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(71) Applicant: **Shonan Design Co., Ltd.**

**Sagamihara-shi,
Kanagawa-ken 2291132 (JP)**

(72) Inventors:

- **MATSUOKA, Yasuhiko**
Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)
- **SUZUKI, Hidekazu**
Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)
- **TANAKA, Nobuyuki**
Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)
- **KASUGA, Tomonobu**
Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)
- **ONSO, Keiichiro**
Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)
- **MATSUYAMA, Reiji**
Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **MIZUNO, Hisashi**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **TAKASE, Akira**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **OI, Takaharu**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **MATSUMURA, Minoru**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **KITA, Taro**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **KAMATA, Kazuki**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

• **KIKUCHIHARA, Masato**

Shonan Design Co., Ltd
Kanagawa 229-1132 (JP)

(74) Representative: **Gesthuysen, von Rohr & Eggert**
Patentanwälte

**Huyssenallee 100
45128 Essen (DE)**

(54) **RESIN PATTERN TO BE BURNT AND PRECISION CASTING METHOD USING THE RESIN PATTERN**

(57) In order to satisfy the requirements for satisfactory levels of melting burn-off characteristics in response to heat application, high temperature burn-off characteristics and ease of residual ash removal that a resin model should assure as an alternative to a wax model, the burn-off resin model according to the present invention, which can be used in the lost wax process, is manufactured by forming a liquid resin compound containing 1 to 30 wt. %

of a plasticizer (D) and 1 to 20wt. % of a wax component (E) blended into a double fluid reactive setting liquid urethane resin (C) constituted of a multifunctional polyol component (A) and a multifunctional polyisocyanate component (B) and then by setting the liquid resin compound within a working life of 5 minutes or less.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a precision casting method achieved by adopting a lost wax process. The present invention proposes the use of resin models satisfying a specific range of requirements as a means for addressing the fundamental problems of conventional wax models used in the lost wax process.

BACKGROUND ART

[0002] A precision casting method achieved by adopting the lost wax process in the related art is explained in full detail.

[0003] The lost wax process includes manufacturing steps in which; a wax model achieving a shape identical to the shape of a cast product is manufactured by pouring a melted wax component into a die used for wax model mass production, cooling the wax component and then disengaging the wax from the die; a hollow casting mold is manufactured by coating the surface of the wax model with a refractory material, heating the wax model to cause the wax model to melt and flow out and then burning off the wax through high temperature baking; and a molten alloy is poured into the hollow casting mold, after which the alloy is cooled and set and the cast product is taken out by splitting off the casting mold.

[0004] To explain this process in further detail, when manufacturing a wax model by injection-molding the wax component in the die, the injection temperature, the injection pressure, the injection pressure holding time and the cooling and disengaging temperature are controlled so as to manufacture a wax model with a specific level of quality. The manufactured wax model is stored in a thermostatic chamber sustaining a constant temperature so as to maintain its dimensional accuracy. This wax model is then brazed to a sprue model prepared separately and thus, an integrated unit is assembled. The entire model assembly is referred to as a tree. Since the shape of this tree is directly reflected in the gating system plan, numerous factors such as the properties of the molten metal, the size and shape of the cast product, the casting conditions and the ease of disengagement from the tree are taken into consideration when designing the tree shape.

[0005] The tree thus manufactured is repeatedly dipped in a coating slurry and dried to form coated layers thereupon. The binder used in the coating slurry may be choroidal silica, ethyl silicate, a hybrid or the like. The slurry is prepared by blending such a binder with a filler constituted of a fine refractory powder. The wax model is immersed in the slurry thus prepared, is then lifted out of the slurry, sprinkled with stucco and dried. The stucco grains may be zircon-sand grains or molochite grains. The coating process is completed by repeating these steps several times.

[0006] Next, the wax model is caused to flow out of the casting mold through the autoclave method by setting the temperature to 120 to 150°C. This process is referred to as dewaxing. The shell casting mold resulting from the dewaxing step is baked by raising the temperature in steps within a range of 700 to 1000°C in a high-temperature baking furnace in order to remove the residual wax and unburned carbon particles and also to improve the strength of the casting mold. A molten alloy is cast into the casting mold thus produced and after the alloy becomes cooled, the casting mold is split away with a knockout machine. Then, the cast product is taken out and runners, weirs and the like are cut away and removed. Next, any residual refractory material is eliminated through blasting. In addition, any repairable portions are repaired through welding, the surface is finished through grinding and finally, the casting undergoes a heat treatment to become a cast alloy product.

[0007] Numerous research and development efforts have been made to date with regard to models used in the lost wax process described above. First, the wax component constituting wax models used in the lost wax process is normally a blend of paraffin, rosin, carnauba wax and terephthalic acid. Possible compositions that may be adopted for the wax component are described in detail in Casting Guidebook (edited by the Japanese Casters Association). In addition, the efficacy of a wax component containing melamine particles blended therein has been reported in recent years (see Japanese Unexamined Patent Publication No.H5-38549). While the use of the wax model is advantageous in that the wax component becomes melted at high temperature and allows for easy dewaxing, there is a limit to the extent to which the mechanical strength of the model itself can be improved as long as a burn-off wax model is utilized. Another type of model, achieved through a combination of a wax model and a synthetic resin laminated thereupon, has also been proposed. Japanese Unexamined Patent Publication No.H5-23791 discloses a model achieved by forming a synthetic resin film over the wax surface. Japanese Unexamined Patent Publication No.H5-329174 discloses an dental inlay casting model constituted with a heat meltable resin. In addition, the Japanese Unexamined Patent Publication No.H7-9084 discloses a model achieved by laminating a lost wax base on a photocuring resin sheet. Japanese Unexamined Patent Publication No.H7-299542 discloses a model achieved by applying a wax plastic material onto an ornamental model with fine features constituted of cotton yarn and a synthetic material. Japanese Unexamined Patent Publication No.H7-47443, on the other hand, discloses a model achieved by inserting a photocuring resin model or heat meltable resin laminated model into a die and injection-molding wax. Furthermore, Japanese Unexamined Patent Publication No. 2000-263186 discloses a model achieved by laminating a lost wax base on an ultraviolet curing resin model.

As the examples quoted above indicate, partial or full use of a synthetic resin in the material used to form a model has become increasingly common. In most applications, the synthetic resin is used to better ensure that the shape of the wax model is retained in a desirable manner and to facilitate model production through simple processes. Namely, advances made in the area of digitized molding technology have spurred wider application of photocuring resins and thermoplastic resins in molding processes.

[0008] The precision casting method disclosed in Japanese Unexamined Patent Publication No. 2000-210755, in which a synthetic resin model is used as a substitute for a wax model in the lost wax process, is most closely related to the present invention. In this method, a reaction injection molded thermosetting polyurethane foam model is prepared, a shell mold is formed around the model, the model is dewaxed through heat treatment, the shell mold is hardened and then a molten pure metal or a molten alloy is cast. However, it is fundamentally different from the present invention, which proposes a precision casting method in which a model constituted with urethane foam or non-foam urethane containing, as essential constituents thereof, a plasticizer and a wax material, is used as a substitute for a wax model in the lost wax process.

[0009] The materials and the manufacturing steps adopted to manufacture resin models in the related art are now explained. Numerous and diverse technologies for resin model production have been proposed in the related art. Wooden or plastic sheets and rods are machined and bonded to manufacture a model in the most basic process. Dried bract and Japanese white pine with their superior dimensional accuracy are favored by wooden pattern producers who manufacture casting models. When manufacturing a model, the directionality of wooden pieces are canceled out and deformation is avoided by combining the wooden pieces so as to mix their directionality. As a result, a high precision wooden model, which retains a high level of precision over time, is manufactured.

[0010] In the design model industry engaged in plastic model production, models are manufactured by machining and bonding sheets and rods constituted of Bakelite, acrylic, PP, vinyl chloride or the like. In recent years, chemical wood achieving superior dimensional accuracy and machinability, which is formed by setting resin microballoons with urethane resin, is widely used and the rapid progress made in CAD/CAM technology has made it possible to have the specific model shape to be achieved specified with data instead of drawings and to manufacture a chemical wood model by machining chemical wood with no directionality on an NC machine.

[0011] In addition, the optical molding method, through which the shape of the model being ordered is specified with CAD data, doughnut-shaped hardened resin disks are formed by radiating computer-controlled beams onto photocuring resin and a three-dimensional resin model is manufactured by sequentially laminating the hardened resin disks, has come to be commonly adopted in recent years. The most marked characteristic of the optical molding method is that a three-dimensional hollow molded object can be manufactured without having to perform any machining process.

[0012] A plaster mold or a resin mold is manufactured through plaster negative or resin negative of a single precision model prepared as described above which is used as a master model and then a plurality of resin models can be replicated by casting a liquid resin into the mold and allowing the liquid resin to set. The liquid resin that is cast into the mold may be a urethane resin, an epoxy resin, an unsaturated polyester resin, an acrylic resin or the like. A specific resin material is selected by taking into consideration the required resin model performance to be achieved.

[0013] When a given product needs to be mass produced, the resin model must be manufactured through a mass production procedure instead of the prototype model production procedure described above. Namely, in mass production applications, the resin model is manufactured through the injection process in which a melted thermoplastic resin is injected into a die under conditions of high pressure and high temperature, and then is disengaged from the die after the resin cools down and becomes hardened. In addition, the RIM method, in which a double fluid reactive liquid resin is injected into a die and the resin becomes hardened while undergoing the process of polymerization inside the die, is considered a very viable method and it has already been adopted in industrial applications as an effective rapid mass production method.

DISCLOSURE OF THE INVENTION

[0014] As explained above, a wax model formed by using a wax component is commonly used when manufacturing a high precision cast product through the lost wax process. While such a wax component is melted out easily at high temperature and has good burn-off characteristics, which proves convenient during the high temperature casting mold baking process, the structures of high precision cast products are becoming increasingly complex and the requirement for the level of dimensional accuracy to be achieved is becoming increasingly rigorous. Thus, there are instances in which the performance level of a typical wax model is no longer satisfactory.

