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METHOD AND APPARATUS FOR DEGASSING LIQUIDS

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2 Sheets-Sheet 1

Fig. 1.

Fig. 1a.

11

Fig. 1b.

12

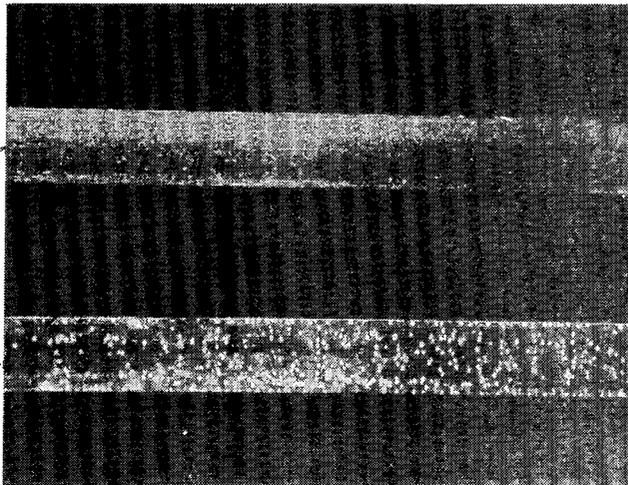
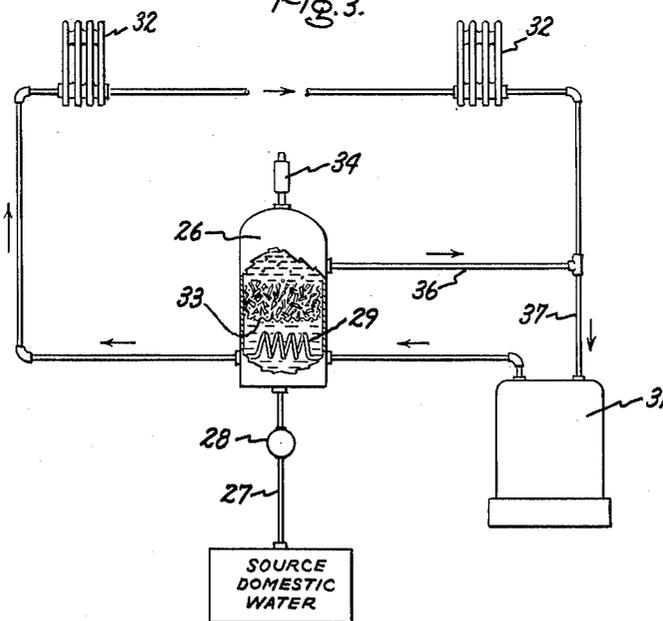


Fig. 3.



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Fig. 2a.

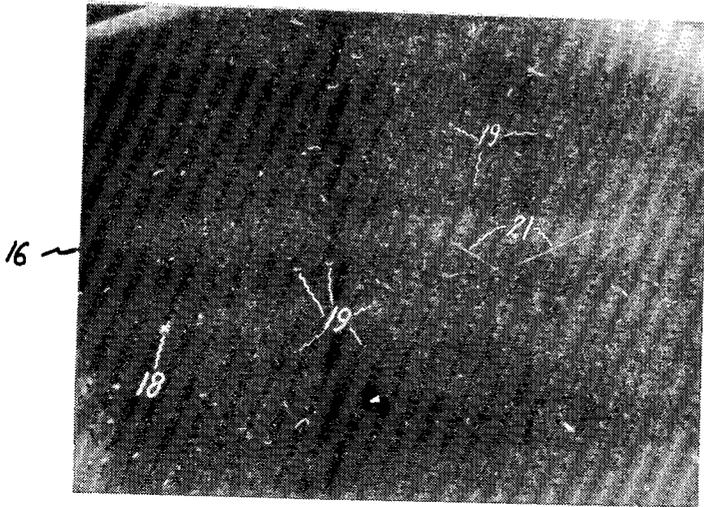
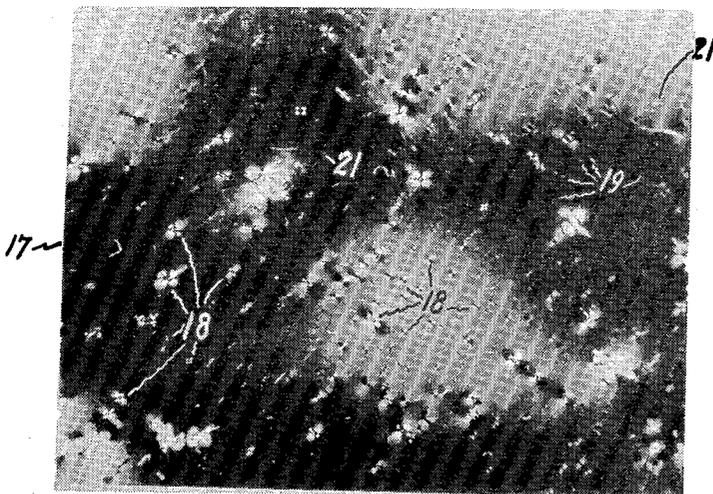


Fig. 2b.



