

- [54] **METHOD OF FABRICATING COMPOSITE OR ENCAPSULATED ARTICLES**
- [75] **Inventor:** Susan L. Oldham, Long Beach, Calif.
- [73] **Assignee:** Hughes Aircraft Company, Los Angeles, Calif.
- [21] **Appl. No.:** 770,917
- [22] **Filed:** Aug. 30, 1985

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 608,614, May 9, 1984, abandoned.
- [51] **Int. Cl.⁴** B29C 39/10; B29C 39/24; B29C 39/42
- [52] **U.S. Cl.** 264/102; 264/500; 264/548; 264/272.11; 264/272.13; 264/331.12; 264/331.16
- [58] **Field of Search** 264/102, 500, 548, 272.11, 264/272.13, 331.12, 331.16

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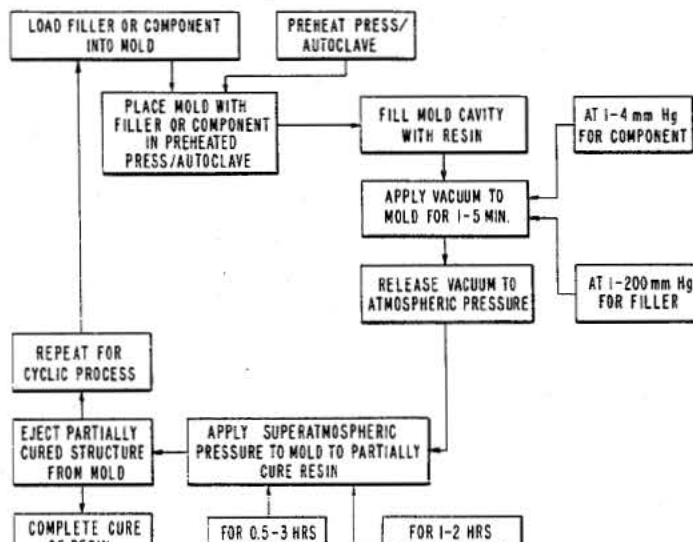
Primary Examiner—Philip Anderson
Attorney, Agent, or Firm—M. E. Lachman; A. W. Karambelas

