

## UNITED STATES PATENT OFFICE

2,628,394

REPLICAS FOR USE IN THE PRODUCTION  
OF REFRACTORY MOLDSIlsabe E. Valyi, New York, N. Y., assignor to  
Emerik Imre Valyi, New York, N. Y.No Drawing. Application June 17, 1950,  
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4 Claims. (Cl. 22—196)

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This invention relates to the precision casting of metals. More particularly, it relates to new and improved replicas (patterns) for the production of refractory molds in precision casting of metals, and to a new and improved composition from which such replicas are produced.

This application is a continuation-in-part of my co-pending application Serial No. 688,335, filed August 3, 1946, for Replicas for Use in the Production of Refractory Molds, and Compositions Therefor, now abandoned.

Metal castings have been made by forcing a molten metal or alloy into a mold made from a refractory composition. The mold was usually made by casting a so-called investment of the refractory about a replica of wax. After the refractory had been set, the wax replica was melted and removed. The set refractory was finally subjected to a high temperature or firing whereby it was brought into final shape and condition to be used as the mold for metal casting.

In principle, the procedure of using the wax replicas above described appears to be simple and attractive. However, in practice it has many shortcomings and disadvantages. Though wax can be easily cast or molded to form the replica, nevertheless such replica does not possess satisfactory dimensional stability. The wax patterns are sensitive to temperature, organic solvents and mechanical actions. At temperatures of 50° F. and below, which may well be met in manufacturing practice, molding waxes tend to become extremely brittle, with the consequence that much breakage of replicas formed thereof takes place during handling. Additionally, at higher temperatures, the wax replicas become soft and easily undergo plastic deformation under the influence of small stresses, resulting in loss of dimensional accuracy in the final mold. Furthermore, replicas of wax undergo undesirable ageing effects upon storage. In many cases, even manual handling of such replicas deformed them so as to render them unsuitable for use.

Attempts have been made to overcome the defects of wax replicas by forming the replicas from high molecular weight commercial resins. However, replicas of such materials were unsatisfactory in that they tended to warp and deform during the casting, setting, and drying of the investment mold. Additionally, when such high

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molecular weight resins were injection-molded, it was necessary to use steel molds to withstand the high molding temperatures and pressures which were required.

An object of this invention is to provide a new and improved replica for the production of a refractory mold to be used in precision casting of metals and alloys.

Another object of this invention is to provide a replica which undergoes substantially no deformation during the production of a refractory mold to be used in precision casting of metals and alloys.

An additional object of this invention is to provide a replica for the production of a refractory mold to be used in precision casting of metals and alloys and which is characterized by high chemical and mechanical stability.

A further object of this invention is to provide a replica which does not crack the mold due to thermal expansion.

Another object is to provide a replica having improved thermal expansion characteristics.

A still further object of this invention is to provide a replica having the above characteristics which can be molded at lower pressures and temperatures than the usual high molecular weight resins.

Other and additional objects of the invention will become apparent hereinafter.

The above objects are accomplished, in general, by producing the replica from resins having a sufficiently low molecular weight to impart the above characteristics.

Although replicas consisting of the low molecular weight resins are satisfactory, fillers or plasticizers, or mixtures thereof, can be incorporated into the low molecular weight resin if desired, and such compositions employed for the production of replicas.

In practicing this invention, to produce a desired metal casting there is first prepared a metal die from a positive. This die, which may be formed of a soft metal or alloy, such as tin babbitt, lead babbitt, or preferably a zinc base alloy or similar soft metal, is produced by casting and subsequent pressing and is utilized to produce any number of the low molecular weight resin replicas. Each replica or plurality of replicas, as may be necessary, may be appropriately mounted



by the use of a sprue forming extension and a flask is placed around the set-up. The mold composition is introduced into the flask and the flask is left at room temperature or subjected to a slightly elevated temperature until the mold composition has set. Thereafter, the flask is placed in an oven for firing the mold. During the firing cycle, the replica undergoes combustion, leaving a cavity in the mold corresponding precisely to the shape of the replica. The fired mold is then removed from the oven and used in the desired metal molding or casting procedure.

The details and manner of practicing the invention will become apparent by reference to the following specific examples, it being understood that the examples are merely illustrative embodiments of the invention and that the scope of the invention is not limited thereto.

#### Example I

A die made from a zinc base alloy was prepared in the usual way by casting such alloy around a steel positive and followed up by repressing to insure perfect surface and sharp edges. The die consisted of two parts which fitted together and provided a cavity of the desired shape between them. This cavity was completely enclosed except for a channel to the outside, said channel consisting of a groove in each zinc base alloy face.

