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METHOD OF FORMING A BACKING FOR METAL SHELLS

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ABSTRACT OF THE DISCLOSURE

A two-part backing composition useful for backing metal shells comprises Part A and Part B wherein; Part A comprises a pliable, workable, thermoconductive, particulate metal aggregate of metal particles having an average size of between 60 and 400 mesh; from 0.2 to 18 parts by weight of a heat activated nonvolatile binder per 100 parts by weight of metal particles and an effective amount of a catalyst for the thermosetting resin of Part B; and Part B comprises a thermosetting resin. The metal aggregate can be cured to a rigid porous structure which is thereafter filled with the thermosetting resin and the entire combination cured to a strong, structurally stable backing.

BACKGROUND OF THE INVENTION

At the present time, many varieties of molds and dies are used to form intricately designed shapes reproduced from an original article that might otherwise have to be hand crafted. Such hand crafting is very expensive and requires much time. Many types of molds are used for this purpose, the most successful of which, however, is the mold prepared by electrodepositing nickel, or some other metal, on the original part that is to be reproduced. The deposition of the nickel continues until the metal layer becomes relatively self-sustaining, which is at a thickness of about 0.1 to 5 mm. Although self-sustaining, this metal mold or shell does not have a high degree of structural integrity, strength, or toughness to withstand continual molding procedures and pressure developed during manufacturing and consequently must be backed with a relatively rigid and strong backing material to prevent fracturing, rupturing and distortion of the thin shell walls. Also, to insure rapid reproduction of the desired molded parts, the shell, which holds the molded part, should be able to cool rapidly, solidifying the part for immediate removal and subsequent reception of further molding material. Consequently, the backing material should be thermoconductive to dissipate heat as fast as possible.

Backings have been prepared from a molten metal which is poured on and around the back of the mold shell. However, shrinkage problems occur when the metal cools and freezes. The shrinkage will cause a distortion on the mold and voids may form between the backing and the shell, not supporting the shell at that particular point. Other attempts have been made to provide a backing for such metal shells as exemplified in U.S. Pat. 3,434,182 issued to Paul S. Peterson. That patent describes a backing layer formed of a solid block of material having a cavity therein of a size sufficient to receive the shell. The mold shell is fastened at its peripheral edges to the block and the mold face portions are backed by filling the opening or cavity in the block of material with elongated rods positioned so that ends of the rods abut directly against the mold shell. The rods are then tightly packed into the opening of the block material and molten metal is poured into the openings to insure good structural integrity. This type of backing is disadvantageous in many respects. First, the solid backing portion of the material must be preformed. Further, the addition of cooling lines and other molding accessories would be more difficult. Also, "trees," which are protrusions and other plating irregularities, which are caused by plating bath impurities, must be removed.

At the present time to applicant's knowledge, there is no known convenient, inexpensive method for backing metal shells which provide a tough, strong, structurally integral thermoconductive backing around the shell.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a two-part backing composition useful for backing metal shells comprising, Part A and Part B wherein; Part A comprises a pliable, workable, thermoconductive particulate metal aggregate of metal particles having an average size of between 60 and 400 mesh; from 0.2 to 18 parts by weight of a heat-activated, nonvolatile binder per 100 parts by weight of metal particles; and an effective amount of a catalyst for the thermosetting resin of Part B, and Part B comprises a heat-activated thermoseting resin. The metal used in conjunction with the present invention is preferably iron, aluminum, or copper. A preferred catalyst is the zinc salt of trifluoromethane sulfonic acid.

