriers of a similar type, such as monochloropentafluoroethane (Freon 115), octafluoro-cyclobutane (Freon C–118), dichlorotetrafluoroethane (Freon 114) and the like. When such higher boiling-point carriers are utilized, it is desirable to mix them with a sufficient amount of lower boiling-point carrier, such as liquefied monochlorodifluoromethane (Freon 22), so that the resulting liquid carrier shall have the desired low boiling point.

The desired liquid carrier for the solid ingredients of the composition may also be formed of a mixture of other liquids or liquefied gases particularly when the used resinous binder forms a true or colloidal solution in such mixture of liquids. For instance, polymerized isobutylmethacrylate may be used with a liquid carrier consisting of 90% dichlorodifluoromethane (Freon 12) mixed with 10% dichloromonofluoromethane (Freon 21). Ethyl cellulose and polymerized vinyl acetate form colloidal solutions in liquefied dichlorodifluoromethane (Freon 12) mixed with 30% or more of liquefied dichloromonofluoromethane (Freon 21).

Liquefied monochlorodifluoromethane has proven especially suitable as a carrier for use in coating compositions which are to be applied to casting patterns of pure frozen mercury because it is a gas at normal temperature, is in the liquid state at the temperature of the frozen mercury pattern, it has a high vapor pressure and volatilizes in a short period of time at temperatures below −40° C. The liquid carrier should be present in a sufficient amount as to enable it to hold suspended or dispersed or in colloidal solution the organic resinous binder particles, and, if stirred or agitated, to hold suspended or dispersed the refractory particles and raised temperature binder particles. A sufficient amount of the liquid carrier should be present to provide, together with the solid composition ingredients, a slurry of the desired viscosity, variable in accordance with the intricacies of the pattern, so that it shall readily penetrate all narrow pattern crevices. For coating intricate frozen mercury patterns, the viscosity of the slurry for preparing the inner shell layer should be about 100 to 150 centipoises at −60° C. so that the slurry when applied will penetrate into indentations and small or narrow openings and will form a thin film or stratum on thin closely spaced fins or the like. For less intricate patterns, the viscosity of the slurry may be higher, up to about 250 centipoises at −60° C. The slurry for the outer backing shell layer

may have a still higher viscosity, such as from 400 to 1600 centipoises at —60° C.

The raised temperature binder for the refractory particles is so chosen as to become effective as a binder for the refractory particles at or above normal temperatures and which, after becoming effective, binds the refractory particles together at the casting temperature of substantially all metals and alloys, such as metals or alloys having a fusion point of approximately 1800° C. or higher, as well as at low and intermediate temperatures. Inorganic binders which become effective at temperatures ranging from 350° to 1250° have proven especially suitable. Various compounds or mixtures of compounds have proven suitable as raised temperature binder for shell-forming coating compositions of the invention.

According to a phase of the invention, strong thin porous shell molds of the type described above may be formed over frozen mercury patterns by combining the refractory particles with raised temperature binders which consist wholly or partly of a metal borate or of compounds which react to form a metal borate. Because they become effective as a binder for the refractory particle material at lower temperatures, the alkali metal borates (including metal tetraborates) or compounds which react to form such alkali metal borates are specially suitable.

According to a phase of the invention, very desirable raised temperature binders for the refractory particles of such thin shell molds are provided by a combination of an alkali metal fluoride with a boron compound, such as boric acid or boric oxide. Suitable alkali metal fluorides are the fluorides of sodium, potassium, lithium, beryllium. Other fluorides of the elements of group 1*a* and 2*a* of the periodic table are also suitable for use as such raised temperature binder ingredients for the refractory particles of such thin shell molds.

When combining an alkali metal fluoride with a boron compound, such as boric acid or boric oxide, to provide a raised temperature binder for the refractory particles of such thin shell molds, the relative proportions of the metal fluoride and the boron compound may vary over a wide range and the amount of the boron compound may range from incidental impurities up to a substantial proportion. In general, the proportions of these ingredients may vary from 99% of the metal fluoride with 1% of the boron compound to about 33% of the alkali metal fluoride with about 67% of the boron compound. It is good practice to combine the alkali metal fluoride with 5% to 35% of boric acid or similar boron compounds for use as a raised temperature binder for the refractory particles of such thin shell molds.

As an example, in commercial practice, highly satisfactory strong thin shell molds are obtained by combining the refractory particles with a raised temperature binder consisting of about 75% of the alkali metal fluoride in the form of sodium fluoride and 25% boric acid.

The amount of the raised temperature binder which is combined with the refractory particles for forming the thin shell mold may vary over a wide range and particularly from about .25% to 2.0% of the total solid ingredients of the investment composition. Good results are obtained by combining the refractory particles with .25% to 1% of the raised temperature binder consisting of about 75% of the alkali metal fluoride and 25% of boric acid.

When a thin shell mold containing refractory particles and a small amount, such as 0.5% to 2%, of such raised temperature binder is heated to red heat or about 1000° C., the small amount of these binder ingredients become effective in binding the refractory particles of the thin mold shell into a strong mold structure into which molten metal of high melting temperature may be poured for forming excellent castings. It was believed that when such shell mold is heated to red heat, a part of the metal fluoride reacts with the boron compound and that the excess of the metal fluoride reacts with the refractory particles, and that as a result of these and possibly other reactions the refractory particles become bound into a strong thin shell mold.

Similar results are obtained if investment compositions of similar refractory particles are combined with a raised temperature binder formed of metal borates (including metal tetraborates) such as sodium, potassium or beryllium borate or the tetraborates of these and similar metals or mixtures of such metal borates and metal fluorides. When thin shell molds formed with such binder compositions are heated to red heat or 1000° C. to render effective the binding action of such raised temperature binder and drive off the resinous low temperature binder, there are obtained strong thin porous shell molds suitable for casting high temperature metal to form complicated castings.

The investment coating composition of the type described above should contain sufficient raised temperature binder to bind the refractory particles together after the shell mold has been heated to a temperature sufficient to modify the organic resinous binder and also during the casting of molten metal into the shell mold. In general, depending upon the binder chosen, amounts of raised temperature binder varying from about .25% to 5% of the total amount of solids in the coating composition (after the carrier vaporizes) have given satisfactory results. In compositions for preparing both the inner shell layer and also the outer shell layer, good results are obtained with the amount of the raised temperature binder forming .5% to 5% and even somewhat higher up to 7% of the solids in the composition (after the carrier evaporates).

The coating composition for producing the outer backing shell layer of a shell mold composed of two or more shell layers, such as backing shell layer **29** (Fig. 4) or backing shell layer **38** (Fig. 8) or backing shell layer **48** (Fig. 10), may be formed of essentially the same ingredients as utilized to form the inner shell layer. However, the refractory particles of the coating composition for the backing-shell layer are chosen to be partly of fine particle size as used for the inner shell layer and partly of coarse particles. As the coarse refractory particles, any suitable refractory particle material capable of resisting high temperatures may be used. The coarse refractory particles may consist of the materials as described above for forming the inner shell layer, including zirconium silicate, zirconium oxide, or beryllium, magnesium or silicon oxide. Also refractory materials such as prefired firebrick particles, prefired silica sand, micaceous material such as vermiculite, an aluminum silicate, such as sillimanite or mullite, or a mixture of two or more of such refractory particle materials. The size of the coarse particles may vary over a wide range, and may have, for instance, an average particle size of —12 mesh to +60 mesh.

Thin shell molds of the invention may be formed with a single shell-forming coating composition as by applying superposed coating strata thereof in any desired manner, such as by dipping, spraying, brushing or pouring, to form a self-supporting thin shell mold of the required thickness. Such thin self-supporting shell mold may also be formed with inner and outer shell layers produced out of different coating compositions, both of which contain the same type of refractory particle material. In actual practice, it has been found desirable to form thin self-supporting shell molds of the invention having an inner shell layer produced with a coating composition containing essentially fine refractory particles and an outer backing shell layer produced with a coating composition containing both coarse and fine refractory particles. The coarse refractory particles give the outer backing shell layer greater strength in resisting lateral movement of the relatively thin walls of the shell mold when molten metal of high temperature is cast into the mold cavity.

A shell mold having such coarse-particle backing layer exhibits also greater porosity or permeability in permitting the escape of gases evolved in the mold cavity when hot metal is cast into it. When coating compositions for forming the backing shell layer are made up with the coarse refractory particles only, they tend to settle from the coating slurry composition, and it is more difficult to apply a uniform coating stratum with such composition. This difficulty is avoided by preparing the backing-layer coating composition with a sufficient addition of fine-grade refractory particles to the coarse-grade particles to substantially hold the coarse refractory particles in suspension within the composition slurry. Good results are obtained with backing-layer slurry compositions wherein the proportion of the fine refractory particles to the coarse refractory particles vary over the range between about 3 to 2 and 1 to 1. Depending on the character and the shape of the article to be cast and the size thereof, the proportion of fine to the coarse particles may be varied over the range between 3 to 2 and 2 to 3.