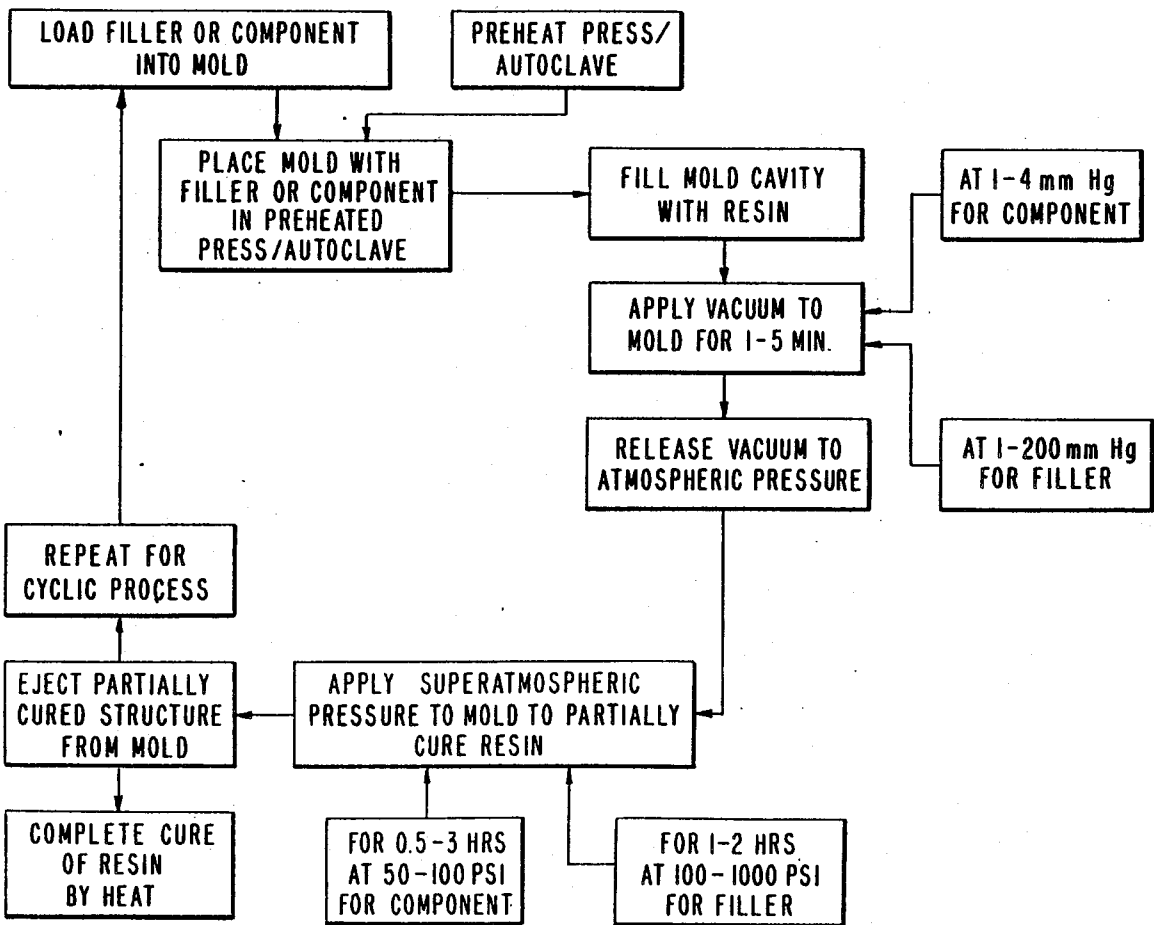
[57] **ABSTRACT**

A method for encapsulating an electrical component or forming a resin based filler reinforced composite article which comprises providing a rigid mold having a cavity and an opening in one surface of the mold connected to the cavity, and a chamber in which the mold is placed for applying heat and varying pressure to the mold contents. The chamber is preheated to the curing temperature of the resin and is maintained at this temperature. The component or filler is loaded into the mold cavity and the mold is placed in the preheated chamber. Then the mold cavity is filled with a low viscosity heat curable, thermosetting resin such as an epoxy resin. Next, the mold cavity is evacuated to a subatmospheric pressure to impose a vacuum on the mold to impregnate the component or filler with the resin, degas the mold cavity contents, and expand any voids in the resin. The vacuum is released to atmospheric pressure to collapse any gas bubbles remaining in the mold contents. Then, a superatmospheric pressure is applied to the mold to burst any gas bubbles and cause the resin to compact and encapsulate the component or filler. The temperature and the superatmospheric pressure are maintained for a time sufficient to partially cure the resin and form a unitary structure which can be ejected from the mold. The ejected structure is then subjected to further heating to completely cure the resin. The method may be performed in cyclic fashion to form continuously in sequence a plurality of encapsulated components or composite articles.

Composite articles so formed are useful as structures, such as antenna waveguides, for space applications. Electrical components encapsulated by the process of the present invention have high voltage resistance.

25 Claims, 1 Drawing Figure





METHOD OF FABRICATING COMPOSITE OR ENCAPSULATED ARTICLES

This application is a continuation-in-part of patent application Ser. No. 608,614, filed May 9, 1984 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of fabricating lightweight, composite materials, as well as to a method of encapsulating electrical components to provide increased resistance to electrical stress. More particularly with regard to the former, this invention relates to a method of preparing epoxy resin based filler reinforced composite members exhibiting improved performance characteristics such as reduced weight and thermal expansion coefficients.

2. Description of the Prior Art

The successful utilization of filler reinforced composites in aerospace applications, such as antenna fabrication, imposes several important requirements on the filler reinforced composite. A feature of primary importance is that the composite have strength and dimensional stability characteristics (e.g. a low linear coefficient of thermal expansion) calculated to withstand the rigors of environmental temperature cycling.