[0015] Namely, the wax model is problematic in that edges cannot be formed with ease, in that fine ribs cannot be formed with ease, in that fine ribs tend to break readily, in that portions with small wall thicknesses must be handled with the utmost care when disengaging the model and in that there is a technical limit in the production of a wax model with extremely thin portions, i.e., portions with wall thicknesses equal to or less than 1 mm. In addition, since the surface hardness of the manufactured wax model is low, it tends to be easily scarred, its dimensional accuracy tends to be

inconsistent and it is susceptible to damage in the event of a fall or an impact occurring during transportation. There is another problem in that since the shape of the manufactured wax model can change readily during the summer, it must be stored in a temperature-controlled environment. In particular, the utmost care must be taken when transporting the wax model during the summer. Furthermore, the wax material, which is a relatively low molecular organic substance, becomes soft at approximately 80°C. The problems of the wax model discussed above are mostly attributable to the characteristics of the wax material. While concentrated efforts are being made in researching alternative wax component compositions in order to address the problems described above, the basic characteristics of the wax material, i.e., it is an organic substance with a low melting point, which becomes melted at a temperature slightly higher than normal temperature but remains in a crystallized solid state at normal temperature, makes it difficult to address the fundamental problems in an effective manner.

[0016] Accordingly, the inventor of the present invention et al. conceived the present invention based upon a finding that a resin model constituted with a liquid resin compound satisfying a specific range of requirements can be effectively used as an alternative to the wax model, which was made through focused research into possible resin compositions that would satisfy the requirements for a specific level of heat induced melt-out performance, a specific level of high temperature burn-off performance and a specific level of residual ash removal performance and thus could be used to form a resin model as an alternative without the problems of the wax model.

[0017] The burn-off resin model according to the present invention, which can be used in the lost wax process, is manufactured by forming a liquid resin compound containing 1 to 30 wt.% of a plasticizer (D) and 1 to 20wt.% of a wax component (E) blended into the double fluid reactive setting liquid urethane resin (C) constituted of a multifunctional polyol component (A) and a multifunctional polyisocyanate component (B) and then by setting the liquid resin compound within a working life of 5 minutes or less. It is particularly desirable to set the length of the working life to 1 to 2 minutes.

[0018] In addition, it is desirable that the multifunctional polyol component (A) in the double fluid reactive setting liquid urethane resin have an average functional radix of 2.8 or larger and that the multifunctional polyisocyanate component (B) in the double fluid reactive setting liquid urethane resin have an average functional radix of 2.0 or larger, with the ratio NCO/OH achieving a value within a range of 0.7 to 1.0.

[0019] It is also desirable that the plasticizer (D) be micro-dispersed through phase separation when the double liquid reactive setting liquid urethane resin (C) undergoes the process of reaction hardening.

[0020] Moreover, the double fluid reactive setting liquid urethane resin (C) should preferably contain 2 to 25 wt.% of polyether chains having a chemical structure indicated in the chemical structural formula below.

(Chemical structural formula)



[0021] In addition, it is desirable that the wax component (E) be provided in the form of grains, flakes or lumps, each formed in a size that allows it to be contained in a space of approximately 1 cm³.

[0022] It is also desirable to foam the double fluid reactive setting liquid urethane resin (C) with water by adding 0.01 to 1.0 wt.% of water (F) into the double fluid reactive setting liquid urethane resin (C) (claim 6) and to blend an organic solvent (G) into the double fluid reactive setting liquid urethane resin (C) so as to achieve an organic solvent content of 10 to 25 wt.%.

[0023] Furthermore, it is desirable that fine particles (H) of a natural high molecular filler be added into the double fluid reactive setting liquid urethane resin (C) at a ratio of 1 to 10%.

[0024] Moreover, it is desirable to use the burn-off resin model described above in the lost wax process in high precision production.

BEST MODE FOR CARRYING OUT THE INVENTION

[0025] An explanation is first given on the constituents and the composition of the double fluid reactive setting liquid urethane resin (C) used in the present invention. The skeleton of the double fluid reactive setting liquid urethane resin (C) is achieved by using two different types of liquid, one constituted with a multifunctional polyol component (A) and the other constituted with a multifunctional polyisocyanate component (B), and this particular composition of the double fluid mixture induces a chemical reaction at normal temperatures, which generates heat and induces hardening. A plasticizer (D) and a wax component (E) contained in the double liquid reactive setting liquid urethane resin (C) may be blended into either the multifunctional polyol component (A) or the multifunctional polyisocyanate component (B), or they may be blended into both of them. In addition, since a water component (F) chemically reacts with the multifunctional

isocyanate component (B), it is preblended into the multifunctional polyol component (A). Natural cellulose-type waste (H), which chemically reacts with the polyisocyanate component (B), is preblended into the multifunctional polyol component (A). An organic solvent (G) may be blended in either the multifunctional polyol component (A) or the multifunctional polyisocyanate component (B) or it may be blended in both of them.

[0026] The individual constituents are now explained.

[0027] The multifunctional polyol component (A) may be a low molecular polyol, a polyether polyol, an amine polyol, a polyester polyol, an acrylic polyol or a polybutadiene polyol. Alternatively, castor oil and its derivatives may also be used to constitute the multifunctional polyol component (A).

[0028] Examples of the low molecular polyol include ethylene glycol, propylene glycol, 1-4 butanediol, glycerine, trimethyl propane, and pentaerythritol.

[0029] The polyether polyol may be a polyether polyol achieving a specific molecular weight obtained by adding ethylene oxide or propylene oxide into the low molecular polyol. A primary or secondary terminal hydroxyl group can be achieved in the polyether polyol by blending an additional constituent in a specific manner, e.g., by adding ethylene oxide by itself, adding propylene oxide by itself, adding a mixture of ethylene oxide and propylene oxide or adding ethylene oxide and propylene oxide separately in sequence. Various types of polyether polyols with ethylene oxide and propylene oxide rendering diverse hydrophilic/hydrophobic properties in their additional chains can be achieved by varying the reactivity of the hydroxyl group terminal through the different blending methods. Alternatively, poly tetramethylene ether glycol obtained through cationic polymerization of THF, which is often referred to as PTMG, may be used.

[0030] An amine polyol is a substance achieved by adding ethylene oxide or propylene oxide to a low molecular amine such as ammonia, ethylene diamine or polyethylene polyamine. Thus, the amine polyol, which contains tertiary nitrogen within its molecule, is a polyol retaining an effect of promoting the reaction of isocyanate. An amine polyol containing ammonia as a starter is trifunctional, an amine polyol containing an ethylene diamine as a starter is quadrafunctional and an amine polyol containing polyethylene polyamine as a starter is multifunctional more than four functions. This constitutes an essential element of the present invention according to which the resin needs to be set rapidly.

[0031] The polyester polyol may be a condensed polyester polyol having a hydroxyl group constituting a molecular terminal achieved by esterifying a dibasic acid and a low molecular polyol. By selecting specific types of dibasic acid and low molecular diol · triol, adjusting the molecular weight and using a small quantity of a multifunctional low molecular polyol, diverse types of polyester polyols can be prepared. The dibasic acid which is often used to prepare a condensed polyester polyol is adipic acid. The low molecular diol may be ethylene glycol, propylene glycol, 1-4 butanediol or the like, whereas the low molecular triol may be glycerine, trimethyl propane or glycerine or trimethyl propane containing a small quantity of alkylene oxide. In addition, the functional radix and the molecular weight of an Σ -caprolactam ring-opening polymerization-type polyester polyol can be adjusted by controlling the ring-opening polymerization starter type and the quantity of the starter used for the ring-opening polymerization. Highly diverse chains, e.g., polyester chains and polyether chains, can be formed by alkylene oxide. Alternatively, a carbonate diol obtained by opening the ring of ethylene carbonate may be used.

[0032] An acrylic polyol is an acrylic oligomer having a plurality of hydroxyl groups in an acrylic chain, which is formed by polymerizing an acrylic monomer containing a hydroxyl group terminal with methyl acrylate or methyl meta-acrylate. Various types of acrylic polyols formed by selecting specific acrylic monomers and adjusting their molecular weights are commercially available. A liquid resin dissolved in an organic solvent, with a high molecular weight achieved by raising the extent of polymerization to a level at which film formation is enabled, constitutes a paint with superior weather resistance due to slight cross-linking induced by aliphatic polyisocyanate.

[0033] A polybutadiene polyol is a copolymer of butadiene containing a hydroxyl group at a terminal thereof and a compound having double bonds. It is a polyol with a relatively high level of hydrophobic property.

[0034] A urethane modified polyol with a hydroxyl group terminal obtained by joining such multifunctional polyols via polyisocyanate may be used as well. In such a case, the viscosity tends to increase since the molecular weight increases slightly due to oligomerization resulting from the urethane modification. For this reason, it is desirable to form the urethane modified polyol by using only part of the multifunctional polyols.

[0035] One of the multifunctional polyols listed above may be used by itself, or two or more multifunctional polyols may be used in combination. Under normal circumstances, the molecular structure is designed by blending various types of multifunctional polyol constituents in specific quantities in order to satisfy numerous requirements corresponding to a given purpose of use. Such a multifunctional polyol component (A) includes an active hydroxyl group at a molecular terminal and the manner with which it reacts with isocyanate is determined by the type of hydroxyl group at the molecular terminal.

[0036] In particular, polyether polyols and polyester polyols have high levels of affinity with water and also contain minute quantities of water. Such extremely low water contents do not cause any concern as long as the polyols are used in aqueous foam urethane. However, if they are used in non-foam urethane, it is necessary to rigorously control the water content to keep it at the lowest possible level. For this reason, the multifunctional polyol component (A) is manufactured through heating, mixing and dehydrating steps.

[0037] The polyol component contains at least two hydroxyl groups in a single molecule, whereas the multifunctional polyisocyanate component (B) is a compound containing at least two isocyanate groups in a single molecule. The isocyanate groups, which are functional groups with an extremely high level of reactivity, react with hydroxyl groups containing active hydrogen, amino groups and thiol groups. Since isocyanate groups generally react with amino groups and thiol groups instantaneously, they are normally used only in combination with a less reactive isocyanate component or less reactive aromatic amines, but they still react fairly quickly and for this reason, such a combination is not commonly used.