The following are specific examples of shell-forming coating compositions suitable for preparing the inner shell layer of thin shell molds of the invention of the type shown in Figs. 2 to 10.

Example A–1

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	10,500.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° C. with molar solution in benzene	141.8
Ethyl cellulose that has been ethylated to an extent of 46.5% to 48.5% and having a viscosity of 20 centipoises when a 5% solution thereof is dissolved in a mixture of 80% toluene and 20% ethanol	47.3
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	94.5
Boric acid	46.2
Sodium fluoride	140.7
Zirconium silicate, —325 mesh particle size	18,425.5

Example A–2

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	10,500.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° C. with molar solution in benezene	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 particle size	7,923.7

Example A–3

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	1,950.0
Polymerized vinyl acetate having viscosity of 700 to 900 centipoises at 20° C. with molar solution in benzene	27.0
Phenol-formaldehyde condensation product condensed to intermediate soluble stage	13.5
Borax, anhydrous	43.5
Zirconium silicate, —325 mesh particle size	2,615.7

The following are examples of coating compositions which are suitable for preparing the outer shell layer of shell molds of the type shown in Figs. 2, 4, Figs. 6 to 8 and Figs. 9 to 11.

Example B–1

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	18,000.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° C. with molar solution in benzene	400.0
Ethyl cellulose ethylated to an extent of 46.5% to 48.5% and having a viscosity of 20 centipoises when a 5% solution thereof is dissolved in a mixture of 80% toluene and 20% ethanol	132.0
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	148.0
Sodium fluoride	54.0
Boric acid	18.0
Zirconium silicate, —14 mesh, +25 mesh particle size	14,568.0
Zirconium silicate, —325 mesh particle size	23,952.0

Example B–2

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	8,900.0
Polymerized vinyl acetate having a viscosity of 900 centipoises at 20° C. with molar solution in benzene	225.0
Ethyl cellulose, ethylated to from 46.5% to 48.5% and a 5% solution of which in 80% toluene and 20% ethyl alcohol has a viscosity of 20 centipoises	75.0
Boric acid	8.9
Sodium fluoride	27.3
Zirconium silicate, —325 mesh particle size	7,865.4
Aluminum silicate (mullite), —14 mesh, +35 mesh particle size	11,798.3

In general, the shell-forming coating compositions given above in Example A–1 to A–3 are suitable for producing the outer backing shell layer by substituting for the fine refractory particle ingredients thereof, a mixture of coarse refractory particles with fine refractory particles proportioned in the manner given above for the refractory particle ingredients of the foregoing Examples B–1 to B–2. Furthermore, the amount of the liquid carrier, such as liquefied monochlorodifluoromethane, present in the examples of the coating compositions given above may be increased (or decreased) for decreasing (or increasing) the viscosity of the coating composition in accordance with the particular requirements and the particular shape of the frozen mercury pattern of the cast article that is to be produced with a thin-walled shell mold of the invention.

Any of the shell-forming coating compositions given in Examples A–1 through A–3 may be utilized for forming the inner shell layer of a thin-wall shell mold of the invention and any of the compositions given in Examples B–1 through B–5 may be utilized in preparing the outer backing shell layer of such shell mold.

In producing shell molds of the invention, it is also of advantage to use shell-forming coating compositions of the type given in the foregoing examples which contain the combination of polymerized vinyl acetate and ethyl cellulose as the organic resinous material, either with or without a thermosetting resin ingredient, such as phenol-formaldehyde condensation product. When a phenol-formaldehyde condensation product is utilized in the shell-forming coating composition, it does not become effective as a binder for the refractory particles until it is converted by the applied heat into its infusible insoluble state, thus supplementing the organic resinous binder ingredients in binding the refractory particles together at temperatures in the range from about 450° to 1000° C., and becoming modified into vapors, thereby giving the thin shell mold its desired great porosity.

In preparing the inner shell layer of a shell mold con-

sisting of one or more shell layers, it is also desirable to utilize as the raised temperature binder in the inner shell layer an alkali metal compound or a mixture of alkali metal compounds, such as a metal fluoride or a metal borate or a mixture of a metal fluoride and boron compound. The hardness of the inner surface of the mold cavity may be controlled by varying the percentage of such raised temperature binder that is used in forming the shell mold. Compounds containing an alkali metal compound or a mixture of alkali metal compounds are particularly suitable, such as sodium fluoride, sodium borate, or sodium tetraborate, or a mixture of sodium fluoride and sodium borate or sodium tetraborate, or compounds which react to provide sodium borate or sodium tetraborate or a mixture of sodium fluoride or sodium borate or sodium tetraborate.

In preparing a slurry of the shell-forming compositions for producing shell molds of the invention, the solid ingredients of the composition are precooled to a temperature below the freezing temperature of the frozen mercury pattern and then thoroughly mixed with the liquefied monochlorodifluoromethane, which is also maintained at such low temperature.

To facilitate the mixture of the raised temperature binder with the refractory particles, a premixture of the raised temperature binder with a portion of the refractory material is prepared prior to mixing the solid ingredients with the liquefied carrier or solvent, such as monochlorodifluoromethane. For instance, in preparing the composition disclosed in Example A–1, the sodium fluoride and boric acid are premixed with a portion of the zirconium silicate to approximately 1 part of the combined weight of the sodium fluoride and boric acid and this premixture may be suitably ground, as in a ball or pebble mill, for approximately six hours. This premixture, and the other solid ingredients of the composition, are then precooled to a temperature below the freezing temperature of the frozen mercury pattern, and added to the liquefied monochlorodifluoromethane which is also maintained at such low temperature.

The following is an example of investment coating compositions for preparing the buffer layer of shell molds of the type shown at **47** in Fig. 11. This composition may also be utilized for preparing a shell mold layer or shell mold of the invention in which a raised temperature binder is not present.

Example C–1

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	22,000.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° C. with molar solution in benzene	378.0
Phenol-formaldehyde condensation product condensed to its intermediate stage	189.0
Zirconium silicate, —325 mesh particle size	37,233.0

In general, the shell-forming coating compositions, given above in Examples A–1 to A–3, which are suitable for producing the inner shell layer may be modified to serve for producing the buffer layer, of the type shown at **47** in Fig. 11, by omitting the high temperature binder from the corresponding coating composition for the inner shell layer.

Shell molds of the invention which contain the raised temperature binder have proven very effective for casting metals of high melting temperatures, such as cobalt-chromium-nickel alloys (Vitalium) or stainless steel alloys, into articles such as gas turbine buckets, gas turbine vanes or the like.

In order to render the raised temperature binder effective the shell mold has to be subjected to a baking or firing treatment at elevated temperatures, at which the raised temperature binder becomes effective in binding the refractory particles into a self-supporting shell, and at which the low temperature resinous binder is fully, or at least partially modified into a vapor and driven off to render the mold porous.

Baking temperatures in the range of about 800° C. to 1200° C. give good results. At such baking temperatures, the low temperature organic resinous binder is modified to provide a vapor which exudes or is driven off through the mold walls thereby rendering the shell mold porous, and the raised temperature binder becomes effective in binding the refractory particles together.

After the shell molds of the invention from which the mercury has been removed, are fired with the raised temperature binder present, the metal may be cast therein by any desirable method, such as by static or centrifugal casting, or the molten metal may be cast in the shell mold under pressure or under vacuum. Thus, a shell mold such as shown at **21** in Fig. 4, may be suspended in a suitable vessel, such as in flask **24**, of Fig. 5, and supported therein by any suitable loose-particle refractory material such as loose sand which is placed or blown around the shell mold. When the shell mold is intricate and it is difficult for the loose refractory material to flow into the fine crevices, the flask **24** is vibrated to assist in packing the loose refractory particles. The hot molten metal is cast into the cavity of the thin-walled shell mold **21** so held suspended within flask **24**. Since the shell mold of the invention is thin and porous, it permits gases to pass through walls of the shell mold during vasting of the molten metal.

When casting small parts, such as turbine buckets, it is good practice to combine a substantial number of individual frozen mercury patterns into a cluster and form the thin shell mold of the invention around such pattern cluster as shown, for instance, in Fig. 3–A, and described in application Serial No. 291,643, as filed on June 4, 1952, by S. J. Sindeband, now Patent No. 2,711,570, assigned to Mercast Corporation. The resulting shell mold has a common, generally vertical hollow runner with a plurality of transverse hollow runners to which are joined the inlet ends of the upwardly projecting individual shell molds. The hot molten metal is poured through a gate into the top of the common runner, and because of the high porosity of the individual shell molds, the hot molten metal flows freely through the transverse runners and therefrom through their open bottom ends into the individual shell molds, rising therein until they are all filled as the metal is poured into the common runner.

According to a phase of the invention strong thin porous shell molds may be formed over frozen mercury patterns by combining the refractory particles with raised temperature binders which consist wholly or partly of primary, secondary or tertiary ammonium phospates $NH_4H_2PO_4$, $(NH_4)_2HPH_4$ and $(NH_4)_3PO_4$, in small particle size, such as of —150 to —135 mesh particle size, or a mixture of an alkali metal and an ammonium phosphate, such as microcosmic salt, or a mixture of one or more of the foregoing compounds with binder ingredients which consists of an alkali metal fluoride together with a boron compound, such as boric acid or boric oxide, or alkali metal borates, or alkali metal fluorides only.