In addition, for complex structures such as antennae, structures molded from epoxy resin based composites are preferred over metal structures since the composite can be molded directly, thereby avoiding costly machining operations. Glass and graphite fiber reinforced epoxy based composites are finding growing use in aerospace applications because of their high strength-to-weight ratio. These composite materials, because of their relatively low coefficient of thermal expansion (α), find wide application in structural components such as antenna used in space. Such materials are described, for example, by H. S. Katz and J. V. Milewski, in the book entitled "Handbook of Fillers and Reinforcements for Plastics," Chapter 19, Hollow Spherical Fillers, Van Nostrand Reinhold Company, New York, 1978, pages 326 to 330. In a space environment where one face of the structural member is subjected to constant sunlight while the opposite face of the member is in darkness, the face exposed to sunlight is heated considerably more than the opposed face. Such non-uniform heating causes uneven expansions of the structural members making up the antenna with the resultant distortion of the antenna from its desired shape. Thus, aerospace use requires that some critical antenna structural components exhibit a dimensional stability over a ten year lifetime in the operating range of 54° to 115° F. (12° to 46° C.) and have densities equal to or less than 0.9 grams/cm³. When the structural components are electroplated with a metal layer to provide, for example, utility as an electromagnetic interference (EMI) shielding or a conductive path in an antenna waveguide structure, the metal coating layer must also withstand thermal cycling in the extremes of the space environment without loss of adhesion.

Furthermore, in another area of current interest, it is recognized that high voltage power supplies and pulse forming networks for aerospace use must meet high standards of performance and reliability for long periods under extreme environmental conditions. To assure trouble-free operation of components within the assem-

bly, the components, such as magnetic coils, capacitors, diode arrays, transformers, stator generators, and resistor networks, are commonly encapsulated with synthetic resin materials to provide electrical insulation to the components. Such encapsulants for electrical and electronic components are described, for example, in the book by Katz et al, previously referenced, at page 327. The conventional encapsulation processes used are batch processes, i.e., processes which are not in continuous production, but rather are carried out on a limited number of items at one time.

Because of their excellent adhesion, good mechanical, humidity and chemical properties, epoxy resins are used extensively both as encapsulants for electronic components and in combination with glass and graphite fibers and microballoons in the manufacture of the previously discussed high performance reinforced composite structures, such as antenna. The encapsulated article or filled epoxy resin composite is molded using conventional molding techniques, such as compression molding or transfer molding, in which the required materials including the resin are loaded into a mold, and curing of the resin is effected under increased pressure, with the load being applied directly to the mold by the action of a contained media, namely a gas for pneumatic pressure or a liquid for hydraulic pressure. In compression molding, the pressure is applied to a platen which then presses on an opening in the mold which communicates with the mold cavity. In transfer molding, the pressure is applied to a transfer ram which then presses on the mold contents through the opening in the mold. Problems encountered in the molding of the epoxy systems and especially filled epoxy resin systems have limited the use of these resins as encapsulants, as well as for the fabrication of structural composites useful in a space environment. In molding filler reinforced composites, the problem is aggravated due to the fact that high filler loadings, e.g. 40 to 60 percent by weight, are required in the epoxy resin based composite structures to achieve the required low α value and corresponding high dimensional stability. Thus, when using transfer molding or batch encapsulation techniques, the use of high filler contents in the epoxy system impedes adequate resin flow into the mold because of the high viscosity of such a resin system. This, in turn, results in varying filler orientations and distributions within the geometrical areas in the complex structures being molded, with a resultant loss in α and ultimate dimensional stability, as well as erratic adhesion of metal layers plated on the surfaces of the structure. This problem is further aggravated when hollow particulates such as glass or graphite microballoons are used as filler materials since the high viscosity filled epoxy resin may have unpredictable densities due to microballoon fractures and voids in the filler/resin mixture. Further, high viscosity resins are unable to penetrate and impregnate the filler to provide homogenous systems.