[0038] The polyisocyanate component may be constituted with an aromatic polyisocyanate, an aliphatic polyisocyanate, or an alicyclic isocyanate. Typical examples of the aromatic polyisocyanate include tolylenediisocyanate and diphenylmethane diisocyanate. Due to the particulars of its chemical reaction manifesting during the production process, tolylenediisocyanate is obtained as a mixture of various isomers, and various industrial products with varying mixing ratios of the 2,4-body and the 2,6-body, e.g., TDI-100 (2,4-TDI 100%), TDI-80 (2,4-TDI 80%, 2,6-TDI 20%) and TDI-65 (2,4-TDI 65%, 2,6-TDI 35%), are commercially available. Likewise, due to the particulars of the chemical reaction occurring during the manufacturing process, diphenylmethane diisocyanate, too, is obtained as a mixture of various isomers, and is used in the form of either pure MDI or polymeric MDI in industrial applications. The pure MDI is a dicaryonic, whereas the polymeric MDI is a multicaryonic. While the pure MDI is isolated through distillation, the polymeric MDI is obtained as residue. Since the number of multicaryons in the polymeric MDI changes under different manufacturing conditions, various types of polymeric MDI are produced and are offered as commercial products by numerous manufacturers. In addition, other examples of aromatic polyisocyanates include naphthalene diisocyanate achieved by adding an isocyanate group to a naphthalene nucleus and tolidine diisocyanate. Examples of the aliphatic polyisocyanate include hexamethylene diisocyanate, isophorone diisocyanate, xylene diisocyanate and lysine diisocyanate. The alicyclic polyisocyanate may be hydrogenated xylene diisocyanate obtained by hydrogenating xylene diisocyanate or hydrogenated MDI obtained by hydrogenating MDI.

[0039] Generally speaking, polyisocyanates are highly reactive and, in particular, volatile polyisocyanates are highly toxic. For this reason, they are normally used after undergoing various types of metamorphisms. Such a metamorphism may be urethane modification, dimerization, trimerization, polycarbonimidization, urea modification, pre-polymerization and blocking. Through these metamorphisms, self condensation is induced by taking advantage of the higher reactivity of the isocyanate groups, or the isocyanate groups are joined via an active component while leaving a terminal isocyanate group.

[0040] The specific range applied to the double fluid reactive setting liquid urethane resin (C) according to the present invention constituted with the multifunctional polyol component (A) and the multifunctional polyisocyanate component (B) is now explained.

[0041] The double fluid reactive setting liquid urethane resin (C) containing as resin constituents thereof the multifunctional polyol component (A) and the multifunctional polyisocyanate component (B) contains 2 to 20 wt. % of polyether chains, as indicated in the chemical structure formula presented below.

(Chemical structure formula)



[0042] Polyether chains will be introduced by using polyether to constitute the multifunctional polyol component (A). Alternatively, they may be introduced via a polyether ester if a polyester polyol is used. Otherwise, polyether chains may be introduced by way of a so-called quasi-prepolymer, with a terminal isocyanate joined with a polyether, which can be used as a multifunctional polyisocyanate component (B). The polyether chains constitute the soft component of the urethane resin, and polyether chains derived from propylene oxide, in particular, are extremely soft. When such extremely soft polyether chains are heated to high temperature during the dewaxing and baking processes, they become thermally decomposed and the thermally decomposed polyether chains become liquefied, flow out and burn off readily. The present invention takes full advantage of these characteristics by ensuring that the liquid resin according to the present invention contains 2 to 25 wt. % of polyether chains. The full effect of the polyether chains does not manifest if the polyether chain content is less than 2 wt. %. Once the polyether chain content exceeds 20 wt. %, the ratio of the soft component becomes too high and, as a result, the hardened object becomes softened, making it difficult to keep the level of hardness required of the model. For this reason, the more desirable polyether chain content is 5 to 20 wt. %.

[0043] The multifunctional polyol component (A) and the multifunctional polyisocyanate component (B) are blended in quantities determined by calculating the NCO radix and the OH radix and setting the NCO/OH ratio of the NCO radix and the OH radix to a value close to 1.0 in the case of non-foam urethane. The NCO/OH ratio of the multifunctional

polyol component (A) and the multifunctional polyisocyanate component (B) to constitute urethane foam is set to 1.0 to 1,1, i.e., in a range where the NCO value is larger than the OH value. When $\text{NCO/OH} = 1.0$, the numbers of the isocyanate groups and the hydroxyl groups are equal to each other and at this setting, the reaction ends when both types of groups are all used in the reaction. In other words, it is a setting at which the maximum strength is realized. According to the present invention, NCO/OH is set to a range of 0.7 to 1.0, i.e., in a range where the NCO value is smaller than the OH value. Under normal circumstances, urethane molecules are not designed in such an NCO-short range. The molecular design in this unusual NCO/OH range is enabled according to the present invention, since the multifunctional polyisocyanate component with an average functional radix 2.1 or greater and the multifunctional polyol component with an average functional radix of 3.0 or greater are used and, as a result, a three-dimensional network structure is achieved even in the range over which the value of NCO/OH is 1.0 or less. While there are more OH groups than NCO groups in this state, multifunctional monomers are used and, for this reason, the monomers become completely linked to constitute a principal chain without the functional groups achieving complete reaction. The excess OH groups are retained in the principle chains when the reaction ends. This is considered to help sustain a high level of hydrophilic property, which facilitates micro dispersion of the highly hydrophobic plasticizer through phase separation.

[0044] For the reasons discussed above, NCO/OH is set to 0.7 to 1.0 and more desirably to 0.8 to 0.9. Once the NCO/OH ratio becomes equal to or less than 0.7, the number of isocyanate groups relative to the number of hydroxyl groups becomes too small and, as a result, a three-dimensional network structure cannot be achieved in the reactively set resin compound, which leads to a major reduction in the hardness and ultimately the resin becomes too soft to retain the original shape. If, on the other hand, the NCO/OH ratio is equal to or greater than 1.0, the number of excess isocyanate groups becomes too large and too many isocyanate groups will be left unused in the reaction when the resin needs to be disengaged from the die. This may lead to undesirable results such as failure to achieve a specific level of hardness and inconsistent color at the surface of the hardened object.

[0045] As a catalyst that promotes the chemical reaction of the multifunctional polyol component (A) and the multifunctional polyisocyanate component (B), a metal catalyst or an amine catalyst may be used. Examples of a metal catalyst that may be used include octylic zinc, octylic lead, dibutyltin denatured, dibutyltin diacetate and the like. Examples of an amine catalyst that may be used include triethylene diamine, NN-dimethyl piperazine, N-methyl morpholine and the like. The catalyst is normally added into the polyol component. Under normal circumstances, the multifunctional polyol component (A) contains 1 to 1000 ppm of catalyst and the working life is thus adjusted. According to the present invention, the catalyst is added in the multifunctional polyol component (A) so has to set the length of time over which work is enabled, i.e., the working life, to 5 minutes or less. If the working life is set to 5 minutes or more, the setting-disengaging time exceeds five hours, which may become problematic for resin model production. If the working life is less than 1 minute, the reaction viscosity rises quickly, making it difficult to secure a sufficient length of time for the double fluid mixing and casting processes. For these reasons, the working life should be set to 1 to 2 minutes.

[0046] Next, the plasticizer (D) used in the present invention is explained.

[0047] The plasticizer (D) used in the present invention is an inactive chemical compound having no functional group that induces a chemical reaction with volatility insignificant enough to be disregarded. The plasticizer (D) may be an ester plasticizer, an ether plasticizer or an ester/ether plasticizer. More specifically, typical examples of the ester plasticizer are dioctyl adipate (DOA), dioctyl phthalate (DOP) and dibutyl phthalate (DBP). Alternatively, benzyl acetate, benzoic butyl, benzoic octyl, benzoic isopentyl, ethylene glycol benzoic diester, polyethylene glycol benzoic diester, propylene glycol benzoic diester, poly propylene glycol benzoic diester, ethylene glycol dioleate, polyethylene glycol dioleate, propylene glycol dioleate and polypropylene glycol dioleate. Examples of the ether plasticizer include ethylene glycol dibutyl ether, ethylene glycol diphenyl ether, diethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol diethyl ether, diethylene glycol ethyl butyl ether, diethylene glycol dibutyl ether, triethylene glycol diethyl ether, triethylene glycol diethyl ether, triethylene glycol dibutyl ether, tetraethylene glycol diethyl ether, tetraethylene glycol diethyl ether and the like. Examples of the ethyl/ester plasticizer include ethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol mono phenyl ether acetate and the like.

[0048] The plasticizer (D) is used in a quantity that amounts to 2 to 20wt.% relative to the entire weight of the double fluid reactive setting liquid urethane resin (C). If the content of the plasticizer (D) exceeds 20 wt.%, the plasticizer (D) bleeds over the surface of the resin model readily to cause stickiness. If, on the other hand, the plasticizer (D) is used in a quantity amounting to less than 2wt.% the thermally decomposed and melted resin does not flow out readily during the dewaxing/baking processes since the plasticizer (D), which is a highly viscous liquid at room temperature but has a lower level of viscosity at higher temperatures, is not contained in sufficient quantity. While it is desirable to take full advantage of these characteristics of the plasticizer by using a greater quantity of the plasticizer (D), an excessively high plasticizer content in the resin results in bleeding of the plasticizer over the surface of the hardened object and the surface becomes tacky and sticky, as described earlier. Accordingly, the present invention was conceived based upon the finding that a maximum content for the plasticizer (D) can be achieved by rapidly setting the resin within less than 5 minutes of working life and trapping the plasticizer (D) having undergone phase separation from the cured resin in the

three-dimensional network structure of the cured resin in a state of micro dispersion.

[0049] Such phase separation micro dispersion can be regarded as a state in which the plasticizer (D) is enclosed by the cured resin assuming a honeycomb structure. The cured resin assuming the honeycomb structure has superior physical strength, and the honeycomb structure can also be regarded as a three-dimensional structure within which the plasticizer (D) is secured within the honeycomb and is not allowed to be released to the outside. The structure does not allow the plasticizer (D) to bleed over the surface of the hardened object to induce tackiness even when the plasticizer is contained at a relatively high ratio. If the phase separation micro dispersion structure is not adopted, the plasticizer is dissolved into the hardened resin, and once it reaches the saturation level, the plasticizer becomes bled over the surface of the hardened object to result in tackiness. If the extent of bleeding is significant, the surface becomes sticky. The phase separation micro dispersion structure can be observed through an electron microscope. The formation of the phase separation micro dispersion structure needs to be aided by rapidly hardening the resin within a working life of 5 minutes or less. Preferably, the working life should be set to 3 minutes or less, and even more desirably to 1 to 2 minutes. If the working life is set to 5 minutes or more, the process of phase separation micro dispersion cannot be completed with ease, and since it will take a day or more to disengage the model during the model production, the model production will become an extremely slow process.