An ammonium phosphate of small particle size is of advantage as raised temperature binder when used in combination with an organic resinous binder that is effective in binding the refractory particles at low temperatures, because the ammonium phosphate starts to decompose at about 350° to 450° C. and to react with the refractory particles and cause them to become bound before the low temperature binder is substantially modified into a vapor or driven off, thus giving the mold good strength throughout the entire baking or hardening range. To render it fully effective, it should be heated to above 500° C., preferably to at least 600° C.

In compositions for preparing both the inner shell layer

and also the outer shell layer, the amount of the ammonium phosphate raised temperature binder may be .5% to 5% and up to 7% or 10% of the solids of the composition (after the carrier evaporates). It is good practice to use about 2% to 4% of the ammonium phosphate binder. In commercial practice, good results are obtained with about 3.5% of the ammonium phosphate as a raised temperature binder for the refractory particles of shell molds of the type shown in Figs. 4 to 10.

When shell mold material of the invention containing refractory particles combined with fine particles of a small binder addition consisting of ammonium phosphate is heated or baked at 450° C. and higher, the ammonium phosphate content reacts with the refractory particles and causes them to become bound into a hard shell mold. It is believed that when the binder particles of ammonium phosphate are heated to 450° C. and higher they decompose into phosphoric acid which reacts with the refractory particles and brings about the binding of the refractory particles into hard shell mold material.

In preparing a slurry of the shell forming compositions containing as a raised temperature binder an ammonium phosphate of small particle size for producing therewith thin porous shell molds of the invention, the solid ingredients of the investment composition are precooled to a temperature below the freezing temperature of the frozen mercury pattern and then thoroughly mixed with the liquefied carrier, such as monochlorodifluoromethane, which is also maintained at such low temperature.

To facilitate the mixture of the ammonium phosphate raised temperature binder with the refractory particles, a premixture of this binder with a portion of the refractory material is prepared prior to mixing the solid ingredients with the liquid carrier. As an example, the ammonium phosphate particles are mixed with equal proportions of the zirconium silicate particles and the premixture thus formed is suspended in a liquid in which the ammonium phosphate is insoluble, such as carbontetrachloride. The liquid suspension thus prepared is then ground in a suitable grinding device, such as a ball or pebble mill, for about 9 to 10 hours. After evaporation of the carbontetrachloride, this premixture together with the remainder of solid ingredients of the investment composition are precooled to below the freezing temperature of the mercury pattern and then thoroughly mixed with the liquefied carrier such as monochlorodifluoromethane, which is also maintained at such low temperatures.

Below are specific examples of shell-forming investment composition having an ammonium phosphate raised temperature binder and suitable for forming the entire shell mold or only the inner shell layer of thin porous self-supporting shell molds of the invention, such as described in connection with Figs. 2 to 10.

Example D–1

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	21,000.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° C. with molar solution in benzene	284.0
Ethyl cellulose that has been ethylated to an extent of 46.5% to 48.5% and having a viscosity of 20 centipoises when a 5% solution thereof is dissolved in a mixture of 80% toluene and 20% ethanol	94.0
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	189.0
Primary ammonium phosphate, —325 mesh particle size	1,325.0
Zirconium silicate, —325 mesh particle size	35,925.0

Below are specific examples of coating compositions having an ammonium phosphate raised temperature binder and suitable for forming the outer shell layer of shell molds of the type shown in Figs. 2, 4, Figs. 6 to 8 and Figs. 9 to 11.

Example E–1

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	18,000.0
Polymerized vinyl acetate having a viscosity of 900 centipoises at 20° C. with molar solution in benzene	400.0
Ethyl cellulose, ethylated from 46.5% to 48.5% and a 5% solution of which in 80% toluene and 20% ethyl alcohol has a viscosity of 20 centipoises	132.0
Primary ammonium phosphate, —325 mesh particle size	500.0
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	148.0
Aluminum silicate (Mullite) of —14 mesh, +25 mesh particle size	14,568.0
Zirconium silicate, —325 mesh particle size	23,952.0

Example E–2

	Grams
Liquefied monochlorodifluoromethane (Freon 22)	18,800.0
Polymerized vinyl acetate having a viscosity of 700 to 900 centipoises at 20° C. with molar solution in benzene	400.0
Ethyl cellulose, ethylated to an extent of 46.5% to 48.5% and having a viscosity of 20 centipoises when a 5% solution thereof is dissolved in a mixture of 80% toluene and 20% ethanol	132.0
Phenol-formaldehyde condensation product condensed to its intermediate soluble stage	148.0
Primary ammonium phosphate, —325 mesh particle size	800.0
Zirconium silicate, —325 mesh particle size	23,952.0
Mullite (aluminum silicate), —14 mesh, +35 mesh particle size	14,568.0

In general, the shell-forming coating compositions given above in Examples A–1 to A–3, B–1 to B–2 are suitable for producing the inner and outer backing shell layers respectively, of the present invention by substituting for the alkali-metal salt base binder of about 3.5% of primary ammonium phosphate of —325 mesh particle size. Similarly the amount of the liquid carrier may be increased or decreased in accordance with the particular requirements.

According to a phase of the invention, thin porous shell molds are formed over frozen mercury patterns with investment coating compositions of the type herein described by forming the outer shell layer with compositions containing an ammonium phosphate as raised temperature binder and forming the inner shell layer with compositions containing as raised temperature binder alkali metal salt base compound, such as given in Examples A–1 to A–3. The raised temperature binders consisting of alkali metal salt base compounds start becoming effective as binder for the refractory investment particles at higher temperatures than the ammonium phosphate particle binder which starts becoming effective as such binder at temperatures between about 350° to 450° C. Accordingly less care is required in the baking of the shell molds having in both shell layers, or at least in the outer shell layer an ammonium phosphate particle binder of the type given in Examples D–1 to E–2.

When casting molten ferrous metals, or other metals which tend to react with or absorb phosphorus from the mold material, it is of advantage to form the inner shell layer with a raised temperature binder formed of an alkali metal salt base compound, such as consisting of an alkali metal fluoride plus boric acid. Thus if the inner shell layer is formed with an ammonium phosphate as

the raised temperature binder, the ferrous metal has the tendency to absorb phosphorus from the mold. On the other hand, if the inner shell layer is formed with a raised temperature binder composed of an alkali metal salt base compound, the inner shell layer prevents the molten ferrous or like metal being cast from absorbing phosphorus from the outer shell layer while the ammonium phosphate in the outer backing shell layer assures that the shell mold will not sag or become distorted when, in processing, it is heated to a raised temperature at which the raised temperature binders become effective and causes the refractory particles to become bound into a self-supporting porous thin shell mold from which all resin binder ingredients have been expelled.

Such combination of different high temperature binder ingredients in the inner shell layer and the outer backing shell layer of shell mold of the invention is also of great advantage because the presence of the alkali metal binder compound or compounds on the exterior surface of the inner shell layer and of the ammonium phosphate at the interior surface of the outer backing shell layer results in the formation of a weak junction stratum or interface between the inner and outer shell layers of the shell mold of the invention. This weak junction stratum is capable of yielding and permits the inner shell layer to slightly contract or expand, for instance, when metal having a very high melting point is cast into the mold cavity or when hot molten metal cast into the mold cavity cools and contracts about cores, or like wall portions of the mold.

In order to render the raised temperature binders effective, the shell mold containing the ammonium phosphate binder particles is subjected to a baking or firing treatment at elevated temperatures, at which the ammonium phosphate binder content becomes effective in causing the refractory particles to become bound into a self-supporting thin shell mold and at which the low temperature resinous binder is fully, or at least partially modified into a vapor and driven off to render the shell mold porous.

Baking temperatures above 530° C. and particularly between 1000° C. to 1200° C. are desirable. At the baking temperatures, the low temperature organic resinous binder that is adherent to a frozen mercury pattern is modified to provide a vapor which exudes or is expelled through the mold walls thereby rendering the shell mold porous while the raised temperature binder becomes effective in binding the refractory particles together. When sodium fluoride and boric acid are used as the raised temperature binder of the inner shell layer and primary ammonium phosphate is used as the raised temperature binder of the outer backing shell layer, the refractory particles with the sodium fluoride and the boric acid in the inner shell layer are modified at the baking temperatures to form a strong hard inner shell layer, and the refractory particles with the ammonium phosphate in the outer shell layer are modified at the baking temperatures into a strong hard outer shell layer which backs up the inner shell layer and forms with it a strong, thin porous shell mold.

As the inner and outer shell layers with their different raised temperature binders are baked and hardened at about 1000° C., the stratum or interface between the two shell layers provides only a relatively weak bond between them, which permits the inner shell layer to yield when hot metal is cast into the mold cavity or when the cooling metal cast into the mold cavity contracts about cores or other inserts of the shell mold.