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**METHOD AND APPARATUS FOR
DEGASSING LIQUIDS**

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6 Claims. (Cl. 328—233)

ABSTRACT OF THE DISCLOSURE

A process for removing residual gases from a liquid by immersing in the liquid during the degassing thereof at reduced pressure a quantity of solid material, whose surface is inert, which has a low surface energy and which has pores or roughness of microscopic size. The low surface energy materials disclosed and for which criteria are recited resist complete wetting by the liquid being degassed and thereby provide a source of preferred sites where bubbles of gas dissolved in the liquid will nucleate, grow and be transported by buoyant force or agitation to the free surface of the liquid for removal. Directions for the selection and preparation of the low surface energy degassing material are set forth and the degassing of epoxy resin as well as an apparatus improvement for the degassing of make-up water for a domestic hot water heating system are described.

This invention is directed to an improved method for removing residual gases from liquids, for example, viscous resins used in the preparation of polymeric castings, such as epoxy resin castings.

The presence of voids in potting compounds or in resin castings is undesirable not only because they induce local centers of high stress, which can cause failure under thermal cycling, but also because such voids can have a detrimental effect on electrical properties of the resin material. Likewise, removal of gases from dielectric fluids is most important to the proper operation and longevity of such fluids. It has been shown, for example, that voids located along the core of an epoxy resin insulator used for high voltage transmission lines lower the electrical breakdown strength of the insulator as the result of electrical discharge that takes place in the voids. Such discharge causes degradation of the solid resin material, e.g., by causing local hot spots and failure by corona fatigue. As a result the presence of gases or voids, if known or suspected, will limit the voltage to which a dielectric fluid or insulator can be exposed, that is, the voltage applied must be kept below the corona starting voltage to prevent electrical discharge and consequent degradation.

By conventional techniques, resins being prepared for casting are degassed by holding the resin in the liquid state at a reduced pressure (and in some cases at an elevated temperature). Under such a condition the equilibrium solubility of any given gas in liquid is reduced. However, little, if any, bubble nucleation occurs during such conventional degassing and the rate of degassing is controlled by the rate of molecular diffusion of the gaseous species through the resin. Rapid agitation is commonly used to bring fluid from the interior of the bulk of the liquid to the surface but the degassing time required even with agitation is quite long in high viscosity resins. As a practical matter, the degassing time is often limited by the fact that the components of the resin have already been mixed and are proceeding to a state of cure. In any

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event, it is of considerable economical advantage to be able to reduce the degassing time by a significant amount.

Although this invention is described with respect to liquid resins, it is equally applicable to the degassing of dielectric fluids or other liquids in which dissolved gases pose a problem.

Voids in a resin casting prepared with a resin material which has been inadequately degassed occur, because after the resin is poured into the mold, bubbles form at nucleation sites on the surface of the mold, and are trapped as the resin cures. The use of certain mold release agents, as for example, polytetrafluoroethylene, increases this tendency for nucleation at the surface of the mold and, since the use of such mold release agents is relatively common, it becomes increasingly important to insure that a rapid, thorough degassing may be effected prior to the casting step. In the absence of such effective degassing procedures, defective castings result in considerable material waste, when the presence of such voids may be detected upon examination. In those cases in which the presence of the voids escapes detection the cost of replacement after the defect has been encountered during operation is even more expensive.

At the temperature and pressure used for conventional degassing procedures in the preparation of epoxy resin for making resin castings, for example, the rate of degassing is so slow that the resin becomes supersaturated with gas compared to the equilibrium concentration at ambient pressures and temperatures. Relatively few bubbles (which would quickly rise and be removed from the surface) form in such supersaturated resin, because in the absence of nucleation sites bubble formation is subject to the statistical laws of homogeneous nucleation. Experiments in systems free of nucleation sites have shown that tremendous supersaturations, superheats, or negative pressures are necessary before bubbles can be generated in a liquid under such conditions. However, in systems where heterogeneous nucleation can occur, such as occurs in nucleate boiling, the driving force required to produce bubbles is relatively small. This behavior is well-illustrated in copending application S.N. 348,727—Gaertner, filed Mar. 2, 1964 and assigned to the assignee of this invention.

It is therefore a prime object of this invention to provide a substantially improved degassing process for the preparation of liquids substantially free of entrained gas.

It is another object of this invention to provide an improved process for the degassing of viscous liquid resins.

It is still another object of this invention to provide a process for insuring the preparation of more effective dielectric fluids, e.g. for transformers.

A further object of this invention is the provision of an improved system for obviating undesirable noise and decreased heat transfer by the collection of air in hot water heating systems.