[0050] When the plasticizer (D) is contained in the double fluid reactive setting liquid resin (C), it needs to be uniformly dissolved in the liquid resin, whereas the phase separation micro dispersion of the plasticizer from the cured resin is promoted during the reactive setting stage so that the micro dispersed plasticizer is trapped by the time the reactive setting process is completed, thereby preventing bleeding of the plasticizer onto the surface. The composition of the double fluid reactive setting liquid resin must be designed so as to strike an optimal balance by taking into consideration the factors discussed above. Namely, the composition must be designed within the range over which the hydrophilic and hydrophobic properties of the plasticizer (D) and the reactive setting resin are perfectly balanced. For this reason, it is effective to form the hydrophilic segment with an alkylene oxide chain and to form the hydrophobic segment with a hydrocarbon chain. The properties of the hydrophilic segment and the hydrophobic segment are determined by selecting a specific type of raw monomer. A certain degree of dissociation should be assured with regard to the balance between the hydrophilic property and the hydrophobic property. If the double fluid reactive setting liquid resin (C) contains a large number of ethylene oxide chains, the hydrophilic property becomes more pronounced, whereas if the ethylene oxide chains are replaced with propylene oxide chains, the level of hydrophilic property is lowered. If ethylene oxide chains or propylene oxide chains are used in a smaller quantity, the hydrophobic property of the double fluid reactive setting liquid resin (C) becomes more pronounced. By adjusting the types of hydrophobic and hydrophilic segments and their quantities the hydrophilic property and the hydrophobic property of the double fluid reactive setting liquid resin can be adjusted over a specific range. In addition, by adjusting the type and quantity of the plasticizer (D), the hydrophilic property and the hydrophobic property of the plasticizer (D) itself can be adjusted within a certain range. For instance, if the terminal of the plasticizer is constituted with alkyl ether, the level of the hydrophobic property increases as it changes to methyl ether, to ethyl ether, to butyl ether, and then to phenyl ether. By adjusting the chemical structure and the quantity of the plasticizer (D) and also by adjusting the chemical structure and the quantity of the double fluid reactive setting liquid resin (C), the range over which the phase separation micro dispersion is achieved can be controlled. The desirable phase separation micro dispersion can be achieved by setting the hydrophobic property of the plasticizer (D) to a relatively high level and setting the hydrophilic property of the resin component to a relatively high level through the method described above.

[0051] Next, the wax component (E) used in the present invention is explained.

[0052] The wax component is an inactive chemical compound having no functional groups that induce a chemical reaction, with volatility the extent of which is insignificant enough to be disregarded. It is a solid substance manifesting crystallization at room temperature. The wax component (E) may be a natural wax that is found in the natural world or a synthetic wax obtained through synthesis. The natural wax is most commonly found in candles. The chemical composition of the natural wax is referred to as wax ester which is constituted with higher fatty acid and higher alcohol. The number of carbons in the higher fatty acid higher alcohol is 16 or higher in most instances. Since it is an ester compound, it has a small residual acid value. In other words, it contains residual free fatty acids. In addition, since numerous types of saturated and unsaturated higher fatty acids exist in the natural environment, certain types of wax contain unsaturated higher fatty acids or hydroxyl acid as well. These waxes have chemical structures close to that of paraffin and are crystallized or uncrystallized solid substances at room temperature. Their melting points are normally approximately 80°C. Typical examples of waxes include candela wax, carnauba wax, rice wax, bees wax, whale wax, montan wax, lanolin wax, alpha wax, cork fiber wax, sugarcane wax, wood wax, sumac wax, micro crystalline wax, and earth wax. Examples of synthetic waxes include polyethylene wax, wax obtained through Fischer-Tropsch synthesis, a waxy copolymer and an ester constituted with such waxy copolymers, wax obtained by adding hydrogen as a catalyst to C₈-C₃₂ animal/vegetable oil or edible oil having straight or branched fat chains, silicon wax and fluorine containing wax. One of these wax substances may be used by itself, a plurality of the wax substances may be used in combination or a wax component containing a third constituent may be used. Such a wax component (E) manifests a pronounced paraffin or

olefinic property, has a high level of hydrophobic property and is in a solid state at room temperature. Thus, it does not readily become dissolved into the multifunctional polyol component (A), the multifunctional polyisocyanate component (B) or the plasticizer (D). For this reason, it does not readily become dissolved when mixed in the double fluid reactive setting liquid urethane resin (C) and mostly remains suspended in the liquid. As the double fluid reactive setting liquid urethane resin (C) becomes rapidly set in this state, the wax becomes enclosed in a solid state within the resin achieving the three-dimensional network structure. Thus, the resin model according to the present invention has an advantage in that since the wax component is not directly exposed at the surface thereof, none of the problems of the conventional wax model arise. The wax component (E) is highly effective in accelerating the flow out of the resin constituents which have become softened, thermally decomposed and melted as heat is applied during the dewaxing baking processes.

[0053] The wax component (E) is added so as to achieve a ratio of 1 to 20 wt.% relative to the double fluid reactive setting liquid urethane resin (C). If the wax content is equal to or less than 1wt.% the desired effect of using the wax component (E) does not manifest during the dewaxing process. If the wax content is equal to or greater than 20 wt.%, on the other hand, the fluidity of the double fluid reactive setting liquid resin (C) becomes poor and the operability of the resin model production is compromised. In addition, the strength of the resin model itself becomes lowered and the likelihood of the resin model becoming cracked or broken during disengaging becomes high. Accordingly, the wax content should be set to a range of 5 to 20wt.% and more desirably to a range of 10 to 15 wt.%.

[0054] The wax component (E) is used in the form of grains, flakes or lumps in a size small enough to be contained within a 1cm³ cube. Such wax grains or lumps may assume a roughly spherical shape, a roughly cubic shape or an irregular shape. In other words, the shape is not limited to true spheres or cubes. Their size should be small enough to be contained in a 1cm³ cube. Their diameter should be, preferably, 1mm (approximately 0.8mm³) or less. These wax particles naturally do not flow into any portion of the model with a wall thickness of 1mm or less. While this prevents uniform distribution of the wax component (E) in the model, it does not pose a problem as long as the casting mold can be manufactured and a high precision cast product is produced by assuring high levels of model shape retention and dimensional accuracy, smooth thermal decomposition, fusion and flow out and a minimum quantity of residual ash resulting from high temperature decomposition. The wax component is allowed to flow into portions of the model with wall thicknesses equal to or greater than 1mm. Since unhardened liquid resin, too, is naturally allowed to flow into these portions with ease, a model with a resin component distributed evenly throughout its entirety can be disengaged from the mold. In a sense, the wax component (E) flowing into the portions of the model with large wall thicknesses in great quantities is advantageous. Namely, when the model is being dewaxed and baked, the melting flow out decomposition burning process tends to be slowed down in thick portions. The presence of the wax component (E) in relatively large quantities fixed by the cured resin in these portions and ensures smooth melting flow out - decomposition - burning during the dewaxing and baking processes.

[0055] The water component (F) is constituted of H₂O. The water component (F) includes; 1) the water blended in on purpose, 2) small quantities of water that become mixed into the raw chemical materials during normal manufacturing steps and 3) water in the air absorbed into the raw materials. The water component (F) according to the present invention includes them. Carbon dioxide gas generated through the chemical reaction between the water component (F) and the multifunctional polyisocyanate is used as a foaming agent. In other words, the water component is used to foam urethane with the water. Thus, a model constituted with a resin foam containing the plasticizer (D), the wax component (E) and air bubbles is achieved. Such a resin model constituted of foam achieved within a specific controlled foam formation range retains a firm shape and is highly effective during the dewaxing baking processes in which it is heated, becomes melted and decomposed, flows out and becomes burnt.

[0056] The main factor that determines the expansion ratio is the quantity of the water component (F), and sub factors such as the presence/absence of water at the die surface and the temperature and the humidity of the surrounding air also affect the expansion ratio. The water component (F) is included at a ratio of 0.01 to 1.0 wt.% relative to the double fluid reactive setting liquid urethane resin (C). It is desirable to set the water content to 0.03 to 0.5 wt.%, and is even more desirable to set it to 0.08 to 0.15 wt.%. If the ratio of the water component (F) is equal to or greater than 1.0 wt.%, air bubbles tend to concentrate at the resin surface in a large quantity, which reduces the thickness of the skin layer at the model surface. Such a thin skin layer tends to become broken readily during the disengaging process, to allow air bubble cavities to be exposed at the model surface, which leaves the model surface in an irregular undesirable state. In other words, the foaming level must be controlled to a very low level. A foam regulator is used when a foaming urethane in order to regulate the size of the bubbles. According to the present invention, too, a foam regulator is added so as to regulate the size of the bubbles.

[0057] The water content (F) is normally blended in the multifunctional polyol component (A). The quantity of the water component added and then blended evenly into the multifunctional polyol component (A) is controlled by implementing metering for trace amounts of water through the Karl Fischer method. The water component blended in the multifunctional polyol component (A) may be pure water or it may be a substance containing water as long as it does not adversely affect the processes of model production. For instance, the water component may be provided as a surface active agent aqueous solution, a dye aqueous solution, a water-based glue, a resin aqueous solution or the like.

[0058] The surface active agent aqueous solution that may be used is an aqueous solution containing a negative ion surface active agent, a positive ion surface active agent, a nonionic surface active agent, an amphoteric surface active agent or a high molecular surface active agent. No particular restrictions are imposed with regard to the surface active agent content in the aqueous solution. In other words, a liquid detergent containing a great deal of water or a solid or powder detergent with a low water content may be used. The surface active agent aqueous solution is blended into the multifunctional polyol component (A). It may be evenly dissolved in the multifunctional polyol component (A) or it may be blended in a dispersed and suspended state.

[0059] A surface active agent is normally constituted with hydrophobic groups formed with extended chain alkyl groups and hydrophilic groups which become dissolved into water easily. Since the plasticizer component (D) and the wax component (E) with high levels of hydrophobic property are present in the blend, the surface active agent is assumed to be oriented toward these components with high hydrophobic property.