After baking the shell molds of the invention, the metal may be cast therein by any desirable method, such as by static or centrifugal casting or the molten metal may be cast in the shell mold under pressure or under vacuum. Thus, a shell mold such as shown at **21** in Fig. 4, may be suspended in a suitable vessel, such as in flask **24**, of Fig. 5, and supported therein by any suitable loose particle refractory material, such as loose sand which is placed or blown around the shell mold. When it is difficult for the loose refractory material to flow into the fine crevices of an intricate shell mold, the flask **24** is vibrated to assist in packing the loose refractory particles. The hot molten metal is cast into the cavity of the thin-walled shell mold **21** so held suspended within flask **24**. Since the shell mold of the invention is thin and porous, it permits gases to pass through walls of the shell mold during casting of the molten metal.

The shell mold may be easily removed from the casting. If the cast metal may be quenched in liquids, such as oil or water, the casting may be quenched and a considerable portion of the refractory material will fall off during the quenching operation. The remainder of the shell mold may be removed by blasting, such as sand blasting.

Shell molds of the invention—in the form of a two-layer shell mold shown in Figs. 2 and 4, and Figs. 7 and 8, or in the form of a single layer shell mold as shown in Fig. 5—may be produced without the raised temperature binder by omitting it from the shell-forming coating compositions which are applied to the frozen mercury pattern for forming thereon the shell mold.

In accordance with a phase of the invention, shell molds of the invention which have been prepared without the raised temperature binder—after drying into a self-supporting shell mold and removal of the liquefied mercury from the mold cavity—are combined with a raised temperature binder by impregnating such self-supporting shell mold with a solution of a raised temperature binder which is effective in the same way as the raised temperature binder embodied in the shell-forming coating compositions of the type explained hereinabove.

In other words, in accordance with the invention, shell molds of the invention, which do not contain a raised temperature binder, are impregnated with a solution containing a raised temperature binder, which—after evaporation or driving off of the liquid carrier—becomes effective as a binder for the refractory particles of the shell mold at temperatures ranging from above normal temperature up to the temperature below that of at which the organic resinous binder of the shell mold becomes modified to at least partially lose its binding properties, such as at temperatures from about 450° C. to 600° C., and which added raised temperature binder, after becoming effective, binds the refractory particles together from below normal temperatures up to the high temperatures of molten metal and metal alloys that are cast into the mold cavity.

By way of example, a self-supporting thin-wall two-layer shell mold of the invention, is prepared on a frozen mercury pattern, by first forming the inner shell layer with the composition of Example C–1, and after completing the inner shell layer, the outer shell layer is formed thereover with the composition of Example E–1 from which the ammonium phosphate ingredient has been omitted. The two-layer shell mold so formed on the frozen mercury is then dried until all the carrier or solvent thereof has been driven off while the frozen mercury pattern remains in the mold cavity. Thereafter, the frozen mercury pattern is liquefied and removed from the mold cavity and the self-supporting shell mold is then impregnated with a solution containing the raised temperature binder. After impregnation, the solvent is driven off by drying. Thereafter, the shell mold with the raised temperature binder so embodied therein is subjected to the baking treatment in the same way as the hereinbefore described shell molds of the invention containing the raised temperature binder.

Among raised temperature binder impregnating solutions which may be applied in the manner just described are an aqueous solution of phosphoric acid of a strength varying from 10% to 85% or an aqueous solution of ethyl silicate; also aqueous solutions of sodium silicate,

sodium metasilicate and zirconium oxychloride. A small amount of wetting agent, such as about 1% of dioctyl sodium sulfosuccinate may be added to the impregnating solution.

The impregnation of the shell mold in the manner described above may be carried on by immersing the self-supporting shell mold into a bath of the impregnating solution containing the raised temperature binder and maintaining it therein for a sufficient time for the solution to completely penetrate the shell mold. Alternatively, the shell mold may be left immersed in the impregnated solution for a shorter time which permits penetration of the raised temperature binder to certain depth of the shell, thus impregnating only an outer backing region of the shell mold with the raised temperature binder.

The time such shell mold is exposed to the impregnating solution will vary with the thickness of the shell mold, the concentration of the impregnating solution, and the depth of penetration desired, depending upon the particular metals that are to be cast into the shell mold. When a concentrated or saturated solution of the impregnating liquid is utilized and the shell mold is comparatively thin, less than a minute may be required, whereas several minutes may be required when the shell mold is comparatively thick, such as shell molds having a thickness ranging from approximately ¼ to ⅜ of an inch. In general, the concentration of the solution and the time of impregnation should be sufficient to incorporate in the shell mold from approximately .25% to 5% of the raised temperature binder based on the total weight of the mold.

The following examples illustrate raised temperature binder compositions that are satisfactory for impregnation of shell molds composed of a refractory material and a low temperature organic resinous binder that is adherent to a frozen mercury pattern:

Example F–1

	Grams
Sodium metasilicate	462.0
Dioctyl sodium sulfosuccinate	10.0
Water	1,000.0

Example F–2

	Grams
Phosphoric acid, 85% solution	50.0
Dioctyl sodium sulfosuccinate	1.0
Water	4,000.0

Example F–3

	Grams
Zirconium tetrachloride	1,000.0
Water	4,000.0

The zirconium tetrachloride reacts with the water to form soluble zirconium oxychloride ($ZrOCl_2$). A wetting agent may be added.

The solution of the Example F–3 is suitable for embodying a raised temperature binder in shell molds of the invention containing polyvinyl acetate as the low temperature resin binder.

In general, thin-wall shell molds of the invention which do not contain the raised temperature binder—and suitable for impregnation with a raised temperature binder in the manner just described—may be produced on a frozen mercury pattern by using the inner shell layer the shell-forming compositions of Examples A–1 through A–3 or D–1 from which the raised temperature binder was omitted. Similarly the outer backing shell layer may be formed over such inner shell layer by using shell-forming compositions of Example B–1 through B–2 from which the raised temperature binder was omitted.

In making shell molds of the invention which combine refractory particles with a low-temperature resinous binder and a raised temperature inorganic binder as disclosed heeinabove, much stronger and superior shell molds are obtained if the amount of the organic resinous binder is at least about .5% and does not exceed about 2% of the solid investment ingredients applied to form the shell mold. For best results the resinous binder ingredients should be between 1% to 1.5% of these solid investment ingredients. The amount of the organic resinous binder may also be between 0.5% and 5% as disclosed in our prior application Serial No. 257,328, filed Nov. 20, 1951, now abandoned.

It will be apparent to all those skilled in the art that the novel principles of the invention disclosed herein in connection with specific exemplifications thereof will suggest various other modifications and applications of the same. It is accordingly desired that in the present invention they shall not be limited to the specific exemplification thereof described herein.

What we claim is:

1. An investment composition for application in the form of a layer of film to a frozen mercury pattern below the freezing temperature of the pattern material and producing a shell-like mold around said pattern, said composition comprising as composition ingredients a refractory material of small particle size constituting a predominant amount of the normally solid composition ingredients, an organic resinous binder for said refractory particles that is adherent to the frozen mercury pattern when a film or layer of the composition is applied thereto comprising a mixture of polymerized vinyl acetate and ethyl cellulose that has been materially ethylated, which mixture constitutes .25% to 5% of said solid ingredients and is present in an amount sufficient to bind the refractory particles in the applied layer or film of said composition together over a temperature range from below said freezing temperature up to at least a temperature 90° C. higher than said freezing temperature, and said polymerized vinyl acetate and ethyl cellulose each being present in an amount sufficient to provide at least a substantial portion of the binding action of said mixture over said temperature range, and a liquid carrier for said refractory particles and said binder that is in the liquid state at temperatures below said freezing temperature and has a boiling point below 0° C., said carrier being present in an amount sufficient to hold dispersed said solid composition ingredients and provide a slurry of sufficiently low viscosity at below said freezing temperature to enable said composition to be applied to the frozen mercury pattern in the form of a layer or film for forming thereover a shell mold.

2. A composition for application in the form of a layer or film to a frozen mercury pattern below the freezing temperature of the pattern material, said composition comprising as composition ingredients a refractory material of small particle size constituting a predominant amount of the normally solid composition ingredients, an organic resinous binder for said refractory particles that is adherent to the frozen mercury pattern when a film or layer of the composition is applied thereto, said binder comprising a mixture of polymerized vinyl acetate and ethyl cellulose that has been ethylated to the extent of at least 46.5% which mixture constitutes .25% to 5% of said solid ingredients and is present in an amount sufficient to bind the refractory particles in the applied layer or film of said composition together over a temperature range from below said freezing temperature up to at least a temperature 90° C. higher than said freezing temperature, and said polymerized vinyl acetate and ethyl cellulose each being present in an amount sufficient to provide at least a substantial portion of the binding action of said mixture over said temperature range, and an organic liquid carrier for said binder that is in the liquid state at temperatures below said freezing temperature and has a boiling point below 0° C., said carrier being present in an amount sufficient to hold dispersed said binder particles and to provide with the solid ingredients of the composition a slurry of sufficiently low viscosity at said freezing temperature to enable said composition to be applied to the

frozen mercury pattern in the form of a layer or film and forming thereover said shell mold.