Polystyrene having an intrinsic viscosity in toluene of 0.142, corresponding to a viscosity average molecular weight of 9500 was heated in a chamber to 200° C. and forced into the die through the above channel under a driving pressure of approximately 250 pounds per square inch. The die was split open, and the injection molded, polystyrene replica removed.

The replica was easily removed from the die with no tendency toward adherence to the die surface. It possessed sufficient toughness for use as a replica in the precision casting process.

No deformation or warpage were observed when the replica was exposed to temperatures up to 45° C., a temperature at which a replica made from the usual commercial molding grades (high molecular weight) polystyrene would deform extensively. No sinks or depressions were formed in the flat surfaces even on parts of heavy cross-section.

On firing of the replica, vapors were evolved on decomposition. However, combustion proceeded smoothly, with no harmful changes in shape and without producing any cracks in the mold.

#### Example II

A polymethyl methacrylate resin, having an intrinsic viscosity in acetone of 0.15, corresponding to a viscosity average molecular weight of 25,000 was forced into a die, prepared as set forth in Example I, at a temperature of approximately 200° C. and under a driving pressure of approximately 300 pounds per square inch. The die was opened and, after the molded replica had been stripped, several of them were assembled in a flask and invested. The mold thus formed was subjected to the usual drying and firing cycle, during which the polymethyl methacrylate replica burned out. Stainless steel castings made on a centrifugal casting machine from the refractory mold had very good surfaces and their dimensions showed that the plastic replica had suffered no deformation and no dimensional changes other than thermal expansion.

#### Example III

Using a similar die and procedure as in Example I, polystyrene, having an intrinsic viscosity in toluene of 0.20, corresponding to a viscosity average molecular weight of 13,000 was molded under a pressure of approximately 300 pounds per square inch and at a temperature of approximately 190° C.

#### Example IV

Same as Example I, except that polystyrene having an intrinsic viscosity in toluene of 0.20, corresponding to a viscosity average molecular weight of 13,000, to which had been added 15% by weight dioctylphthalate as a plasticizer, was molded under a pressure of 250 pounds per square inch at a temperature of approximately 190° C.

#### Example V

Same as Example I, except that polystyrene, having an intrinsic viscosity in toluene of 0.281, corresponding to a viscosity average molecular weight of 19,000, was molded at a temperature of about 200° C. under a driving pressure of approximately 350 pounds per square inch.

#### Example VI

Same as Example I, except that a polyethylene sample of molecular weight 10,000, into which had been incorporated 30% by weight of paraffin wax, was molded at a temperature of approximately 90° C. under a driving pressure of approximately 200 pounds per square inch.

#### Additional examples

	I. V. <sup>1</sup>	M. W. <sup>2</sup>	M. T. <sup>3</sup>	M. P. <sup>4</sup>
			° C.	
VII. Polystyrene.....	.40	26,500	185	500
VIII. Polystyrene.....	.55	36,500	200	500
IX. Polystyrene.....	.65	43,500	190	1,000
X. Polystyrene.....	.75	50,000	200	1,000

<sup>1</sup> Intrinsic viscosity in toluene.

<sup>2</sup> Viscosity average molecular weight.

<sup>3</sup> Molding temperature.

<sup>4</sup> Molding pressure in pounds per square inch.

Replicas according to all of the above examples were found to have the characteristics enumerated under Example I.

As seen from the examples, polystyrene having an intrinsic viscosity in toluene of the range 0.14 to 0.75 may be used. However, the range of 0.40 to 0.65 is preferred for reasons of molding economy.

This entire intrinsic viscosity range is well below that of the usual commercial injection molding grades of polystyrene which are of the order of 1.3 to 2.0.

The invention is not restricted to the specific low molecular weight resins disclosed in the examples. In general the following low molecular weight resins in molecular weight ranges sufficiently low to impart the desired characteristics may be used:

1. Copolymers of styrene with other chlorine-free monomers;
2. Acrylate-type polymers, such as polyethyl methacrylate and polyethyl acrylate;
3. Chlorine-free vinyl resins, such as polyvinyl acetate; and
4. Cellulose derivatives, such as cellulose acetate, cellulose acetate butyrate, and cellulose acetate propionate.