In addition, with regard to encapsulants for electrical components, state-of-the-art heat curable epoxy resin systems used as encapsulating resins have the disadvantage that the viscosity of the resin at working temperatures, e.g. 100° C., (75° F.), are quite high, e.g., 500 centipoise (cps), and such resins are not intruded completely into crevices present in the electrical component. Thus, the insulation is often incomplete and defective.

It is the primary object of the present invention to provide a method for molding filled thermosetting res-

ins such as polyimides, bismaleimides, and particularly epoxy resins, to provide resin based filler reinforced composite structural components which have a low coefficient of thermal expansion rendering the composite relatively insensitive to environmental temperature cycling while possessing desirable performance properties of low density, high strength, and amenability to the plating of adherent metal films and coatings.

It is a further object of the present invention to provide a method for encapsulating electrical components or devices to provide components or devices having improved reliability and improved electrical properties.

Another object of the present invention is to provide methods of the type described above which can be performed in cyclic and continuous fashion.

SUMMARY OF THE INVENTION

The above objectives are achieved in accordance with the present invention, which is directed to a method for encapsulating an electrical component or forming a resin based filler reinforced composite article which comprises providing a rigid mold having a cavity and an opening in one surface of the mold connected to the cavity, and a chamber in which the mold is placed for applying heat and varying pressure to the mold contents. The chamber is preheated to the curing temperature of the resin and is maintained at this temperature. The component or filler is loaded into the mold cavity and the mold is placed in the preheated chamber. Then the mold cavity is filled with a low viscosity heat curable, thermosetting resin such as an epoxy resin. Next, the mold cavity is evacuated to a subatmospheric pressure to impose a vacuum on the mold to impregnate the component or filler with the resin, degas the mold cavity contents, and expand any voids in the resin. The vacuum is released to atmospheric pressure to collapse any gas bubbles remaining in the mold contents. Then, a superatmospheric pressure is applied to the mold to burst any gas bubbles and cause the resin to compact and encapsulate the component or filler. The temperature and the superatmospheric pressure are maintained for a time sufficient to partially cure the resin and form a unitary structure which can be ejected from the mold. The ejected structure is then subjected to further heating to completely cure the resin. The method may be performed in cyclic fashion to form continuously in sequence a plurality of encapsulated components or composite articles.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE presents a flow chart representation of the process steps for two preferred embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The heat curable, thermosetting resins employed in the molding compositions used in this invention can be any low-viscosity, liquid heat curable resin. Preferred heat curable resins are low-viscosity epoxy resins having 1,2 epoxy groups or mixtures of such resins, and include cycloaliphatic epoxy resins, such as the glycidyl ethers of polyphenols, epoxy resins, liquid bisphenol-A diglycidyl ether epoxy resins (such as that sold under trademark as EPON 815 by Shell Chemical Company). In addition, other resin compositions, such as polyimide compositions and bismaleimide compositions, having appropriate viscosities, gel times, green strengths, and

dielectric properties may be used in the practice of the present invention.

Epoxy resins preferred in the practice of the method of the present invention are polyglycidyl aromatic amines, i.e. N-glycidyl amino compounds conventionally prepared by reacting a halohydrin such as epichlorohydrin with an amine. Examples of those preferred polyglycidyl aromatic amines include diglycidyl aniline, diglycidyl orthotoluidine and tetraglycidyl metaxylylene diamine.

The epoxy resins are admixed with polyfunctional curing agents to provide heat curable epoxy resins which are cross-linkable at a moderate temperature, e.g. about 100° C., to form thermoset articles. Suitable polyfunctional curing agents include polycarboxylic acid anhydrides of which nadic methyl anhydride (i.e. a maleic anhydride adduct of methyl cyclopentadiene), methyl tetrahydrophthalic anhydride and methyl hexahydrophthalic anhydride are exemplary. Polycarboxylic acid anhydride compounds are preferred curing agents for polyglycidyl aromatic amine based epoxy resins. In preparing heat curable, thermosetting epoxy resin compositions, the epoxy resin is mixed with the curing agent in proportions from about 0.6 to about 1.0 of the stoichiometric proportions.