3. In a destructible shell mold, a shell-shape structure having thin shell walls and an inner cavity surface layer comprising as shell ingredients a predominant amount of refractory material of small particle size to provide a relatively smooth inner surface, an organic resinous binder for said refractory particles comprising a mixture of polymerized vinyl acetate and ethyl cellulose that has been ethylated to at least about 46.5% said mixture of polymerized vinyl acetate and ethyl cellulose constituting .25 to 5% of the said solid composition ingredients and being present in an amount sufficient to bind the refractory particles together into a self-supporting shell mold structure.

4. In a destructible shell mold having a cavity of a shape corresponding to an object to be cast, a generally shell-like shaped inner shell layer having an inner surface forming the mold cavity and comprising as layer ingredients, a predominant amount of refractory material and the cavity surface of said layer having refractory material of a particle size small enough to provide a relatively smooth inner surface and an organic resinous binder for said refractory particles comprising a mixture of polymerized vinyl acetate and an ethyl cellulose that has been materially ethylated, and said polymerized vinyl acetate and ethyl cellulose constituting .25% to 5% of said layer ingredients and being present in the mixture in an amount sufficient to provide a substantial portion of the binding action, and a supporting shell layer overlying said inner shell layer which corresponds substantially in shape to said inner shell layer and forms with it a self-supporting shell mold structure having relatively thin walls, said supporting shell layer comprising as layer ingredients a predominant amount of refractory particles consisting of a substantial portion of fine particles mixed with a substantial portion of coarse particles, and an organic resinous binder for the refractory particles in the supporting shell layer comprising a mixture of polymerized vinyl acetate and an ethyl cellulose that has been materially ethylated, said mixture of polymerized vinyl acetate and ethyl cellulose in the supporting structure constituting .25% to 5% of the supporting layer ingredients and being present in an amount sufficient to bind the refractory particles in the supporting shell layer together.

5. The method of preparing a shell mold which comprises applying to a frozen mercury pattern at very low temperatures below the freezing point of the pattern material a slurry-like investment composition comprising as solid composition ingredients a refractory material of small particles constituting a predominant amount of the solid composition ingredients, an organic resinous binder for the refractory particles that is adherent to the frozen mercury pattern and which comprises a mixture of polymerized vinyl acetate and ethyl cellulose that has been materially ethylated, which mixture constitutes .25% to 5% of said solid composition ingredients and is present in sufficient amount to cause said solid composition ingredients to adhere to each other and to adhere as coating strata to said pattern from said very low temperatures up to at least a temperature 90° C. higher than said freezing temperature and a liquid carrier for said binder which carrier is in the liquid state at said very low temperatures and has a boiling point below 0° C. and is present in an amount sufficient to hold dispersed said binder and to provide with the refractory particles a slurry of sufficiently low viscosity at very low temperatures to enable the composition to be applied to the frozen mercury pattern, drying the applied coating strata at said very low temperatures and below the boiling point of said carrier until the shell mold structure is formed of the applied composition, subjecting the coated pattern to such temperature that the mercury will liquefy, and then removing the liquefied mercury from the so formed shell mold structure.

6. A slurry-like investment composition for application as a shell layer or coating film and producing a shell-like mold over a frozen mercury pattern below the freezing temperature of the pattern material, said composition comprising as solid ingredients which form an applied shell layer refractory particles which for the inner shell layer are of fine particle size, an inorganic binder for the refractory particles constituting .25% to 7% of said solid ingredients and becoming effective as a binder for the refractory particles on heating to a raised temperature between 350° C. and 1250° C., which inorganic binder is effective and is present in sufficient amount upon becoming effective to bind the refractory particles of a shell layer into a firm structure, an organic binder comprising a mixture of polymerized vinyl acetate and ethyl cellulose which has been materially ethylated, which mixture constitutes .25% to 5% of said solid ingredients, and is effective and is present in sufficient amount to bind the refractory particles and the inorganic binder into a shaped shell layer over temperatures from below said freezing temperature up to temperatures at which said inorganic binder becomes effective in binding the refractory particles, and a liquid carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder at temperatures below said freezing temperature, and has a boiling point a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity at below said freezing temperature, to enable said composition to be applied to said pattern in the form of a layer or film for forming thereover a shell mold.

7. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, and said carrier being selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

8. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

9. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an ammonium phosphate of fine particle size.

10. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an alkali metal fluoride together with boric acid.

11. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an alkali metal fluoride together with boric oxide.

12. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an ammonium phosphate of fine particle size, and said carrier being an organic solvent selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

13. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an alkali metal fluoride together with boric acid, and said carrier being an organic solvent selected from the group consisting of monochlorodifluoromethane, methyl chloride, and a mixture of monochlorodifluoromethane and methyl chloride.

14. A slurry-like investment composition as claimed in claim 6, said ethyl cellulose having been ethylated to

at least 30%, said inorganic binder comprising an alkali metal fluoride together with boric oxide, and said carrier being an organic solvent selected from the group consisting of monochlorodifluoromethane, methyl chloride, and a mixture of monochlorodifluoromethane and methyl chloride.

15. In a destructible shell mold having a cavity of a shape corresponding to an object to be cast, at least one generally shell-like shell layer having an inner surface forming the mold cavity and comprising as solid ingredients a predominant amount of refractory material and the cavity surface of said shell layer having refractory material of a particle size small enough to provide a relatively smooth inner surface, an inorganic binder for the refractory particles constituting .25% to 5% of said solid ingredients and becoming effective as a binder for the refractory particles when heated to a raised temperature between 350° C. and 1200° C., which inorganic binder is effective and is present in sufficient amount upon becoming effective to bind the refractory particles of a shell layer of said shell mold into a firm structure, and an organic resinous binder for said refractory particles and inorganic binder comprising a mixture of polymerized vinyl acetate and ethyl cellulose which has been materially ethylated, which mixture constitutes .25% to 5% of said solid ingredients and being effective and present in sufficient amount to bind the refractory particles and the inorganic binder into a shaped shell layer over temperatures from below said freezing temperature up to temperatures at which said inorganic binder becomes effective in binding the refractory particles.

16. A shell mold as claimed in claim 15, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

17. A shell mold as claimed in claim 15, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an ammonium phosphate of fine particle size.

18. A shell mold as claimed in claim 15, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an alkali metal fluoride together with boric acid.

19. A shell mold as claimed in claim 15, said ethyl cellulose having been ethylated to at least 30%, said inorganic binder comprising an alkali metal fluoride together with boric oxide.

20. The method of preparing a shell mold with a frozen pattern of mercury, which comprises applying to said pattern a slurry-like investment composition in an amount sufficient to form a thin shell layer while said pattern and the slurry are at temperatures below the freezing temperature of the pattern material, said composition comprising as normally solid ingredients which form an applied shell layer refractory particles constituting a predominant amount of said ingredients and which at least for the inner shell layer have fine particle size, an inorganic binder constituting .5% to 5% of said solid ingredients and which is ineffective as a binder for the refractory material when the composition is applied to said pattern, but becomes effective as a binder and is sufficient in amount to bind said refractory particles into a firm shell layer when heated to a raised temperature between 150° C. to 1250° C., an organic binder for the refractory particles and the inorganic binder comprising a mixture of polymerized vinyl acetate and ethyl cellulose that has been ethylated to at least 30%, and constituting .25% to 5% of said solid ingredients, which organic binder is effective and is present in sufficient amount to cause the refractory particles and the inorganic binder to be bound into a shaped shell layer at temperatures from below said freezing temperature up to a temperature at which said inorganic binder becomes effective as a binder for the refractory particles, and a liquid carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder at temperatures below said freezing temperature, and has a boiling point within a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity at below said freezing temperature to enable said composition to be applied to said pattern in the form of a layer or film for forming thereover a shell mold, drying the shell mold formed of the applied composition while held on said pattern at below said freezing temperature and below said boiling point, thereafter liquefying the material of said pattern and removing it from the shell mold, and thereafter heating the shell mold to render said inorganic binder effective in binding the refractory particles into a shell mold and to drive off said organic binder to render said shell mold porous.

21. The method of preparing a shell mold as claimed in claim 20, said carrier being selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

22. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

23. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising an ammonium phosphate of fine particle size.

24. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising an alkali metal fluoride together with boric acid.

25. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising an alkali metal fluoride together with boric oxide.

26. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising an ammonium phosphate of fine particle size, said carrier being an organic solvent selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

27. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising an alkali metal fluoride together with boric acid, said carrier being an organic solvent selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

28. The method of preparing a shell mold as claimed in claim 20, said inorganic binder comprising an alkali metal fluoride together with boric oxide, said carrier being an organic solvent selected from the group consisting of monochlorodifluoromethane, methyl chloride, and a mixture of monochlorodifluoromethane and methyl chloride.