[0060] A dye aqueous solution is a solution containing dissolved there in a dye with hydrophilic groups, and water-based glue is a type of high molecular surface active agent assuming the form of a cellulose type high molecular aqueous solution.

[0061] A resin aqueous solution is an aqueous solution of a resin with a high level of hydrophilic property, and typical examples of such resin aqueous solutions include vinyl acetate and EVA.

[0062] When aqueous foaming the resin, a foam regulator is used in order to achieve the highest possible level of uniformity in the size of the bubbles. A foam regulator is a type of surface active agent. It is most commonly manufactured by adding alkylene oxide to silicon. By adding a foam regulator when aqueous foaming the model, the model can be formed as a foam model containing bubbles with a relatively uniform size. While the strength of the model is lowered, a great advantage is achieved during the dewaxing baking processes since the quantities of the components that become dewaxed and baked are greatly reduced. No particularly rigorous requirements need to be satisfied with regard to the model strength, and the model only needs to have a level of strength that allows it to be disengaged smoothly. In addition, the disengaged model only needs to achieve a level of strength that allows it to be transported without breakage. It should also undergo a minimum extent of change in its shape while it is stored at room temperature and should assure a sufficient level of strength to withstand the refractory coating process. The resin model according to the present invention containing the plasticizer and the wax component assures a satisfactory level of strength meeting such requirements.

[0063] Next, the organic solvent (G) used in the present invention is explained.

[0064] An inactive organic solvent that does not chemically react with isocyanate should be selected for the organic solvent (G). Examples of the inactive organic solvent include an aromatic organic solvent, an ester organic solvent, an ether organic solvent, an aliphatic organic solvent and a chlorine-based organic solvent. The requirements that the organic solvent (G) must satisfy are that it dissolves the multifunctional polyether (A), the multifunctional polyisocyanate (B) and the plasticizer (D), that it only has a mild odor, that it does not generate any toxic gas when it is burned and that it is economical. The organic solvent (G) satisfying such requirements should be preferably an aromatic organic solvent such as toluene or xylene.

[0065] Since the organic solvent (G) tends to become gasified readily while the double fluid reactive setting liquid resin (C) is heated and gels, it also acts as a foaming agent. In addition, the organic solvent (G) remains trapped in small quantities inside the hardened and disengaged model. The presence of the organic solvent (G) remaining in the portions of the model with wall thicknesses equal to or greater than 1 mm, which do not burn easily helps burn the thick portions more efficiently during the dewaxing - sintering processes. It also achieves a great advantage in that it lowers the viscosity of the resin to improve the operability of the model production.

[0066] Next, an explanation is given on the fine particles of a natural high molecular waste (H) used in the present invention.

[0067] The fine natural high molecular waste particles (H) may be fine particles of paper waste, wood waste or fabric waste. Examples of fine paper waste particles include fine particles of newspaper, advertising fliers, copying paper, wrapping paper and corrugated cardboard. Examples of fine wood waste particles include fine particles of building lumber waste, civil engineering lumber waste, furniture wood waste, wood fabrication leavings, scrub plant waste and sawdust. Examples of fine fabric waste particles include fine particles of cotton cloth, linen cloth and wool cloth. More specifically, fine paper particles may be obtained by shredding used office paper, fine wood waste particles may be sawdust generated when a wooden structure is dismantled, disassembled and scrapped and fine fabric waste particles may be obtained from fabric waste cut into a single-fiber state.

[0068] It is desirable to blend these fine natural high molecular waste particles (H) into the multifunctional polyol component (A). Since the specific gravity of the fine natural high molecular waste particles (H) is very close to the specific gravity of the multifunctional polyol component (A), the fine particles are allowed to remain suspended in the liquid without settling or rising to the surface, and the fine waste particles mixed in the multifunctional polyol component can be dispersed uniformly with relative ease. If air is trapped inside the fine natural high molecular waste particles (H), it will make it difficult to mix and disperse the fine waste particles (H) in the liquid containing the multifunctional polyol component

(A). In such a case, the fine natural high molecular waste particles (H) should be deaerated at a lowered pressure level to remove the air and ultimately to facilitate the process of mixing and dispersing.

[0069] The fine natural high molecular waste pieces (H) are normally hydrophilic and thus contain a certain level of moisture. Accordingly, as the fine natural high molecular waste pieces (H) are mixed and dispersed in the multifunctional polyol component (A), the water contained in the fine natural high molecular waste particles (H) is added into the multifunctional polyol component (A) to result in an increase in the water content of the multifunctional polyol component (A). For this reason, it is necessary to control the water content of the multifunctional polyol component (A) by factoring in the quantity of water in the fine natural high molecular waste particles (H) mixed in the multifunctional polyol component (A).

[0070] A balancing agent, a stabilizer, a coloring agent, a flammable filler and a diluent are added into the double fluid reactive setting liquid resin (C). A hindered phenol oxidation inhibitor or a hindered amine oxidation inhibitor is used as the stabilizer. An organic dye or powdered carbon is an effective coloring agent. A pigment that becomes residual ash through the baking process is not desirable. In addition, no flame retardant should be added. The flammable filler should contain 1 to 10% microballoons or carbon powder. Resin microballoons are fine lightweight particles with a true specific gravity of 0.15 to 0.50g/cc and a particle diameter within the range of 15 to 100 μm , and are available as commercial products such as UCAR Phenolic Microballoons (manufactured by Union Carbide) and Matsumoto Microsphere (manufactured by Matsumoto Yushi Pharmaceuticals Co. Ltd.). By using a flammable filler containing resin microballoons, air is embedded into the resin model, which promotes the decomposition, flow out and burn off during the dewaxing and baking processes and reduces the quantity of residual ash. The content of the resin microballoons should be within a range of 0.1 to 10 wt.% relative to the weight of the resin model. If the resin microballoons are contained at 10 wt.% or higher, the reactive setting liquid resin (B) becomes grainy and smooth fluidity cannot be achieved. For this reason, the resin microballoons content should be 3 to 8 wt.%.

[0071] The present invention proposes an optimal resin composition satisfying a specific range of requirements to be adopted in a burn-off model used in high precision casting. A resin model assures greater strength compared to a wax model. At the same time, the resin model must facilitate speedy production to assure good cost performance. Since resin models are not intended for mass production in the first place, various types of resin models need to be manufactured in small quantities in a speedy manner in industrial applications. Accordingly, the inventor of the present invention et al. conducted a great deal of research into the optimal resin composition to be adopted in burn off models constituted of a reactive setting resin that becomes set rapidly, instead of a resin model constituted of a thermoplastic resin injected into a die.

[0072] It is conceivable that if the hardened resin is extremely hard, the process of melting, decomposition, flow out and burn off of the heated resin becomes slowed down, which may allow expanded resin to crack and damage the casting mold. For this reason, the resin model having become hardened needs to soften quickly so as to allow the stress of the expanded resin to be dispersed through the gate and the air bleed. The inventor of the present invention et al. found that the stress could be spread most effectively when the hardness of the hardened burn off resin model was 20 to 55 and even more desirably 30 to 50 in the shore-D hardness scale. If the hardness of the resin model at 80°C is equal to or greater than 55 in the shore-D hardness scale, the stress of the expanded hardened resin cannot be dispersed to the gate or the air bleed efficiently, allowing the resin to keep expanding until the force of the expansion damages the casting mold. If, on the other hand, the hardness of the resin model at 80°C is equal to or less than 20 in the shore-D hardness scale, the resin model hardness at summer temperatures is equal to or less than 40 in the shore-D hardness scale, which is not high enough to withstand the disengaging process during the resin model production and may cause deformation of the resin model due to forced disengaging stress.

[0073] Thus, factors such as the quantity and the skeletal structure of the resin, the speed with which the resin becomes set, the composition of the plasticizer, the composition of the wax component that becomes melted, flows out and is burnt off, the hardness of the hardened resin and the foaming control must be taken into consideration when determining the composition of the resin used to form a burn-off model, and the inventor of the present invention et al. completed the present invention by ascertaining the optimal range over which the best balance is achieved among these factors.

[0074] First, embodiments of the double fluid reactive setting liquid urethane resin (C) are described below.

(Embodiment 1 - liquid resin)

[0075] 34.0 wt. units of crude MDI (NCO = 32%), 14.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer and 2.0 wt. units of polypropylene glycol (MW = 200) were placed in a three-neck flask, the mixture was evenly agitated to ensure that the added substances were dissolved, the mixture was gradually heated and was agitated for 5 hours at 80°C, thereby inducing a urethane producing reaction. A urethane prepolymer with NCO at its terminals was thus formed. The ratio of NCO was 20.9%. Then, 0.01 wt. units of an antifoaming agent was added and blended into the mixture, thereby forming a multifunctional polyisocyanate component.

[0076] Next, 5.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300), 18.0 wt. units of trimethylol propane

propylene oxide adduct (MW = 400) and 10.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.015% through the Karl Fischer method. After the mixture cooled down, 0.01 wt. units of an antifoaming agent and a trace amount of octylic zinc/xylene solution (10% solution) were added into the mixture to adjust its working life to 3 minutes. Then, 5.0 wt. units of beeswax to constitute the wax component was added into the mixture, and thus, the multifunctional polyol component was prepared.

[0077] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 0.88, the plasticizer content was calculated to be 24.0 wt. % the polyether chain content was calculated to be 21.7 wt. % the wax component content was calculated to be 10.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 3.43 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.33.

(Comparison example 1 - liquid resin)

[0078] 43.0 wt. units of crude MDI (NCO = 32%), 4.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer and 2.0 wt. units of polypropylene glycol (MW = 200) were placed in a three-neck flask, the mixture was evenly agitated to ensure that the added substances were dissolved, the mixture was gradually heated and was agitated for 5 hours at 80°C thereby inducing a urethane producing reaction. A urethane prepolymer with NCO at its terminals was thus formed. The ratio of NCO was 25.0%. Then, 0.01 wt. units of an antifoaming agent was added and blended into the mixture, thereby forming a multifunctional polyisocyanate component.

[0079] Next, 5.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300) and 45.0 wt. units of bisphenol propylene oxide adduct (MW = 400) were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.015% through the Karl Fischer method.

[0080] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 1.02, the plasticizer content was calculated to be 5.0 wt. % the polyether chain content was calculated to be 23.4 wt. % the wax component content was calculated to be 0.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 2.26 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.32.