Metal shells used for molding may be backed according to the present invention by placing a suitable amount of a pliable, workable, thermoconductive, particulate metal aggregate (Part A) on the back surface of a shell, the aggregate comprising metal particles having an average size of between 60 and 400 mesh, from 2 to 18 parts by weight of a heat-activated non-volatile binder per 100 parts by weight of metal particles, and an effective amount of a catalyst for heat-activated thermosetting resin; compacting said metal aggregate into relatively close contact around said shell; heating the metal aggregate at a temperature of from about 220° F. (100° C.) to 400° F. (200° C.) until cured forming a porous structure backing said shell; saturating said porous structure with a heat-activated thermosetting resin (Part B); and curing the resin at a temperature of from about 250° F. (120° C.) to 400° F. (200° C.) for about ½ to 48 hours.

In the preferred embodiment, the system for backing metal shells comprises a latent epoxy catalyst, a heat-activated thermosetting resin to be later cured by said catalyst, and a metal powder. The metal powder is pre-coated with a binder dispersion of the same or another latent epoxy catalyst and a thermosetting resin. The metal shell, generally an electroformed metal shell, in the preferred method of the present invention, is placed in or attached to a box after which the coated metal powder is compacted or tamped behind the formed shell. The compacted material or "pre-form" can be left in the box or removed and allowed to partially cure to a hard state in an oven. The metal aggregate cures into a relatively rigid, structurally integral and self-sustaining porous structure. As a thermosetting resin will be later "wicked up" into this porous structure, the pores herein preferably have a pore size range from 0.03 to 100 microns, and more preferably the average pore size is in the neighborhood of 40 microns. In the most preferred embodiment the present voids in the porous structure is between 40 and 50 percent. When the porous structure is filled with the resin, the percent voids is reduced to about 2½ to 5 percent.

After the metal aggregate is cured, the backing and shell combination is preferably placed on small supporting pieces of a suitable material, preferably a loose nonwoven bonded fibrous material. Prewarmed thermosetting resin is poured beneath the piece until it contacts the piece and is then allowed to wick up into and saturate the backing material by capillary action. When the resin is no longer being depleted, or saturation of the porous backing material is complete, the entire piece may be wiped off and placed in a clean container and oven cured.

The cured piece is hard, tough, strong and yet easily tapped or machined.

The metal particulate aggregate is preferably prepared by premixing the binder resin and binder catalyst together forming the total binder for the metal particles. The metal used should be thermoconductive and nonreactive with the metal shell that is backed. Examples of metals which may be used are iron or steel, aluminum, copper, nickel, etc. and combinations thereof. After the binder is prepared, the metal powder, the system catalyst, or catalyst for Part B, and the binder are mixed until homogeneous or the metal powder is uniformly coated with the binder material. The resulting aggregate is a soft, pliable and easily workable material and may conveniently be molded around most surfaces. The material preferably sticks somewhat to the metal shell to insure conformability thereto and good thermoconductivity after curing. The cured metal aggregate is a porous self-sustaining structure and carries therein a catalyst in an accessible state for curing the thermosetting resin after it saturates the porous metal aggregate.

The durability and structural integrity of the porous metal aggregate backing material is greatly enhanced by the addition of the thermosetting resin. The preferred thermosetting resin is a standard bisphenol A-epichlorohydrin epoxy resin. Examples of other thermosetting resins which may used are epichlorohydrin-bisphenol A epoxy resins and epichlorohydrin novolak epoxy resins of a wide range of equivalent weights, preferably from about 150 to 200; polyesters, alkyds, phenolics, melamine-aldehyde, urea-aldehyde, cyanamides and allyl types such as diallyl phthalate, or combinations thereof all used with suitable catalysts.

The catalyst used for curing the heat-activated thermosetting resin which is used to fill the porous cured metal aggregate is included with and in the metal aggregate and the type used is dependent on the thermosetting resin used which information is within the skill of the art. Catalysts which are preferred for use with epoxy resins are zinc trifluoro-methane-sulfonate, dicyanamide, melamine, and most preferably, dicyandiamide hexakis-imidazole nickel (II) chloride, or combinations thereof, Care must be taken when using catalysts having loosely-bound metal ions (e.g., managanous trifluoromethane sulfonate) to prevent displacement of the metal ion by those from the metal used as fillter. Such dispelacement decreases the shelf life of the coated metal powder and can be predicted by reference to a table of electrochemical potentials. The amount of catalyst employed should be from about 0.2 to 60 parts by weight catalyst per 100 parts of Part B and preferably 0.2 to 12 parts by weight catalyst per 100 parts of Part B.