29. The method of producing a porous self-supporting shell mold in the form of a porous thin shell layer over the exposed surfaces of a casting pattern formed of frozen mercury, which method comprises preparing a liquid slurry-like investment composition which will adhere to said frozen pattern when applied thereto as coating strata at low temperatures below the freezing temperature of said pattern metal, which investment composition comprises as normally solid ingredients refractory particles constituting a predominant amount of said ingredients applied to form the shell layer, an inorganic raised temperature binder for the refractory particles that is ineffective as a binder for the refractory particles when the composition is applied to said casting pattern but which becomes effective as a binder for the refractory particles at a raised temperature between about 350° to 1250° C., which raised temperature binder constitutes about 0.1% to 5%

by weight of said solid composition ingredients, and which after becoming effective binds the refractory particles into a firm shell layer at temperatures from 0° C. up to the high casting temperature of metals having a melting temperature of at least about 700° C., a synthetic organic resinous binder for the refractory particles and the raised temperature binder, which organic binder constitutes about 0.25% to 5% by weight of said solid ingredients and has the property of causing said composition to adhere as a shell layer to said pattern over a medium temperature range from said low temperatures up to said raised temperature, which organic binder is present in an amount sufficient to cause the refractory material and the raised temperature binder to adhere to the pattern and to bind the refractory material and the raised temperature binder into a shell layer over said medium temperature range, and a carrier which is an organic solvent, and is liquid and at least a colloidal solvent for said organic binder at said low temperatures and has a boiling point a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity to enable said composition to be applied in the form of a shell layer to said pattern, thereafter applying said composition to said pattern at said low temperatures as coating strata until there is formed a shell layer which adheres to said pattern and has a thickness of at most about one-quarter inch and which after making the raised temperature binder effective renders the shell layer self-supporting and porous, thereafter drying the shell layer adhering to said pattern at said low temperatures and below the boiling point of the liquid carrier to solidify said shell layer, thereafter liquefying the metal of the pattern and removing the liquefied pattern metal from the solidified shell layer to provide the shell mold, and then heating the shell mold 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.

30. The method for producing a shell mold as claimed in claim 29, wherein the shell layer is formed by first applying to the frozen casting pattern one coating stratum of said coating composition while said composition and said pattern are at said low temperatures, and after at least partially drying the exterior of said one coating stratum at said low temperatures, applying to the exterior of said one coating stratum at least one superposed coating stratum of the same or of similar coating composition while said applied compositions and said pattern are at said low temperatures, and at least partially drying the exterior surface of said superposed coating stratum at said low temperatures.

31. The method for producing a shell mold as claimed in claim 29, wherein the thin shell layer is formed by first applying at said low temperatures to the frozen metal pattern at least one stratum of said coating composition containing said fine refractory particles to provide an inner layer formation having a relatively smooth mold cavity surface, and thereafter applying over said inner layer formation at said low temperatures at least one superposed coating stratum of a similar investment composition having the refractory particle material, partly in the form of coarse particles of +60 to −20 mesh particle size and partly in the form of fine particles, with the fine particles being present in an amount sufficient to maintain the coarse particles in suspension within said composition, for forming with said superposed coating strata an outer backing layer formation which supports said inner layer formation and constitutes therewith a self-supporting shell mold.

32. The method of producing a shell mold as claimed in claim 29, said carrier having a boiling point within a temperature range 30° C. higher than said freezing temperature.

33. The method of producing a shell mold as claimed in claim 29, said carrier being a compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

34. The method of producing a shell mold as claimed in claim 29, said organic compound being selected from the group consisting of polymerized vinyl acetate, ethyl cellulose which has been materially ethylated, and a mixture of polymerized vinyl acetate and ethyl cellulose which has been materially ethylated, copolymers of acrylonitrile and butadiene, polymerized isobutyl methacrylate and normal butyl methacrylate.

35. The method of producing a shell mold as claimed in claim 29, said organic compound being selected from the group consisting of polymerized vinyl acetate, ethyl cellulose which has been materially ethylated, and a mixture of polymerized vinyl acetate and ethyl cellulose which has been materially ethylated, copolymers of acrylonitrile and butadiene, polymerized isobutyl methacrylate and normal butyl methacrylate, said carrier having a boiling point within a temperature range 30° C. higher than said freezing temperature.

36. The method of producing a shell mold as claimed in claim 29, said organic compound being selected from the group consisting of polymerized vinyl acetate, ethyl cellulose which has been materially ethylated, and a mixture of polymerized vinyl acetate and ethyl cellulose which has been materially ethylated, copolymers of acrylonitrile and butadiene, polymerized isobutyl methacrylate and normal butyl methacrylate, said carrier being a compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

37. The method of preparing a shell mold with a frozen mercury pattern of an object to be cast, which comprises applying to said frozen pattern an investment coating composition in the form of a slurry suitable for forming a thin shell layer while said pattern and slurry are at low temperatures below the freezing temperature of the pattern material, said coating composition comprising as solid ingredients which form said shell layer refractory particles constituting a predominant amount of said ingredients with the refractory particles applied to form the inner mold cavity surface being of fine particle size, an inorganic raised temperature binder comprising ammonium phosphate of small particle size which constitute .5% to 5% of said ingredients and having the property and being sufficient to provide at a raised decomposition temperature sufficient phosphoric acid to bind together the refractory particles of said shell layer over temperatures from normal temperature between about −20° C. to 50° C. up to the casting temperature of metals having a high melting temperature, an organic binder for said refractory material and said raised temperature binder constituting 0.25% to 5% of said ingredients, which organic binder has the property of adhering to said pattern and is present in an amount sufficient to cause said refractory particles and said raised temperature binder to be bound into a firm shell layer over temperatures from said low temperatures up to said raised temperature at which the raised temperature binder becomes effective in binding said refractory particles into a shell layer and causing the organic binder to be modified and be driven off as vapors, and a liquid carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder at said low temperatures and has a boiling point within a temperature range between said freezing temperature and 40° C. higher

than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to at least hold dispersed said solid ingredients and to provide with said ingredients a slurry of sufficiently low viscosity to enable the composition to be applied as a shell layer or film to said pattern, drying the shell layer formed on the pattern below said freezing temperature and below the boiling point of the solvent to solidify the shell layer into a shell mold, thereafter liquefying said pattern and removing the liquefied pattern material from the shell mold, and then heating the shell mold to a raised temperature which causes the ammonium phosphate particles to decompose and provide phosphoric acid which binds together the refractory particles of the shell mold and which modifies and drives off said organic binder to render the shell mold porous.

38. The method of preparing a shell mold with a frozen mercury pattern of an object to be cast, which comprises applying to said pattern a first investment composition in the form of a slurry suitable for forming a thin shell layer while said pattern and the slurry are at low temperatures below the freezing temperature of the pattern material, said first investment composition comprising as solid ingredients which form said shell layer refractory particles of fine particle size constituting a predominant amount of said ingredients, an inorganic raised temperature binder substantially free of phosphorus compounds constituting 0.5% to 5% of said solid ingredients and having the property and being sufficient to provide at a raised temperature a binding action sufficient to bind together the refractory particles of said shell layer over temperatures from normal temperature between —20° C. to 50° C. up to the casting temperature of metals having a high melting temperature, an organic binder for said refractory particles and said raised temperature binder constituting .25% to 5% of said ingredients, which organic binder has the property of adhering to said pattern and is present in an amount sufficient to cause said refractory particles and said raised temperature binder to be bound into a firm shell layer over temperatures from said low temperatures up to said raised temperature above which the raised temperature binder becomes effective in binding said refractory particles into a shell layer and causing the organic binder to be modified and be driven off, and a liquid carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder at temperatures below said freezing temperature and has a boiling point within a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in amount sufficient to at least hold dispersed said solid ingredients and to provide with said ingredients a slurry of sufficiently low viscosity to enable said composition to be applied in the form of a shell stratum or layer to said pattern and after forming at least one shell stratum out of said first composition over said pattern, forming thereover at least one additional shell stratum superposed thereon by applying over the previous shell stratum a further investment composition similar to the first investment composition but containing ammonium phosphate of small particle size as a raised temperature binder in an amount ranging from 0.5% to 5% of said solid ingredients to provide at a raised decomposition temperature sufficient phosphoric acid to substantially bind together the refractory particles of said additional shell stratum over a temperature range from normal temperature between —20° C. to 50° C. up to the casting temperature of metals having a high melting temperature, drying the shell layer of said strata formed on said pattern below said freezing temperature and below the boiling point of said carrier to solidify the shell layer into a shell mold, liquefying the pattern and removing the liquefied pattern material from said shell mold and then heating the shell mold to a raised temperature which causes the ammonium phosphate particles to decompose and provide phosphoric acid which binds together the refractory particles of the shell mold and which modifies and drives off said organic binder to render the shell mold porous.