Summary of embodiment and comparison example of double fluid reactive setting liquid urethane resin (C) Table 1

composition	embodiment 1 - resin	comparison example 1 - resin
ethylene diamine propylene oxide adduct (mw = 300)	5.0	5.0
ethylene diamine propylene oxide adduct (mw = 400)	7.0	-
trimethylol propane propylene oxide adduct (mw = 400)	18.0	-
DOA	10.0	-
antifoaming agent	0.01	0.01
beeswax	10.0	-
bisphenol PO adduct (mw = 400)	-	45.0
octylic zinc	small quantity	small quantity
total	50.01	50.01
crude MDI NCO = 32%	34.0	43.0
polypropylene glycol (MW = 200)	2.0	2.0
DOA	14.0	5.0
antifoaming agent	0.01	0.01
total	50.01	50.01
grand total	100.02	100.02
double fluid blending ratio (wt. ratio)	1:1	1:1
NCO/OH	0.88	1.02
working life	3 minutes	6 minutes
resin content (wt.%)	66.0 %	95.0 %
plasticizer component content (wt.%)	24.0 %	5.0 %

(continued)

composition	embodiment 1 - resin	comparison example 1 - resin
wax component content	10.0%	0.0%
alkylene oxide chain component (wt.%)	21.7%	23.4%
polyol component average functional radix	3.43	2.26
polyisocyanate component average functional radix	2.33	2.32
* denotes a compound containing alkylene oxide		

(Embodiment 2 - liquid resin)

[0081] 32.0 wt. units of crude MDI (NCO = 32%), 5.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer and 8.0 wt. units of xylene were placed in a three-neck flask. Then, 5.0 wt. units of beeswax to constitute the wax component were added into the mixture and blended through agitation. The ratio of NCO was 20.5%. This mixture was used as the multifunctional polyisocyanate component.

[0082] Next, 5.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300), 7.0 wt. units of ethylene diamine propylene oxide adduct (MW = 400), 16.0 wt. units of trimethylol propane propylene oxide adduct (MW = 400) and 5.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.02% through the Karl Fischer method.

[0083] After the mixture cooled down, 7wt. units of xylene was added blended in and diluted and a very small quantity of octylic zinc/xylene solution (10% solution) were added into the mixture to adjust its working life to 90 seconds. Then, 5.0 wt. units of beeswax to constitute the wax component was added into the mixture, and thus, the multifunctional polyol component was prepared.

[0084] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 0.88, the plasticizer content was calculated to be 10.0 wt. % the polyether chain content was calculated to be 21.7 wt. % the wax component content was calculated to be 13.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 3.40 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.37.

(Comparison example 2 - liquid resin)

[0085] 36.0 wt. units of crude MDI (NCO = 32%), 2.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer, 2.0 wt. units of polypropylene glycol (MW = 200) and 10.0 wt. units of xylene were placed in a three-neck flask. The mixture was evenly agitated to allow the added substance to be dissolved and then, it was gradually heated and was blended for 1 hour at 80°C. The ratio of NCO was 20.5%. This mixture was used as the multifunctional polyisocyanate component.

[0086] Next, 5.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300), 2.0 wt. units of trimethylol propane propylene oxide adduct (MW = 400) and 33.0 wt. units of bisphenol propylene oxide adduct were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.02% through the Karl Fischer method.

[0087] After the mixture cooled down, 10.0 wt. units of xylene was added blended in and diluted, and a very small quantity of octylic zinc/xylene solution (10% solution) were added into the mixture to adjust its working life to 3 minutes. This mixture was used as the multifunctional polyol component.

[0088] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 1.03, the plasticizer content was calculated to be 2.0 wt. % the polyether chain content was calculated to be 21.3 wt. % the wax component content was calculated to be 0.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 2.37 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.33.

Summary of embodiment and comparison example of double fluid reactive setting liquid urethane resin (C) Table 2

composition	embodiment 2 - liquid resin	comparison example 2 - liquid resin
ethylene diamine propylene oxide adduct (MW = 300)*	5.0	5.0

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(continued)

composition	embodiment 2 - liquid resin	comparison example 2 - liquid resin
ethylene diamine propylene oxide adduct (MW = 400)*	7.0	-
trimethylol propane propylene oxide adduct (MW = 400)*	16.0	2.0
DOA	5.0	-
antifoaming agent	0.01	0.01
beeswax	8.0	-
bisphenol PO adduct (MW = 400)	-	33.0
octylic zinc	small quantity	small quantity
xylene	9.0	10.0
total	50.01	50.01
crude MDI NCO = 32%	32.0	36.0
polypropylene glycol (MW = 200)*	-	2.0
DOA	5.0	2.0
antifoaming agent	0.01	0.01
xylene	8.0	10.01
beeswax	5.0	-
total total	50.01	50.01
grand total	100.02	100.02
double fluid blending ratio (wt. ratio)	1:1	1:1
NCO/OH	0.88	1.02
working life	90 seconds	3 minutes
resin content (wt. %)	66.0 %	96.0 %
plasticizer component content (wt. %)	10.0 %	2.0 %
wax component content	13.0%	0.0%
alkylene oxide chain component (wt. %)	21.7%	23.4%
polyol component average functional radix	3.40	2.37
polyisocyanate component average functional radix	2.37	2.33
* denotes a compound containing alkylene oxide		

(Embodiment 3 - liquid resin)

[0089] 32.0 wt. units of crude MDI (NCO = 32%), 5.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer and 8.0 wt. units of xylene were placed in a three-neck flask and were dissolved through agitation. Then, 5.0 wt. units of beeswax to constitute the wax component were added into the mixture and blended through agitation. The ratio of NCO was 20.5%. This mixture was used as the multifunctional polyisocyanate component.

[0090] Next, 7.0 wt. units of ethylene diamine - propylene oxide adduct (MW = 300), 8.0 wt. units of ethylene diamine propylene oxide adduct (MW = 400), 16.0 wt. units of trimethylol propane - propylene oxide adduct (MW = 400) and 5.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.02% through the Karl Fischer method.

[0091] After the mixture cooled down, 0.03 wt. units of water was added into the mixture and it was evenly blended for 1 hour. Then, 9wt. units of xylene was added, blended in and diluted, and a very small quantity of octylic zinc/xylene solution (10% solution) was added into the mixture to adjust its working life to 2 minutes. Then, 5.0 wt. units of beeswax to constitute the wax component was added into the mixture, and thus, the multifunctional polyol component was prepared.

[0092] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 0.77, the plasticizer content was calculated to be 10.0 wt. % the polyether chain content was calculated to be 37 wt.% the wax component content was calculated to be 10.0 wt.

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%, the average functional radix of the multifunctional polyol component was calculated to be 3.30 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.30.

(Comparison example 3 - liquid resin)

[0093] 36.0 wt. units of crude MDI (NCO = 32%), 2.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer, 2.0 wt. units of polypropylene glycol (MW = 200) and 10.0 wt. units of xylene were placed in a three-neck flask and blended through agitation. Then, the mixture was gradually heated and was blended for 1 hour at 80°C. The ratio of NCO was 20.5%. This mixture was used as the multifunctional polyisocyanate component.

[0094] Next, 5.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300), 2.0 wt. units of trimethylol propane propylene oxide adduct (MW = 400) and 33.0 wt. units of bisphenol propylene oxide adduct were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.02% through the Karl Fischer method.

[0095] After the mixture cooled down, 10.0 wt. units of xylene was added blended in and diluted and a very small quantity of octylic zinc/xylene solution (10% solution) were added into the mixture to adjust its working life to 3 minutes. This mixture was used as the multifunctional polyol component.

[0096] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 1.03, the plasticizer content was calculated to be 2.0 wt. % the polyether chain content was calculated to be 21.3 wt. % the wax component content was calculated to be 0.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 2.37 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.33.

Summary of embodiment and comparison example of double fluid reactive setting liquid urethane resin (C)

composition	embodiment 3 - liquid resin	comparison example 3 - liquid resin
ethylene diamine · propylene oxide adduct (MW = 300)*	7.0	5.0
ethylene diamine · propylene oxide adduct (MW = 400)*	8.0	-
trimethylol propane · propylene oxide adduct (MW = 400)*	16.0	2.0
DOA	5.0	-
foam regulator	0.01	0.01
beeswax	5.0	-
bisphenol PO adduct (MW = 400)	-	33.0
octylic zinc	small quantity	small quantity
xylene	9.0	10.0
water	0.03	
total	50.04	50.01
crude MDI NCO = 32%	32.0	36.0
polypropylene glycol(MW = 200)*	-	2.0
DOA	5.0	2.0
xylene	8.0	10.0
beeswax	5.0	-
total total	50.0	50.01
grand total	100.02	100.02
double fluid blending ratio (wt. ratio)	1:1	1:1
NCO/OH	0.82	1.03
working life	2 minutes	3 minutes
resin content (wt.%)	66.0 %	96.0 %
plasticizer component content (wt.%)	10.0 %	2.0 %
wax component content	10.0%	0.0%
alkylene oxide chain component (wt.%)	21.0%	21.3%

(continued)

composition	embodiment 3 - liquid resin	comparison example 3 - liquid resin
polyol component average functional radix	3.30	2.37
polyisocyanate component average functional radix	2.30	2.33
* denotes a compound containing alkylene oxide		

[0097] The values above were calculated by assuming the value of 2.0 for the functional radix of the added water content.

(Embodiment 4 - liquid resin)

[0098] 32.0 wt. units of crude MDI (NCO = 32%), 5.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer and 8.0 wt. units of xylene (MW = 200) were placed in a three-neck flask and were dissolved through agitation. Then, 5.0 wt. units of beeswax to constitute the wax component were added into the mixture and blended through agitation. The ratio of NCO was 20.5%. This mixture was used as the multifunctional polyisocyanate component.

[0099] Next, 7.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300), 8.0 wt. units of ethylene diamine propylene oxide adduct (MW = 400), 16.0 wt. units of trimethylol propane - propylene oxide adduct (MW = 400) and 3.0 wt. units of 2-ethyl hexyl adipate to be used as a plasticizer were placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. The water content in the mixture was measured to be 0.02% through the Karl Fischer method.