Examples of the various components of the backing system of the present invention are illustrated in Table I below. The system resins and binder resins used were epichlorohydrin-bisphenol A epoxy resin, equivalent weight 180–200 ("Epon" 828 available from Shell Chemical Company) and epichlorohydrin-bisphenol A epoxy resin, equivalent weight 450–550 ("Epon" 1001 available from Shell Chemical Company) and combinations thereof.

TABLE I

Binder catalyst	Metal	Binder resin	System resin	System catalyst
$Zn(CF_3SO_3)_2$	Aluminum	"Epon" 828	"Epon" 828	$Zn(CF_3SO_3)_2$.
$Zn(CF_3SO_3)_2$	Steel	do	do	$Zn(CF_3SO_3)_2$.
$Zn(CF_3SO_3)_2$	Aluminum	"Epon" 828 and "Epon" 1001.	do	$Zn(CF_3SO_3)_2$.
$Zn(CF_3SO_3)_2$	Steel	do	do	$Zn(CF_3SO_3)_2$.
Dicyandiamide and hexakis-imidazole nickel (II) chloride.	Aluminum	"Epon" 828	do	Dicyandiamide and hexakisimidazole nickel (II) chloride.
Do	do	do	do	Dicyandiamide.
Do	do	do	do	Melamine.
Do	Steel	do	do	Dicyandiamide and hexakisimidazole nickel (II) chloride.

Part A and Part B of the present invention can be used in varying proportions to vary strength, porosity, etc. Preferably, about 3 to 15 parts of Part A per part of Part B by weight are used. The parts used, particularly Part B, depends on the percent voids in the porous structure. The simplest way to determine how much saturating resin (Part B) to use is to observe when the porous structure is filled. On a weight basis more steel would be used than aluminium to wick up an equal amount of the Part B resin.

One of the biggest advantages of the present invention is that various other components to a backing system can be easily incorporated when the metal aggregate material is in a pliable, sticky and moldable state. Cooling coils can readily be inserted at this time and the material compacted around them. Upon curing of the metal particulate material, the coil and other components are firmly held in place and in no way diminishes the structural integrity of the entire backing. Examples of other components which can be conveniently added to the backing system are alignment aids and selective heating elements.

The procedure of backing a precoated powder, curing, and then allowing the epoxy resin to wick into the porous preform has been described for an epoxy tooling and molding compound using solutions of poly(acrylamide) as binders, as illustrated in Pat. No. 3,056,704, issued to Rothweiler et al. The process described in Rothweiler et al. is, however, unsuited for purposes of the present invention. Because of the use of a volatile binder system, the material cannot be formed on or around the metal shell mold because the release of volatile materials, in close proximity to the shell, causes changes in the strength of the backing which is not crucial to the application of that patent but which is for purposes of the present invention. The Rothweiler et al. patent does not give any suggestion as to the alleviation of this problem for purposes of backing metal shells. The saturation procedures described in that patent are useful, however, for purposes of the present invention.

The invention will be better understood with reference to the following examples wherein all parts are by weight unless otherwise specified.