While replicas according to the above examples are satisfactory in most instances, the proper-



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ties may be further improved by the addition of suitable plasticizers which have been found to reduce the molding temperature or pressure. Such plasticizers also decrease the second order transition temperature of the resin composition so that the rate of expansion of the composition remains essentially linear in the critical mold setting temperature range. This prevents sudden expansion of the replica which is the major cause of mold cracking. The plasticizers must leave no residue in combustion and must be inert to the investment composition.

For polystyrene the following plasticizers have been found useful:

1. O-nitro biphenyl;
2. Hydrogenated terphenyls;
3. Dutrex 20 (Shell Oil Co.);
4. Phthalic acid derivatives
  - a. dioctyl phthalate
  - b. dibutyl phthalate;
5. Sebacic acid derivatives
  - a. dibutyl sebacate
  - b. dioctyl sebacate;
6. Glycolic acid derivatives
  - a. butylphthalyl butyl glycolate.

The plasticizers may be used with the resin compositions of Examples I, III-V and VII-X in proportions from 0 to 40%, preferably in the range of 10% to 20%. The molding temperature and pressure is reduced as a function of the plasticizer content. The preferred range has been found to effect the desired lowering of the second order transition temperature.

In any of the compositions the molding temperature varies inversely with the molding pressure and any suitable combination may be selected.

As indicated above the polystyrenes have been found particularly suitable.

Optionally fillers may be incorporated in the low molecular weight plasticized or unplasticized resin composition from which the replica is made. In general, when a filler, such as carbon black, wood flour, etc. is used, it may constitute from 10% to 40%, preferably from 10% to 20%, by weight of the composition.

The low molecular weight resins are prepared by any of the following methods: For example, the low molecular weight polystyrenes and polymethacrylates can be obtained by polymerizing the appropriate monomer in dilute solution with high catalyst concentration at high temperatures. Preferably, the low molecular weight polystyrene and polymethacrylates are prepared by the addition of a chain-transfer agent, such as carbon tetrachloride, to the polymerizing system. The following are illustrative examples of such method:

(A) A mixture of 50 parts by weight of styrene monomer, 50 parts by weight of carbon tetrachloride, and 1 part of benzoyl peroxide is heated at a temperature of 80° C. for 6 to 8 hours. The resulting polymer is isolated from the reaction mixture and dried.

(B) A mixture containing 500 parts of water, 100 parts of styrene monomer, 25 parts of carbon tetrachloride, 1 part of benzoyl peroxide, and a small amount of a suitable suspending agent is heated with agitation for 10 to 12 hours under reflux conditions. The resulting polymer is subjected to steam distillation and drying.

(C) A mixture containing 100 parts of styrene monomer, 1 part of dodecyl mercaptan and 0.4 gram of benzoyl peroxide was heated for 12 hours

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at 140° C. The resulting polymer is removed from the container and ground into small particles.

The molecular weights mentioned herein were derived from intrinsic viscosity measurements.

The definition of the intrinsic or limiting viscosity  $[\eta]$ , is well known to those familiar with the art to be

$$[\eta] = \lim_{c \rightarrow 0} \left( \frac{\eta_{sp}}{c} \right)$$

that is, the limiting value of the specific viscosity divided by the solution viscosity where the latter approaches zero.

$[\eta]$  was determined by measuring the specific viscosity

$$\eta_{sp} = \frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solution}}}$$

of several highly dilute polymer solutions in a given solvent, dividing the specific viscosities by the concentrations at which they were measured, and plotting the values so obtained against concentration. In this plot of  $\eta_{sp}/c$  versus  $c$  a straight line is obtained whose intercept with the viscosity axis represents the intrinsic viscosity.

The intrinsic viscosity was translated into a molecular weight value by means of the equation

$$[\eta] = K \cdot M$$

wherein the constant  $K$  was assumed to have the value  $1.5 \times 10^{-5}$ .

Other equations and other constants can be used to relate solution viscosity and molecular weight. The molecular weight will vary according to the equation and constants used. The intrinsic viscosity, however, is a definite characterization of a given polymer.

The replicas of this invention can be used with any of the known investment compositions. Investment compositions of the type disclosed in application Serial No. 644,420, filed January 30, 1946, for "Investment Compositions and Method of Producing Refractory Molds Therefrom," now Patent No. 2,521,614 can also be used.

The replicas can be produced by any molding or casting process, such as compression-molding, injection-molding, etc.

The use of a low molecular weight resin as distinguished from the high molecular weight resins commonly used commercially for injection molding, results in the following advantages:

1. Due to the lower softening temperatures of the low molecular weight resin the patterns become softened and drain out of the mold before they have reached a high temperature. This results in a lower total expansion of the pattern within the mold as the temperature of the investment is raised.