Cure accelerators can be employed in preparing the heat curable epoxy resin formulations, and in particular when using polycarboxylic acid anhydrides as curing agents, the preferred accelerators include substituted imidazoles such as 2-ethyl-4-methyl imidazole and organometallic compounds such as stannous octoate, cobalt octoate, and dibutyl tin dilaurate.

Preferred epoxy resin compositions useful in the practice of the present invention and comprising the above-described preferred epoxy resin, curing agent, and accelerator are disclosed in my U.S. Pat. No. 4,559,272, assigned to the present assignee. This resin is particularly useful for providing high electric stress-resistant encapsulated components.

The term "curing" as used herein denotes the conversion of the thermosetting resin into an insoluble and infusible crosslinked product and, as a rule, with simultaneous shaping to give shaped articles.

To prepare resin based filler reinforced composite articles in accordance with one embodiment of the present invention, the epoxy resin in admixture with the curing agent and accelerator may be further mixed before curing with fillers and reinforcing agents, as for example, glass fibers, carbon fibers, graphite fibers, Kevlar fibers, ceramic fibers such as Al₂O₃ or Al₂O₃-SiO₂, ceramic whiskers such as silicon carbide or silicon nitride, glass microballoons, carbon microballoons, phenolic microballoons, ceramic particles, or glass particles, and the mixture is loaded into the mold. However, it is preferred in the practice of the method of the present invention that the mold be prepacked with the filler, i.e. the filler is added first to the mold, followed by the addition of the heat curable resin. If the filler is premixed with the resin and then loaded into the mold, a cured composite with varying filler orientations and distributions within the different geometrical areas of the mold is produced. In the preferred embodiment of the present invention, the components of the filler, such as fibers and microballoons, are pretreated with a titanate or zirconate wetting agent and/or a silane or zirconaluminate sizing agent as discussed below and are mixed mechanically or manually to form a homogenous mixture, which is then added to the mold cavity. Next,

the mold may optionally be vibrated to promote a uniform distribution of the filler in the mold. It has been found by using packing theory that an increased volume percent solids in the resin mixture can be achieved. Packing theory is based on the concept that, since the largest particle size filler in a particular reinforcement system packs to produce the gross volume of the system, the addition of succeeding smaller particles can be done in such a way as to simply occupy the voids between the larger filler without expanding the total volume. This theory is discussed by Harry S. Katz and John V. Milewski, in the book entitled "Handbook of Fillers and Reinforcements for Plastic," Chapter 4, Packing Concepts in Utilization of Filler and Reinforcement Combinations, Van Nostrand Reinhold, 1978. The fillers used in the present invention are chosen on the basis of particle size, shape, and contribution to overall composite properties. This theory applies to the use of solid particulates as well as hollow spheres. Because of the high viscosity of such a highly loaded resin, the mixture could not flow into the mold without damaging the microspheres. To overcome this problem, the mold is pre-packed with the dry filler (i.e. a mixture of microspheres, fibers, and/or whiskers). By applying packing theory as described above, the filler can be packed at a high density and so that segregation of ingredients does not occur. The use of maximum filler loading with a very low viscosity resin and appropriate coupling agents (for good filler-matrix adhesion) results in a material which, when vacuum liquid transfer molded as described herein, provides homogenous, void-free structures.

The composite article formed in accordance with the preferred process embodiment of the present invention is referred to herein as a "fiber reinforced syntactic foam composite," which denotes a composite of a syntactic foam (i.e. a non-porous structure made by incorporating hollow spheres in a liquid resin) and reinforcing fibers dispersed throughout the syntactic foam. The composite article formed in accordance with the present invention is also referred to herein in a more general sense as a "resin based filler reinforced composite," which indicates a composite of a resin and reinforcing filler material.