Example 1

A binder mixture for a metal aggregate was prepared from 5.5 parts by weight of jet-milled dicyandiamide containing approximately 3% fumed silica commercially available as Cab-O-Sil M–5 from the Cabot Corporation, 0.4 parts hexakisimidazole nickel (II) chloride and 100 parts of bisphenol A-epichlorohydrin epoxy resin commercially available as "Epon" 828 from Shell Oil Corporation. A total of 91.5 parts of the binder mixture, 512 parts of aluminum powder commercially available as Al-Meg 100 P from Al-Meg Corporation, 9.8 parts of the jet-milled dicyandiamide, and 0.7 part of hexakis-

imidazole nickel (II) chloride were mixed together for approximately 10 minutes in a sigma blade mixer. The coated powder was tamped into a plastic 290 cc. beaker, removed, and cured at 300° F. (150° C.) for 1 hour. The resulting casting was hard and tough. The casting was placed on an inert support in an aluminum dish. Standard bisphenol A-epichlorohydrin epoxy resin, having an equivalent weight of 150 to 200, ("Epon" 828) was preheated at 250–300° F. (120–150° C.) and poured into the aluminum dish covering the first ⅛ inch of the porous backing structure. The epoxy resin was soaked or saturated into the backing by capillary action and could be followed visually. The epoxy resin, preheated to 250° F. (120° C.) was added as needed. Complete saturation occurred within 1 hour at 250° F. (120° C.). The saturated piece was removed from the resin, wiped off, and allowed to cure 24 hours at 275° F. (135° C.), 4 hours 325° F. (160° C.) and 5 hours at 400° F. (200° C.) in an oven. The completely cured backing material was hard and tough and exhibited a high degree of dimensional stability.

Example 2

An extremely thin (0.1 mm.) electroformed shell of nickel, bearing in three-dimensional relief the configuration desired to be reproduced, was placed in a wooden box 3 x 5 x 6 inches (7.5 x 12.5 x 15 cm.) deep. The metal aggregate material as prepared in Example 1 was placed inside the electroformed shell and tamped in back of the electroformed shell by hand. More aggregate material was added as needed and tamped on top of a previous layer until the shell was completely filled. The backed shell was removed from the wooden box, inverted, and cured in an oven at 300° F. (150° C.) for 1 hour. The composite, while still hot, was placed on 4 blocks of inert material in an aluminum foil pan and bisphenol A-epichlorohydrin epoxy resin preheated to 250° F. (120° C.) was poured into the pan up to a level approximately ⅛ inch (0.3 cm.) on the electroformed backing material. Wicking by capillary action into the porous structure took about 1 hour at 300° F. (150° C.). The piece, however, was allowed to remain at 300° F. (150° C.) for 4 hours. The composite was then removed from the resin, wiped off, and placed in a clean aluminum foil pan and cured in an oven at 300° F. (150° C.) for approximately 63 hours, 350° F. (180° C.) for 2 hours, and 400° F. (200° C.) for 4 hours. The resulting piece was hard and tough and visual observation indicated that no voids were present. No noticeable shrinkage had occurred. Barcol 935 hardness, a well known measurement of the hardness of plastic and metal materials, was 80–89 in all areas.

Example 3

To illustrate the addition of various components in the backing structure, aluminum granules coated according to the procedure set out in Example 1 were tamped to a height of about ¾ inch (1.9 cm.) in a 5 x 6 x 2 inch box (12.5 x 15 x 5 cm.). A curved piece of ¼ inch (0.6 cm.) O.D. copper tubing with compression fittings at each end was coated with an adhesive or binder, to insure stickiness, made from 100 parts of an epichlorohydrin-bisphenol A epoxy resin (Epon 828), 0.4 parts of hexakisimidazole nickel (II) chloride, and 5.5 parts dicyandiamide and the coated piece embedded in the coated granules in the box. The aluminum granule aggregate was tamped in place until the box was filled. Excess granules were removed, the box disassembled, and the composite cured at 300° F. (150° C.) for 1 hour. The hardened composite was placed in warm epoxy resin at 275° F. (120° C.) allowed to saturate the composite for 1½ hours at 300° F. (150° C.) and cured overnight at 300° F. (150° C.), 2 hours at 350° F. (180° C.) and 4 hours at 400° F. (200° C.).