2. The lower total expansion permits large pattern sizes to be used without cracking the investment or otherwise injuring the surface of the mold.

3. The plastic drains out of the mold at such a low temperature that practically all of the combustion can be made to occur outside the mold cavity. This results in a cleaner mold cavity and an improved surface of castings.

4. The low molecular weight resins described above may be molded at much lower temperatures and pressures than the high molecular weight resins. For this reason the production of the pattern is simplified in that the clamping pressures of the machinery, used to mold such low molecular weight resins, are materially reduced, resulting in great economy of operation.



As another result of the lower molding temperature and pressure, wear on and deformation of die cavities is reduced and dies made of metals other than steel may be used. The cost of such dies may often be but a fraction of the cost of a steel die.

5. The low molecular weight resin patterns have less internal strains and, hence, there is a reduced tendency to distort when they are raised to the softening temperature. This results in a more accurate casting than in the case of high molecular weight patterns which have high internal strains and tend to warp during the setting and drying of the investment.

6. In commercial operations the combination of the above qualities results in a very low reject rate both for the patterns and for the castings.

7. Due to the lower molding pressure required for the low molecular weight resins, a die clamping force of only about one-tenth of the force necessary for molding high molecular weight resins is required. This reduces the cost of the injection molding machinery to one-third of that required for conventional high molecular weight plastics.

It is obvious that various changes and modifications can be made in the above description without departing from the nature or spirit of the invention.

What is claimed is:

1. The method of producing refractory molds for industrial precision casting, which comprises embedding in an investment composition a plastic replica consisting essentially of polystyrene having an intrinsic viscosity in toluene of 0.142 to 0.75, corresponding to a calculated viscosity average molecular weight of 9,500 to 50,000, said replica having mold cavity forming parts with exterior surfaces conforming to the exterior surface of the article to be cast, having the property of being rigid at room temperature, softening at higher temperature with thermal expansion in an amount which is insufficient to injure the mold, and being completely combustible at mold firing temperature, subjecting the assembly to conditions of temperature and time to cause solidification of the investment, removal of the replica by softening and combustion to leave a mold cavity, and conversion of the solidified investment to a refractory mold.

2. The method of producing refractory molds for industrial precision casting, which comprises embedding in an investment composition a plastic replica consisting essentially of polystyrene having an intrinsic viscosity in toluene of 0.40 to 0.65 corresponding to a calculated viscosity average molecular weight of 26,500 to 43,500, said replica having mold cavity forming parts with exterior surfaces conforming to the exterior surface of the article to be cast, having the property of being rigid at room temperature, softening at higher temperature with thermal expansion in an amount which is insufficient to injure the mold, and being completely combustible at mold firing temperature, subjecting the assembly to conditions of temperature and time to cause solidification of the

investment, removal of the replica by softening and combustion to leave a mold cavity, and conversion of the solidified investment to a refractory mold.

3. The method of producing refractory molds for industrial precision casting, which comprises embedding in an investment composition a plastic replica consisting essentially of polystyrene having an intrinsic viscosity in toluene of 0.142 to 0.75, corresponding to a calculated viscosity average molecular weight of 9,500 to 50,000, and a plasticizer in an amount not over 40%, said replica having mold cavity forming parts with exterior surfaces conforming to the exterior surface of the article to be cast, having the property of being rigid at room temperature, softening at higher temperature with thermal expansion in an amount which is insufficient to injure the mold, and being completely combustible at mold firing temperature, subjecting the assembly to conditions of temperature and time to cause solidification of the investment, removal of the replica by softening and combustion to leave a mold cavity, and conversion of the solidified investment to a refractory mold.

4. The method of producing refractory molds for industrial precision casting, which comprises embedding in an investment composition a plastic replica consisting essentially of polystyrene having an intrinsic viscosity in toluene of 0.40 to 0.65, corresponding to a calculated viscosity average molecular weight of 26,500 to 43,500, and a plasticizer in an amount of from 10% to 20%, said replica having mold cavity forming parts with exterior surfaces conforming to the exterior surface of the article to be cast, having the property of being rigid at room temperature, softening at higher temperature with thermal expansion in an amount which is insufficient to injure the mold, and being completely combustible at mold firing temperature, subjecting the assembly to conditions of temperature and time to cause solidification of the investment, removal of the replica by softening and combustion to leave a mold cavity, and conversion of the solidified investment to a refractory mold.

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