The compositions of preferred mixtures of resin, fibers, and microspheres used to form fiber-reinforced syntactic foam composites in accordance with one embodiment of the present are discussed in detail in copending patent application Ser. No. 607,847 and U.S. Pat. No. 4,568,603 assigned to the present assignee. Preferred filler materials are fibers and/or whiskers of predetermined length and hollow microspheres of predetermined diameter as discussed in the above-noted copending patent applications. The fibers may be formed of graphite, glass, carbon, ceramic or polyamide, while the hollow microspheres may be formed of glass, silica, phenolic or carbon. The whiskers may be formed of such materials as metal oxides, carbides, halides or nitrides, such as silicon carbide, silicon nitride, sapphire (Al_2O_3), MgO , $MgO-Al_2O_3$, Fe_2O_3 , BeO , MoO_3 , NiO , Cr_2O_3 , ZnO , potassium titanate, or boron. The term "whiskers" is defined in Katz and Milewski, previously referenced, at pages 446-453 as "fibers grown under controlled conditions that lead to the formation of a single crystal" and having minimum length-to-diameter ratios of 10:1 and maximal cross-sectional areas of 7.9×10^{-5} in.² (corresponding to circular cross-sections of 0.010 in. diameter). Typical whiskers

have a diameter of less than one micrometer and high aspect ratios. The internal and surface perfection of whiskers gives them high toughness and nonfriability in handling, high tensile strengths and Young's moduli as compared to fiberglass or polycrystalline fibers. For the discussion herein unless otherwise noted, whiskers are included in the term "fibers".

Carbon fibers useful as reinforcing agents in molding the present filler reinforced composites are high strength, high modulus fibers composed essentially of amorphous carbon but more preferably of graphite or pyrolytic graphite and generally referred to as graphite fiber. One type of graphite fiber which may be used in reinforcing the composites are HM-S graphite fibers (available from the Courtaulds Company of the United Kingdom) which have the following dimensions and physical properties:

Modulus: 50 million psi
(stress/strain): (3.45×10^{11}) pascals
Length: 50 micrometers (μ)
Density: 1.83 gm/cm³
Diameter: 8 micrometers

Whiskers which are particularly useful in practicing the present invention comprise silicon carbide. One type of such whiskers are Silar SC-9 (available from ARCO Metals Company, a Division of Atlantic Richfield Company) which have the following dimensions and physical properties:

Modulus: 70 to 120 million psi
(stress/strain): (4.83×10^{11}) to 8.27×10^{11} pascals
Length: 10 to 80 micrometers
Diameter: 0.8 micrometers
Density: 3.2 gm/cm³

Glass microballoons or hollow microspheres used as fillers are composed essentially of silica and typical glass microballoons which may be used have the following dimensions and physical properties:

Diameter: 10-200 μ
Density: 0.15 to 0.32 gm/cm²

Carbon microballoons are composed primarily of thin-walled carbon balloons and typical ones which may be used have the following dimensions and physical properties:

Diameter: 40 μ
Density: 0.32 gm/cm³

As is known to the art, wetting of fillers, such as graphite fibers, by epoxy resins can be facilitated by the use of titanate wetting agents such as di(dioctylpyrophosphato)ethylene titanate (KR238M available from Kenrich Petrochemical Company of Bayonne, N.J.), tetra(2,2-diallyloxymethyl 1-butoxy) titanium di(tridecyl) phosphite (KR55 available from Kenrich) or titanium di(cumylphenylate)oxyacetate (KR134S, available from Kenrich), whereby compaction and resin penetration of the filler by the resin is enhanced by the presence of such agents, and the use of such sizing and wetting agents represents a preferred practice of the present invention. Coupling agents, such as silanes and zirconaluminates, may be used in conjunction with the titanates to achieve a chemical bond between the organic resin and the inorganic fillers/fibers. The sizing and wetting agents may be dissolved in the mixture of resin, microspheres and fibers; or, preferably they are applied to a mixture of the microspheres and fibers in predetermined proportions by immersing this mixture in a solution of the sizing agent, followed by filtering and drying the mixture to provide a pretreated microsphere/fiber mixture.

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