39. The method of preparing a shell mold with a frozen mercury pattern of an object to be cast, which comprises applying to said pattern a first investment composition in the form of a slurry suitable for forming a thin inner shell layer while said pattern and the slurry are at low temperatures below the freezing temperature of the pattern material, said first coating composition comprising as solid ingredients which form said shell layer refractory particles of fine particle size constituting a predominant amount of said solid ingredients, an inorganic raised temperature binder substantially free of phosphorus constituting 0.5% to 5% of said ingredients and having the property and being sufficient to provide at a raised temperature a binding action sufficient to bind together the refractory particles of said inner shell layer over temperatures from normal temperature between —20° C. to 50° C. up to the casting temperature of metals having a high melting temperature, an organic binder for said refractory particles and said raised temperature binder constituting .25% to 5% of said ingredients, which organic binder has the property of adhering to said pattern and is present in an amount sufficient to cause said refractory particles and said raised temperature binder to be bound into a firm shell layer over temperatures from said freezing temperatures up to said raised temperature above which said raised temperature binder becomes effective in binding the refractory particles into a shell layer and causing the organic binder to be modified and driven off, and a liquid carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder at said low temperatures and has a boiling point within a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to at least hold dispersed said solid ingredients and to provide with said ingredients a slurry of sufficiently low viscosity to enable said composition to be applied as a shell layer or film to said pattern, thereafter applying over the inner shell layer a second investment composition in the form of a slurry for forming an outer backing shell layer while said pattern and said second composition are below said low temperatures, said second composition being similar to the first composition with the exception that the refractory particle material is formed partly of fine refractory particles and partly of coarse refractory particles in the size range from +60 to —60 mesh with the fine particles being in an amount sufficient to maintain the coarse particles in suspension within said slurry, and that the raised temperature binder of the second coating composition comprises ammonium phosphate of small particle size in an amount sufficient to provide at a raised decomposition temperature a sufficient amount of phosphoric acid to substantially bind together the refractory particles of the shell layer formed of the second coating composition, thereafter drying the inner and backing shell layer formed on said pattern below said freezing temperature and below the boiling point of the carrier to solidify said shell layers into a shell mold, thereafter liquefying said pattern and removing the liquefied pattern material from said shell mold, and then heating the shell mold to a raised temperature which causes the ammonium phosphate particles to decompose and provide phosphoric acid which binds together the refractory particles of the shell mold and which modifies the organic binder and drives it off to render the shell mold porous.

40. The method of preparing a shell mold as claimed in claim 37, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

41. The method of preparing a shell mold as claimed in claim 38, said inorganic binder which is substantially free of phosphorus compounds comprising an inorganic compound selected from the group consisting of alkali metal fluorides and an alkali metal fluoride together with a boron compound selected from the group consisting of boric acid, boric oxide and alkali metal borates.

42. The method of preparing a shell mold as claimed in claim 38, said inorganic binder which is substantially free of phosphorus compounds comprising an inorganic compound selected from the group consisting of alkali metal fluorides and an alkali metal fluoride together with a boron compound selected from the group consisting of boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

43. The method of preparing a shell mold as claimed in claim 38, said inorganic binder which is substantially free of phosphorus compounds comprising an alkali metal fluoride together with boric, acid, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

44. The method of preparing a shell mold as claimed in claim 38, said inorganic binder which is substantially free of phosphorus compounds comprising an alkali metal fluoride together with boric oxide, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane and methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

45. The method of preparing a shell mold as claimed in claim 39, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

46. The method of preparing a shell mold as claimed in claim 39, said inorganic binder which is substantially free of phosphorus compounds comprising an inorganic compound selected from the group consisting of alkali metal fluorides and an alkali metal fluoride together with a boron compound selected from the group consisting of boric acid, boric oxide and alkali metal borates.

47. The method of preparing a shell mold as claimed in claim 39, said inorganic binder which is substantially free of phosphorus compounds comprising a compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane and methyl chloride.

48. The method of preparing a shell mold as claimed in claim 39, said inorganic binder which is substantially free of phosphorus compounds comprising an alkali metal fluoride together with boric acid, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

49. The method of preparing a shell mold as claimed in claim 39, said inorganic binder which is substantially free of phosphorus compounds comprising an alkali metal fluoride together with boric oxide, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

50. The method of preparing a shell mold as claimed in claim 38, said organic binder also including a thermosetting organic resin constituting from .3% to 3% of said solid ingredients, said inorganic binder which is substantially free of phosphorus compounds comprising a compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

51. The method of preparing a shell mold as claimed in claim 39, said organic binder also including a thermosetting organic resin constituting from .3% to 3% of said solid ingredients, said inorganic binder which is substantially free of phosphorus compounds comprising an inorganic compound selected from the group consisting of alkali metal fluorides and an alkali metal fluoride together with a boron compound selected from the group consisting of boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride, and a mixture of monochlorodifluoromethane with methyl chloride.

52. The method of preparing a shell mold with a frozen pattern of pattern material consisting predominantly of mercury, which comprises applying to said frozen pattern an investment coating composition in the form of a slurry suitable for forming a thin shell layer while said frozen pattern and the slurry are at temperatures below the freezing temperature of said pattern material, said composition comprising as normally solid ingredients which form the applied shell layer refractory particles constituting a predominant amount of the solid ingredients which form the applied layer, with the refractory particles applied to form the innermost shell layer being of fine particle size, an inorganic binder for the refractory particles constituting .25% to 5% of said ingredients and becoming effective as a binder for the refractory particles at a raised temperature between 350° C. to 1250° C., which raised temperature binder is present in sufficient amount and is effective to bind the refractory particles into a firm shell layer upon heating it at said raised temperature, an organic resinous binder for said refractory particles and said inorganic binder comprising polymerized vinyl acetate which has the property of being adherent to the frozen pattern at below said freezing temperatures and constitutes about .25% to 5% of said solid ingredients and has the property of causing and is present in an amount sufficient to cause the refractory particles and said inorganic binder to adhere to said pattern and to bind the refractory particles and said inorganic binder into a firm shell layer, at temperatures from below said freezing temperature up to at least 50° C., and a carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder below said freezing temperature and has a boiling point a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity to enable said composition to be applied in the from of a shell layer to said pattern, drying the formed shell layer at temperatures below said freezing temperature and the boiling point of the carrier, threafter liquefying said pattern, and then removing the liquefied pattern material from the shell layer to provide a shell mold.

53. The method of preparing a shell mold with a frozen pattern of pattern material consisting predominantly of mercury, which comprises applying to said frozen pattern a first investment coating composition in the form of a slurry suitable for forming a thin inner shell layer while said frozen pattern and the slurry are at temperatures below the freezing temperature of said pattern material, said composition comprising as normally solid ingredients which form the applied shell layer refractory particles constituting a predominant amount

of the solid ingredients which form the applied layer, with the refractory particles applied to form the innermost shell layer being of fine particle size, an inorganic binder for the refractory particles constituting .25% to 5% of said ingredients and becoming effective as a binder for the refractory particles at a raised temperature between 350° C. to 1250° C., which raised temperature binder is present in sufficient amount and is effective to bind the refractory particles into a firm shell layer upon heating it at said raised temperature, an organic resinous binder for said refractory particles and said inorganic binder comprising polymerized vinyl acetate which has the property of being adherent to the frozen pattern at below said freezing temperatures and constitutes .25% to 5% of said solid ingredients and has the property of causing and is present in an amount sufficient to cause the refractory particles and said inorganic binder to adhere to said pattern and to bind the refractory particles and said inorganic binder into a firm shell layer at temperatures from below said freezing temperature up to at least 50° C., and a carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder below said freezing temperature and has a boiling point a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity to enable said composition to be applied in the form of a shell layer to said pattern, thereafter applying over the inner shell layer a second coating composition in the form of a slurry to provide an outer shell layer while said pattern and the second composition are maintained at temperatures below said freezing temperature, said second composition being similar to the first coating composition with the exception that the refractory particles in the second composition consist of a substantial portion of coarse particles mixed with fine particles, drying the applied shell layers below said freezing temperature and below the boiling point of said carrier, thereafter liquefying the pattern, removing the liquefied pattern material from the formed shell layers to provide the shell mold, and then heating the shell mold to a temperature sufficient to cause the inorganic binder to become effective as a binder for the refractory particles of said shell mold and to drive off the organic binder to provide a porous shell mold.