[0100] After the mixture cooled down, 9 wt. units of xylene was added, blended in and diluted and a very small quantity of octylic zinc/xylene solution (10% solution) was added into the mixture to adjust its working life to 3 minutes. Then, 5.0 wt. units of beeswax to constitute the wax component, and 2.0 wt. units of sawdust (sawdust generated when cutting wood) containing 10 wt.% of water was added and thus, the multifunctional polyol component was thus prepared.

[0101] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 0.83, the plasticizer content was calculated to be 8.0 wt. % the polyether chain content was calculated to be 21.0 wt.% the wax component content was calculated to be 10.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 3.30 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.30.

(Comparison example 4 - liquid resin)

[0102] 42.0 wt. units of crude MDI (NCO = 32) and 8.0 wt. units of xylene were placed in a three-neck flask and were dissolved through agitation. Then, the mixture was gradually heated and was blended for 1 hour at 80°C. The ratio of NCO was 26.9%. This mixture was used as the multifunctional polyisocyanate component.

[0103] Next, 5.0 wt. units of ethylene diamine propylene oxide adduct (MW = 300), 3.5 wt. units of trimethylol propane propylene oxide adduct (MW = 400) and 30.0 wt. units of bisphenol propylene oxide adduct was placed in a four-neck flask, and the mixture was thoroughly blended and then dehydrated by agitating the mixture for one hour at 100°C in a vacuum while allowing nitrogen gas to be absorbed therein through capillaries. Then, 1.5 wt. units of water was added and blended for 1 hour through agitation. The water content in the mixture was measured to be 3.02% through the Karl Fischer method.

[0104] After the mixture cooled down, 8.0 wt. units of xylene was added, blended in and diluted and a very small quantity of octylic zinc/xylene solution (10% solution) were added into the mixture to adjust its working life to 3 minutes. This mixture was used as the multifunctional polyol component.

[0105] The blending ratio of the multifunctional polyol component and the multifunctional polyisocyanate component was 1: 1 (by weight). The NCO/OH ratio was calculated to be 0,78, the plasticizer content was calculated to be 0.0 wt. % the polyether chain content was calculated to be 21.3 wt.% the wax component content was calculated to be 0.0 wt. %, the average functional radix of the multifunctional polyol component was calculated to be 2.24 and the average functional radix of the multifunctional polyisocyanate component was calculated to be 2.20.

Summary of embodiment and comparison example of double fluid reactive setting liquid urethane resin (C) Table 4

composition	embodiment 3 - liquid resin	comparison example 3 - liquid resin
ethylene diamine · propylene oxide adduct (MW = 300)*	7.0	5.0
ethylene diamine · propylene oxide adduct (MW = 400)*	8.0	-
trimethylol propane propylene oxide adduct (MW 400)*	16.0	3.5
DOA	3.0	-
foam regulator	0.01	0.01
beeswax	5.0	-
bisphenol PO adduct (MW = 400)	-	30.0
octyllic zinc	small quantity	small quantity
xylene	9.0	10.0
water	-	1.5
sawdust (water content 10%)	2.0	-
total	50.01	50.01
crude MDI NCO = 32%	32.0	42.0
polypropylene glycol (MW = 200)*	-	0.0
DOA	5.0	0.0
xylene	8.0	8.0
beeswax	5.0	-
total total	50.0	50.0
grand total	100.02	100.01
double fluid blending ratio (wt. ratio)	1:1	1:1
NCO/OH	0.77	0.78
working life	3 minutes	3 minutes
resin content (wt.%)	66.0 %	82.0 %
plasticizer component content (wt.%)	8.0 %	0.0 %
wax component content	10.0%	0.0%
alkylene oxide chain component (wt.%)	21.0%	21.3%
polyol component average functional radix	3.30	2,24
polyisocyanate component average functional radix	2.30	2.30
* denotes a compound containing alkylene oxide		

[0106] The values above were calculated by assuming the value of 2.0 for the functional radix of the added water content.

[0107] Next, embodiments and comparison examples of resin models achieved by using these double fluid reactive setting urethane liquid resins (C) are explained.

[0108] Models of an automotive part, each having a gross model weight of 0.8 kg, a maximum wall thickness of 25 mm, a minimum wall thickness of 0.4 mm, a maximum longitudinal measurement of 200 mm, a maximum lateral measurement of 300 millimeters and a maximum height of 200 mm and assuming a complicated shape overall with no leaves or draft, were manufactured through vacuum injection by inverting them from the master models to silicon rubber molds.

[0109] Each master model was prepared through the method described below. Namely, a photocuring acrylic liquid resin was poured into a resin container of an optical molding machine and a thin layer of the liquid resin was formed with the liquid resin supplied onto a supporting stage by slightly lowering the supporting stage, which was installed within the resin container and was allowed to move up/down freely relative to the liquid resin surface. Then, a hardened resin layer in a solid state was formed by irradiating the thin layer with computer-controlled light based upon data indicating the shape of the resin model to be molded. Next, another thin layer was formed over the hardened resin layer by further supplying the reactive setting liquid resin and a new hardened resin layer was formed continuous to the initial hardened

resin layer so as to laminate the initial hardened resin layer by irradiating the new thin layer with computer-controlled light. By repeating this process a predetermined number of times while varying or without varying the pattern formed through the computer controlled irradiation, a plurality of hardened resin layers were formed as an integrated laminated body, and a resin model was molded as a three-dimensional object. The resin model thus formed as a three-dimensional object was then disengaged from the supporting stage in the container and was taken out. The residual liquid resin at the surface of the resin model, which had not undergone the reaction, was washed away with an organic solvent. The organic solvent used to wash away the residual resin was isopropyl alcohol, ethyl alcohol, acetone, ethyl acetate or methyl ethyl ketone. Subsequently, the resin model underwent a post curing process through light irradiation and thus became completely hardened. Any burrs extending over the side surfaces of the hardened resin model were trimmed off with a cutter in a finishing process. The resin model thus formed had a normal appearance with no bleeding or tackiness of the plasticizer observed at the surface thereof. The hardness of the liquid resin instantaneously hardened through the light irradiation was 72 in the shore D hardness scale at 25°C and 59 in the shore D hardness scale at 80°C.

[0110] The resin model was inverted from the master model to the silicon mold through the following procedure. The position of a gate - casting port was determined, a gate constituted with a plastic rod was bonded to the master model and was temporarily tacked inside the container. Then, mold release processing was executed. A transparent RTV silicon liquid resin (Shin-etsu Chemicals Co. Ltd. KE1506) and a hardening agent liquid resin (Shin-etsu Chemicals Co. Ltd. CAT-RG) were placed in a mixing container at a ratio of 20; 1, after they were thoroughly mixed by using an agitator, the mixture was placed in a vacuum defoaming tank where it was alternately left in a vacuum state and in a state of deaeration leak several times and the mixture was defoamed by breaking bubbles of the mixed gas coming up to the surface of the liquid resin. Next, the transparent RTV silicon liquid resin containing the hardening agent was slowly poured into the container within which the master model and the gate had been temporarily tacked. In order to completely eliminate any bubbles formed during the process of pouring the transparent RTV silicon liquid resin, the container was placed in the vacuum tank again and was held therein for 10 minutes at a lowered pressure for defoaming. Then, it was taken out of the vacuum tank and was left to harden at room temperature for 24 hours. As a result, a hardened transparent RTV silicon object enclosing the master model was obtained. The transparent hardened silicon object was cut into two halves along a particle line marked on the master model and the master model was taken out of the hardened transparent silicon object. The front tip of the gate was cut off with a cutter to form a casting port. At the same time, a V-shaped slit was formed with a knife at the transparent silicon mold in order to form an air bleed port. A split-type transparent silicon mold having a casting port and an air bleed port formed at an upper portion thereof was thus prepared. Then, the split-type mold was accurately aligned along positioning screws and was firmly fixed in place with tape. A plastic funnel was inserted at the casting port and was fixed therein to be used as a receptacle for the liquid resin being poured.

[0111] The various types of liquid resins achieved in the embodiments and the comparison examples described above were used to form models through vacuum molding by adopting the following method. A silicon mold was placed inside a vacuum tank, and 50 units of the multifunctional polyol component (A) was poured into one container and 50 units of the multifunctional polyisocyanate component (B) was poured into another container in advance. The pressure inside the vacuum tank was lowered, the container containing the multifunctional polyol component (A) inside the vacuum tank was tilted by rotating a rotary knob which was led from the container to the outside of the vacuum tank and thus, the multifunctional polyol component (A) was poured into the container containing the multifunctional polyisocyanate component (B). Immediately after this, an agitator in the container into which the multifunctional polyisocyanate component (B) had been initially poured started to rotate to thoroughly mix the two fluids. The double fluid mixture was then poured into the plastic funnel fixed to the casting port of the transparent RTV silicon mold by rotating a rotary knob led from the double fluid mixture container to the outside of the vacuum tank. As a result, the double fluid mixture was poured into the space assuming the shape of the model and formed inside the transparent RTV silicon mold. Immediately afterward, the vacuum in the vacuum tank was released and the pressure inside the vacuum tank was reset to normal. It was ensured that the entire procedure was executed efficiently and was completed within approximately 40 seconds. Embodiments and comparison examples of resin models thus manufactured are summarized in Table 5.