Example 4

A binder mixture for metal particles was prepared from 7.3 parts by weight of jet-milled dicyandiamide, 0.6 parts of hexakisimidazole nickel (II) chloride and 100 parts of bisphenol A-epichlorohydrin epoxy resin (Epon 828). A mixture was made of 51 parts of the binder mixture, 1450 parts of steel particles having an average mesh size of 80 to less than 325 (Ancorsteel 1000), and 20.7 parts of dicyandiamide. The mixture was tamped into a 5 x 6 x 2 inch (12.5 x 15 x 5 cm.) wooden box and cured for 90 minutes after which it was placed on four pieces of an inert loose non-woven bonded nylon material in a pan containing bisphenol A-epichlorohydrin epoxy resin (Epon 828) and allowed to become saturated with the resin by wicking the resin into the porous structure. The saturated preformed metal aggregate was then cured overnight at 275° F. (135° C.), 2 hours at 350° F. (180° C.), and 2 hours at 400° F. (200° C.). The backing composite had a compressive strength at 1% deformation of 6.4×10^3 p.s.i. at room temperature and 1.7×10^3 p.s.i. at 300° F. (150° C.).

Example 5

Aluminum granules (Al-Meg 100 P) 512 parts by weight were coated according to the procedures set out in Example 4. A ⅛ inch (0.3 cm.) thick nickel electroformed shell (about 3 inches (7.5 cm.) in diameter and having a circular base) was placed in a 5 x 6 x 2 inch (12.5 x 15 x 5 cm.) wooden box and coated with an adhesive made of the binder mixture of Example 4. Coated aluminum granules were tamped around and in back of the electroform to a depth of ¾ inch (1.9 cm.). A curved cooling coil made from ¼ inch (0.6 cm.) O.D. copper tubing with compression fittings was also coated with the adhesive binder and placed in the box. More coated granules were added and tamped until the box was full. After removal of the box, the backing composite was cured at 275° F. (135° C.) for 90 minutes, placed in a pan of warm 275° F. (135° C.) epichlorohydrin-bisphenol A epoxy resin ("Epon" 828) and then allowed to saturate the composite. The backing composite was then placed in a clean pan and cured overnight at 275° F. (135° C.) and then 8 hours at 350° F. (180° C.).

Example 6

A mixed metal system was prepared from a mixture made of 725 parts by weight of steel granules (Ancorsteel 1000), 256 parts of aluminum granules (Al-Meg 100P), 51 parts of the binder mixture described in Example 4, 0.9 parts of hexakisimidazole nickel (II) chloride, and 12.3 parts of dicyandiamide. The mixture was tamped and filled as described in Example 4. The composite was cured overnight at 275° F. (135° C.), overnight at 350° F. (180° C.) and for 24 hours at 400° F. (200° C.). The resulting piece exhibited a great degree of hardness, toughness, and structural stability.

Example 7

Preparation of a high temperature system.

An electroformed shell of nickel and copper, having a thickness of about 8 mm. was placed in a wooden box with a steel bottom having the dimensions 6 x 5 x 2 inches (15 x 12.5 x 5 cm.). A mixture was made of 1450 parts of steel granules (Ancorsteel 1000), 0.9 parts of hexakisimidazole nickel (II) chloride, 12.3 parts of dicyandiamide, and 51 parts of a binder. The binder was formulated as 75 parts of epichlorohydrin-bisphenol A epoxy resin ("Epon" 828), 25 parts of an epoxy novolac resin having an equivalent weight of 160–180 commercially available from Dow Chemical Company, 0.6 part of the nickel complex, and 7.3 parts of dicyandiamide. The electroform was painted with a small amount of the binder and placed face down on the steel plate. The mixture was tamped around and behind the electroform.