54. The method of preparing a shell mold as claimed in claim 52, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

55. The method of preparing a shell mold as claimed in claim 52, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

56. The method of preparing a shell mold as claimed in claim 52, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

57. The method of preparing a shell mold as claimed in claim 53, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

58. The method of preparing a shell mold as claimed in claim 53, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

59. The method of preparing a shell mold as claimed in claim 53, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

60. The method of preparing shell molds with a frozen mercury pattern of an object to be cast, which comprises applying to said pattern an investment coating composition in the form of a slurry in an amount sufficient to form a thin shell layer while said pattern and the slurry are at temperatures below the freezing temperature of the pattern material, said composition comprising as normally solid ingredients which form the applied shell layer refractory particles constituting a predominant amount of said solid ingredients, and the composition applied to form at least the inner stratum of said shell layer containing substantially only fine refractory particles, an inorganic binder constituting .25% to 5% of said solid ingredients and that is ineffective as a binder for said refractory particles when the composition is applied to said pattern but which becomes effective as a binder for said refractory particles at a raised temperature between about 350° C. to 1250° C., an organic resinous binder for the refractory particles and the inorganic binder comprising ethyl cellulose that has been materially ethylated and which constitutes .25% to 5% of said solid ingredients and is adherent to the pattern and coherent to previously applied layers or films of the same or a similar composition at temperatures below said freezing temperature and which has the property of causing and is present in an amount sufficient to cause the refractory particles and the inorganic binder to adhere to said pattern and to bind said refractory particles and the inorganic binder into a shell layer at temperatures from below said freezing temperature up to a temperature above that at which the inorganic binder becomes effective as a binder for the refractory particles, and a carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder below said freezing temperature and has a boiling point a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity to enable said composition to be applied in the form of a shell layer to said pattern, drying the formed shell layer at temperatures below said freezing temperature and the boiling point of the carrier, liquefying said pattern, removing the liquefied pattern material from said shell layer to provide the shell mold, and then heating the shell mold to a temperature sufficient to cause the inorganic binder to become effective as a binder for the refractory particles and to drive off the ethyl cellulose to render the shell mold porous.

61. The method of preparing shell molds with a frozen mercury pattern of an object to be cast, which comprises applying to said pattern a first investment coating composition in the form of a slurry in an amount sufficient to form a thin inner shell layer while said pattern and the slurry are at temperatures below the freezing temperature of the pattern material, said composition comprising as normally solid ingredients which form the applied shell layer refractory particles constituting a predominant amount of said solid ingredients of the applied layer, and the composition applied to form at least the inner stratum of said shell layer containing substantially only fine refractory particles, an inorganic binder constituting .25% to 5% of said solid ingredients and that

is ineffective as a binder for said refractory particles when the composition is applied to said pattern but which becomes effective as a binder for said refractory particles at a raised temperature ranging between 350° C. to 1250° C., an organic resinous binder for the refractory particles and the inorganic binder comprising ethyl cellulose that has been materially ethylated and which constitutes .25% to 5% of said solid ingredients and is adherent to the pattern and coherent to previously applied layers or films of the same or a similar composition at temperatures below said freezing temperature and which has the property of causing and is present in an amount sufficient to cause the refractory particles and the inorganic binder to adhere to said pattern and to bind said refractory particles and the inorganic binder into a shell layer at temperatures from below said freezing temperature up to a temperature above that at which the inorganic binder becomes effective as a binder for the refractory particles, and a carrier which is an organic solvent and is liquid and at least a colloidal solvent for some of said organic binder below said freezing temperature and has a boiling point a temperature range between said freezing temperature and 40° C. higher than said freezing temperature at atmospheric pressure, said carrier being present in an amount sufficient to hold at least dispersed said solid ingredients and to provide with them a slurry of sufficiently low viscosity to enable said composition to be applied in the form of a shell layer to said pattern, and after forming said inner shell layer, applying over said inner shell layer a second investment composition in the form of a slurry to provide an outer shell layer while said pattern and the second composition are maintained at temperatures below said freezing temperature, said second composition being similar to said first composition with the exception that the refractory particles in the second composition consist of a substantial proportion of coarse particles mixed with fine particles, drying the applied shell layers below said freezing temperature and below the boiling point of said carrier, thereafter liquefying the pattern, removing the liquefied material from the formed shell layers to provide the shell mold, and then heating the shell mold to a temperature sufficient to cause the inorganic binder to become effective as a binder for the refractory particles of said shell mold and to drive off the organic binder to provide a porous shell mold.

62. The method of preparing shell molds as claimed in claim 60, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

63. The method of preparing shell molds as claimed in claim 60, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

64. The method of preparing shell molds as claimed in claim 60, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

65. The method of preparing shell molds as claimed in claim 61, said carrier being an organic solvent compound selected from the group consisting of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

66. The method of preparing shell molds as claimed in claim 61, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates.

67. The method of preparing shell molds as claimed in claim 61, said inorganic binder comprising at least one inorganic compound selected from the group consisting of ammonium phosphates, alkali metal fluorides, boric acid, boric oxide and alkali metal borates, said carrier being an organic solvent compound selected from the group of monochlorodifluoromethane, methyl chloride and a mixture of monochlorodifluoromethane with methyl chloride.

68. In a destructible shell mold, a shell-shaped mold structure having a wall thickness of at most about ⅜ inch and an inner surface forming the cavity of a shape corresponding to the object to be cast and comprising as shell ingredients a predominant amount of refractory particle material, and the inner cavity surface having refractory particle material of sufficiently fine particle size to provide a smooth cavity surface, an inorganic binder for the refractory material that is ineffective as a binder for the refractory material in the shell mold but which becomes effective as a binder for such material at temperatures ranging from approximately 350° C. to 600° C., and which after becoming effective constitutes 0.25% to 5% of the solid shell ingredients and binds and is present in an amount sufficient to bind the refractory material together at temperatures ranging from low temperatures up to the casting temperatures of metals having a high melting temperature, and an organic resinous binder for the refractory material constituting .25% to 5% by weight of the shell ingredients and comprising ethyl cellulose which has been materially ethylated and which has the property of being adherent to a frozen mercury pattern and of binding and being present in an amount sufficient to bind the refractory material and the inorganic binder together at temperatures ranging from below the freezing temperature of mercury up to the temperature at which the inorganic binder becomes effective as a binder for the refractory material, said organic binder having the property of becoming modified when the shell mold is heated to a temperature at which the inorganic binder becomes effective and thereby giving the mold walls of the shell mold high porosity so that gases evolved from metal cast into the mold cavity shall pass substantially freely through said mold walls, the inner stratum of said mold structure facing the mold cavity containing as an inorganic binder a metal fluoride and a boron compound, the outer stratum of said mold structure containing as an inorganic binder primary ammonium phosphate in fine particle size.

69. In a destructible shell mold having a mold cavity of a shape corresponding to the object to be cast, an inner shell layer of small thickness comprising as shell ingredients a predominant amount of refractory material of sufficiently fine particle size to provide a relatively smooth inner surface of the mold cavity, an inorganic binder that is ineffective as a binder for the refractory material in the inner shell layer but which becomes effective as a binder for such material at temperatures ranging from approximately 350° C. to 600° C. and which after becoming effective constitutes 0.25% to 5% of the solid shell ingredients and binds and is present in an amount sufficient to bind the refractory material in the inner shell layer together at temperatures ranging from low temperatures up to the high casting temperatures of metals having a high melting temperature, and an organic resinous binder for the refractory material and the inorganic binder in the inner shell layer comprising ethyl cellulose which has been materially ethylated and which has the property of being adherent to a frozen mercury pattern and of bind and being present in an amount sufficient to bind the refractory material and the inorganic binder in the inner shell layer together at temperatures ranging from below the freezing temperature of mercury up to the temperature at which the inorganic binder becomes effective as a binder for the refractory material, said mold having also a supporting outer shell layer of substantially the same shape as the inner shell layer which overlies and is coherent to the inner shell layer and which provides with the inner shell layer a self-supporting shell mold

having a thickness of at most about ⅜ of an inch depending upon the thickness of the object to be cast, said outer shell layer comprising a predominant amount of refractory material consisting of a substantial portion of fine particles mixed with a substantial portion of coarse particles ranging in size from +60 mesh to −12 mesh, an inorganic binder for the refractory material in the outer shell layer that is ineffective as a binder for the refractory material in the outer shell layer but which has the property of becoming effective as a binder for such material at temperatures ranging from approximately 350° C. to 600° C., and which after becoming effective constitutes 0.25% to 5% of the solid shell ingredients and binds and is present in an amount sufficient to bind the refractory material in the outer shell layer together at temperatures ranging from low temperatures up to said high casting temperatures, and an organic resinous binder for the refractory material and the inorganic binder in the outer shell layer comprising ethyl cellulose which has been materially ethylated, and which organic binder constitutes .25% to 5% by weight of the ingredients of the outer shell layer and has the property of being coherent to the inner shell layer and of causing and being present in an amount sufficient to cause the refractory particles and the inorganic binder in the outer shell layer to cohere to the inner shell layer at temperatures ranging from said freezing temperature up to the temperature at which the inorganic binder in the outer shell layer becomes effective as a binder for the refractory material and to bind the refractory material and the

inorganic binder in the outer shell layer together at temperatures ranging from said freezing temperature up to the temperature at which the inorganic binder in the outer shell layer becomes effective as a binder for the refractory material, said organic binder having the property of becoming modified when the shell mold is heated to a temperature at which the inorganic binder becomes effective and thereby giving the mold walls of the shell mold high porosity so that gases evolved from metal cast into the mold cavity shall pass substantially freely through said mold walls, the inner stratum of said mold structure facing the mold cavity containing as an inorganic binder a metal fluoride and a boron compound, the outer stratum of said mold structure containing as an inorganic binder primary ammonium phosphate in fine particle size.

70. In a shell mold as claimed in claim 68, the refractory particles which form at least the inner cavity surface of the shell mold being selected from the group consisting of zirconium silicate, stabilized zirconia and mixtures thereof.

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