Summary of embodiments and comparison examples of models Table 5

	check items	embodiment1 - model	comparison example1- model	embodiment2 - model	comparison example2-model
resin used	liquid resin	embodimen t1- liquid resin	comparison example1- liquid resin	embodiment2- liquid resin	comparison example2-liquid resin
	type of hardening	double fluid hardening	double fluid hardening	double fluid hardening	double fluid hardening
	working life	3 minutes	6 minutes	90 seconds	3 minutes

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(continued)

	check items	embodiment1 - model	comparison example1- model	embodiment2 - model	comparison example2-model
5	liquid temperature	20°C	20°C	20°C	20°C
	mold temperature	20°C	20°C	20°C	20°C
10	length of time disengaging was enabled	2 hours	next day	30 minutes	12 hours
	post hardening conditions	20 °C/1 day	20 °C/1 day	20 °C/1 day	20 °C/1 day
15	molding method	vacuum injection	vacuum injection	vacuum injection	vacuum injection
	appearance	OK	OK	OK	OK
20	tack	OK	OK	OK	Present
	shape retention	OK	OK	OK	OK
	foam	OK	OK	OK	OK
25	definition	OK	OK	OK	OK
	ribs	OK	OK	OK	OK
	cracking	OK	OK	OK	OK
30	OK indicates "good"				

Summary of embodiments and comparison examples of models

Table 6

	check items	embodiment3- model	comparison example3- model	embodiment4- model	comparison example4- model
35	liquid resin	embodiment3- liquid resin	comparison example3- liquid resin	embodiment4- liquid resin	comparison example4-liquid resin
40	type of hardening	double fluid hardening	double fluid hardening	double fluid hardening	double fluid hardening
	working life	2 minutes	3 minutes	3 minutes	3 minutes
45	liquid temperature	20°C	20 °C	20 °C	20°C
	mold temperature	20°C	20 °C	20°C	20 °C
50	length of time before disengaging was enabled	60 minutes	12 hours	30 minutes	60 minutes
	post hardening conditions	20 °C/1 day	20 °C/1 day	20 °C/1 day	20 °C/1 day
55	molding method	vacuum injection	vacuum injection	vacuum injection	vacuum injection

(continued)

	check items	embodiment3- model	comparison example3- model	embodiment4- model	comparison example4- model
5 10 15	appearance	OK	OK	OK	OK
	tack	OK	slight tacking	OK	Present
	shape retention	OK	OK	OK	void formation
	foam	OK with slight foaming	OK	OK with slight foaming	major foaming*
	definition	OK	OK	OK	OK
	ribs	OK	OK	OK	OK
	cracking	OK	OK	OK	OK
* Large bubbles were formed, leaving voids covered with an extremely thin surface layer in portions with small wall thickness, and thus, good shape retention was not achieved. OK indicates "good".					

[0112] Embodiments and comparison examples in which cast products were manufactured through high precision casting processes by using the resin models constituted of the reactive setting liquid resins achieved in the present invention and the comparison examples thereof are now described.

[0113] Following the model production, high precision casting processes were executed as detailed below.

1. Model preparation: a gate constituted of lost wax was bonded to the resin model.
2. Coating: the resin model was immersed in a slurry constituted with zirconium sol and fused zirconium, was sprinkled with stucco grains constituted with fused zirconium and was dried for a three hours, thereby forming a first coating layer. Next, it was immersed in a slurry constituted with choroidal silica and mullite, was sprinkled with stucco grains constituted with fused silica and was dried for two hours. The coating process was completed by repeating these steps 10 times.
3. Dewaxing: the gait of the coated resin model was heated for approximately one hour by blowing hot air with a dryer. The lost wax portions were thus dewaxed and, at the same time, the process of decomposing, liquefying and melting out the resin model was hastened through heating.
4. Primary baking: after dewaxing, the resin model was set in a gas furnace with the temperature set to gradually rise, was held for 30 minutes at 200°C and thus, the process of decomposing and burning off of the resin model was accelerated through heating. The temperature inside the furnace was further raised to 550°C at which it was held for 60 minutes to burn off the resin model. The temperature was still raised gradually and the resin model was completely burned off and the casting mold was strengthened at 1100°C.
5. Secondary baking: after removing any residual ash remaining inside the casting mold, the casting mold was placed in an electrical furnace and was baked for one hour at 850°C to remove any moisture remaining at the casting mold.
6. Metal fusion: aTi-6 4 alloy was melted in an argon gas current inside a fusing furnace for vacuum fusion casting. The fusing temperature was 1700°C.
7. Casting: immediately after the Ti alloy became melted, it was cast. After the alloy was cast, it was gradually cooled inside the furnace.
8. Die release: the casting die was cracked with a hammer, the cast product was taken out, and after cutting off the runners, the residual refractory material was eliminated through shot blasting or sandblasting.

[0114] Visual inspection: the cast product was visually checked for its external appearance, any void that might have been formed at the surface, the desired extent of edge definition, ribs at thin portions and the like.

[0115] The embodiments and the comparison examples of high precision cast products achieved by using the resin models constituted with reactive hardening liquid resins are summarized in Table 7 and Table 8.

Embodiments and comparison examples of high precision cast products achieved by using resin models Table 7

5	Embodiment/comparison example No.		Embodiment1 - cast product	Comparison example 1 - cast product	Embodiment2 - cast product	Comparison example 2 - cast product
	Embodiment/comparison example No, of model used		Embodiment1 - model	Comparison example - model	Embodiment2 - model	Comparison example 2 - model
10	Casting mold	Hairline cracks in casting mold	OK	Hairline cracks occurred	OK	Hairline cracks occurred
		Major cracking in casting mold	OK	OK	OK	Observed
15	Cast product	External appearance	OK	Slightly deformed	OK	Slightly deformed
		Voids at cast surface	OK	Present	OK	OK
		Damage to portions with small wall thickness	OK	Slight damage	OK	OK
20	OK indicates "good"					

Embodiments and comparison examples of high precision cast products achieved by using resin models Table 8

30	Embodiment/comparison example No.		Embodiment3 - cast product	Comparison example3 -cast product	Embodiment4 - cast product	Comparison example 4 -cast product
	Embodiment/comparison example No of model used		Embodiment3 - model	Comparison example 3 - model	Embodiment4 - model	Comparison example 4 - model
35	Casting mold	Hairline cracks in casting mold	OK	Hairline cracks occurred	OK	Slight hairline cracking
		Major cracking in casting mold	OK	Observed	OK	OK
40	Cast product	External appearance	OK	Deformed	OK	Slightly deformed
		voids at cast surface	OK	Present	OK	Present
		Damage to portions with small wall thickness	OK	OK	OK	Damaged
45	OK indicates "good"					

INDUSTRIAL APPLICABILITY

[0116] In a high precision casting process adopting a lost wax procedure, it is difficult to manufacture a wax model, which is a burn off model, having portions with small wall thicknesses equal to or less than 1 mm, either through machining or through injection molding in a die, due to the insufficient strength of the wax material. According to the present invention, a model having portions with a wall thickness of 0.5 mm can be manufactured with ease. Namely, the present invention, which enables production of high precision cast parts with extremely small wall thicknesses, achieves a great advantage

in that it may be adopted in a wide range of high precision cast components including camera parts, clock parts, electric razor parts, portable telephone parts, automotive parts and aircraft parts.

[0117] It is to be noted that while utmost care must be taken when handling a wax model with a wall thickness of approximately 1 mm to avoid damage to the thin portions and such a wax model still tends to become broken readily, the resin model according to the present invention achieves far greater strength and flexibility compared to those of the wax model.

[0118] In particular, it is extremely difficult to handle wax models in the related art manufactured in greater quantities, e.g., 1000 units to 10,000 units, even if meticulous care is taken. In contrast, the resin model according to the present invention achieving far superior strength and flexibility can be handled with much greater ease.

[0119] In addition, while sharp edges cannot be defined with ease in a wax model, clean sharp edges can be defined without difficulty in the resin model according to the present invention which is covered with resin and the wax component is embedded within the resin skeleton. By using such a resin model having a skeleton thereof formed with resin, a higher level of versatility is afforded with regard to the shapes of models that can be achieved and thus, a distinct advantage is achieved when the present invention is adopted in the production of low profile objects with complicated shapes.

[0120] Furthermore, the wax model in the related art, which is likely to lose its original shape at high temperature, must be stored in a thermostatic chamber. In contrast, the resin model according to the present invention containing the wax component buried inside the resin skeleton sustains a sufficient level of hardness to retain its original shape even at very high temperatures and does not require rigorous management such as storage in a thermostatic chamber.

[0121] Moreover, since the resin model according to the present invention contains a significant quantity of plasticizer, the resin model is allowed to melt, become decomposed and flow out readily during the dewaxing baking processes, without causing cracking of the casting mold. This advantage is further enhanced with the addition of the wax component. The advantages of the resin model according to the present invention are made even more valuable by adding water and thus forming it as a resin foam model with small air bubbles.

Claims

1. A burn-off resin model used in a lost wax process **characterized in:**

that a liquid resin compound is formed with 1 to 30 wt. % of plasticizer (D) and 1 to 20wt. % of a wax component (E) blended a said double fluid reactive setting liquid urethane resin (C) constituted of a multifunctional polyol component (A) and a multifunctional polyisocyanate component (B); and
that said liquid resin compound is set within a working life of 5 minutes or less to form said resin model.

2. A burn-off resin model according to claim 1 **characterized in:**

that said multifunctional polyol component (A) in said double fluid reactive setting liquid urethane resin has an average functional radix of 2.8 or larger and said multifunctional polyisocyanate component (B) in said double fluid reactive setting liquid urethane resin has an average functional radix of 2.0 or larger with an NCO/OH ratio achieving a value within a range of 0.7 to 1.0.

3. A burn-off resin model according to claim 1 or claim 2 **characterized in:**

that said plasticizer (D) is micro-dispersed through phase separation when said double fluid reactive setting liquid urethane resin (C) undergoes the process of reactive setting.

4. A burn-off resin model according to any of claims 1 through 3 **characterized in:**

that said double fluid reactive setting liquid urethane resin (C) contains 2 to 25 wt. % of polyether chains with a chemical structure indicated in the chemical structural formula below.



5. A burn-off resin model according to any of claims 1 through 4 **characterized in:**

that said wax component (E) is provided in the form of grains, flakes or lumps, each formed in a size that allows it to be contained in an approximate volume of 1cm³.

6. A burn-off resin model according to any of claims 1 through 5 **characterized in:**

that said double fluid reactive setting liquid urethane resin (C) is blended with water by adding 0.01 to 1.0 wt. % of water (F) into said double fluid reactive setting liquid urethane resin (C) to induce aqueous foaming.

7. A burn-off resin model according to any of claims 1 through 5 **characterized in:**

that an organic solvent (G) is blended into said double fluid reactive setting liquid urethane resin (C) so as to achieve an organic solvent content of 10 to 25 wt. %.

8. A burn-off resin model according to any of claims 1 through 6 **characterized in;**

that fine particles (H) of a natural high molecular waste are added into said double fluid reactive setting liquid urethane resin (C) so as to achieve a waste particle content of 1 to 10%.

9. A high precision casting method achieved by using a burn-off resin model according to any of claims 1 through 8.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/12853

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ B22C7/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ B22C1/00-25/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-211254 A (Shonan Design Kabushiki Kaisha), 29 July, 2003 (29.07.03), Claims (Family: none)	1-9
E, X	JP 2003-290871 A (Shonan Design Kabushiki Kaisha), 14 October, 2003 (14.10.03), Claims (Family: none)	1-9
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
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