The wooden sides of the box were removed and the backed-up electroform shell placed in an oven to harden at 275° F. (135° C.). After 90 minutes the metal aggregate was hard and porous and the composite was placed on pieces of loose non-woven bonded nylon material in an aluminum tray. Prewarmed epoxy novolac resin (heated to 135° C.) was poured into the tray and the backing allowed to become saturated with the resin at 275° F. (135° C.) for 2½ hours by the aforementioned wicking process. After being removed from the tray and wiped off, the backing was cured at 275° F. (135° C.) overnight, 350° F. (180° C.) for 8 hours, and 400° F. (200° C.) overnight. The resulting piece exhibited a considerable amount of hardness and toughness. The backing material had a compressive strength at 1% deformation of 5.3×10^3 p.s.i. at room temperature and 4.0×10^3 p.s.i. at 150° C.

Example 8

A mixture of 512 parts of aluminum granules (Al-Meg 100P), 51 parts of the binder prepared according to the procedure set out in Example 7, and 0.9 part of hexakisimidazole nickel (II) chloride were used to back an electroformed shell according to the procedure set out in Example 7. A cooling line made from ⅜ inch O.D. copper tubing with compression fittings at each end was coated with the binder formulation and placed about one inch in back of the electroformed shell. The material cured at 1 hour at a temperature of 275° F. (135° C.) after which it was allowed to become saturated with epoxy novolac resin of Example 7. The entire system was cured for 14 hours at 275° F. (135° C.) 8 hours at 350° F. (180° C.), overnight at 400° F. (200° C.). The resulting backing system exhibited excellent strength and durability properties. The backing had a compressive strength at 1% deformation of 5.3×10^3 p.s.i. at room temperature and 3.6×10^3 p.s.i. at 150° C.

Example 9

The binder mixture was made of 7.3 parts by weight of finely ground dicyandiamide, 0.6 part of hexakisimidazole nickel (II) chloride, and 100 parts of a bisphenol A-epichlorohydrin epoxy resin ("Epon" 828). A mixture of 300 parts of this binder, 3450 parts of a copper powder commercially available under the tradename "Amax" electrolytic copper powder type A from U.S. Metal Refining Co., 36.9 parts of dicyandiamide, and 2.7 parts of hexakisimidazole nickel (II) chloride. It was tamped into a 5 x 6 x 2 inch (12.5 x 15 x 5 cm.) wooden box and cured for 90 minutes at a temperature of 275° F. (135° C.) before being placed on pieces of loose nonwoven bonded nylon fibers in a pan containing bisphenol A-epichlorohydrin epoxy resin ("Epon" 828) and allowed to fill the porous structure of the metal aggregate.

The filled system was then cured overnight at 275° F. (135° C.), 8 hours at 350° F., (180° C.), and overnight at 400° F. (200° C.). The cured system had a Barcol 935 hardness of 88 and otherwise exhibited hardness and strength propetries similar to the systems prepared in the above examples.

What is claimed is:

1. A method for backing a metal shell comprising the steps of:
   (a) placing a suitable amount of a pliable, workable, thermoconductive particulate metal aggregate on the back surface of said shell, said aggregate comprising metal particles having an average size of between 60 and 400 mesh, from 0.2 to 18 parts by weight of a heat-activated thermosetting resin binder per 100 parts by weight of metal particles, and a catalyst for a heat-activated thermosetting resin;
   (b) compacting said metal aggregate into relatively close contact around said shell;
   (c) heating the metal aggregate at a temperature of from about 100° C. to 200° C. until cured, forming a self-sustaining porous structure backing said shell;
   (d) saturating said porous structure with a heat-activated thermosetting resin; and
   (e) curing said resin at a temperature of from about 250 to 400° F. for about ½ to 48 hours.

2. The method of claim 1 wherein said binder comprises a heat activated thermosetting epoxy resin and the catalyst for said resin and the resin of step (d) is a combination of dicyandiamide and hexakisimidazole nickel (II) chloride.

3. The method of claim 2 wherein said metal particles are selected from the group consisting of iron, aluminum and copper.

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