These and other objects may be attained by immersing in the liquid during the degassing thereof at reduced pressure a quantity of material, whose surface is inert, has a low surface energy and has pores or roughness of microscopic size, which low surface energy material resists complete wetting by the liquid being degassed and thereby provides a source of preferred sites where bubbles of gas dissolved in the liquid will nucleate, grow and be transported by buoyant force or agitation to the free surface of the liquid for removal.

As described herein a "pore" may be inherently present in the surface or may be artificially created as, for exam-

ple, by abrading with fine emery cloth. Dimensionally a pore is considered microscopic if the width is microscopic and the length and/or depth are macroscopic as in the case of a scratch in the surface. In the case of irregularly shaped pores these are considered microscopic if the dimensions require magnification of at least about 50× to be distinguished.

The exact nature of this invention as well as other objects and advantages thereof will be readily apparent from consideration of the following specification relating to the annexed drawing in which:

FIGS. 1a and 1b are photographic reproductions of two castings prepared under identical conditions except that the resin used to make one of the castings was degassed in the presence of a material immersed therein whose surface has a low surface energy and pores of microscopic size in accordance with this invention.

FIGS. 2a and 2b are photographs taken with polarized light at a magnification of 2× showing representative sections of two 1/8 inch thick epoxy slabs one of which was degassed with a material immersed therein, the surface of which has a low surface energy and pores or roughness of microscopic dimension, but otherwise prepared in an identical manner; and

FIG. 3 is a diagram schematically illustrating a degassing device for hot water heating systems employing the teachings of this invention.

FIGS. 1a and 1b are photographic representations of two epoxy resin bars 11, 12 measuring approximately about 1/4 inch in width, 1/2 inch in depth and 6 inches in length. These bars 11, 12 were degassed at reduced pressures and cast under identical conditions, except that the resin used to cast bar 11 (FIG. 1a) was degassed at reduced pressure having immersed therein 1/8 inch cube pellets of polytetrafluoroethylene with microscopically porous surfaces. The epoxy resin used to make bar 12, which served as a control, was degassed in the same manner as for bar 11, but without the use of the polytetrafluoroethylene pellets. The effect of the immersion of the low surface energy material in the liquid is clearly shown by the relative freedom of the bar 11 from voids.

Another indication of the extent to which the immersion of a nucleation promoter in liquid resin material during the degassing thereof is effective is shown in FIGS. 2a and 2b. Identical epoxy resin material was employed to produce two 1/8 inch thick slab castings 16, 17. Casting 16 (FIG. 2a) was prepared by degassing the liquid resin having immersed therein a concentration of 1/8 inch cube pellets of polytetrafluoroethylene with microporous surfaces.

Casting 17 (FIG. 2b) was prepared in identical manner (degassing under reduced pressure), but without using the pellets. Although neither casting contained macroscopic voids at the time the photographs were made, these photographs, which were taken in polarized light, show in casting 17 in particular many imperfections 18, which appear (under polarized light) to resemble Maltese crosses. These non-crystalline imperfections 18, which are practically invisible in normal illumination were present in much smaller numbers in castings degassed in the presence of the bubble nucleation material. Tests have established that imperfections 18 are spheroidal in shape and have a lower index of refraction than the surrounding resin material. Based upon these facts it has been concluded that these imperfections are aggregates of microscopic bubbles, not yet large enough for spontaneous growth. Small flecks 19 are dust deposits and lines 21 are scratches and are not to be confused with the imperfections 18, which are unmistakable under polarized light.

Although polytetrafluoroethylene has been recited as a preferred low surface energy material other materials may be used having similar qualities of inertness and surfaces having microporosity depending on the liquid being degassed. The following table sets forth a list of materials

exemplary of those useful in the practice of this invention:

Table 1.—Material

- (1) Polystyrene
- (2) Phenol-formaldehyde resin
- (3) Organopolysiloxane adhesive ¹
- (4) Polyethylene
- (5) Isomerized hydrocarbon rubber ²
- (6) Polychlorotrifluoroethylene
- (7) 80:20 copolymer of polytetrafluoroethylene and polychlorotrifluoroethylene
- (8) 60:40 copolymer of polytetrafluoroethylene and polychlorotrifluoroethylene
- (9) Polyethylene terephthalate
- (10) Bis-phenol A polycarbonate (Lexan resin manufactured by General Electric Company)

In general, suitable degassing agents for the practice of this invention are materials selected with the following criteria:

- (a) the material should have a contact wetting angle with the liquid being degassed of greater than about 80°,
- (b) the surface of the material in contact with the liquid being degassed shall have a large concentration of pores of microscopic size, i.e. width and depth thereof,
- (c) the surface shall be insoluble in the liquid being degassed,
- (d) the surface shall be chemically and thermally stable,
- (e) the material shall have a high enough melting point not to soften at operating temperatures and
- (f) if the material is applied as a coating to a substrate, it must adhere well thereto.

As noted hereinabove the surface of the low surface energy material should be microporous and it may be necessary to abrade the surface of certain materials otherwise suitable to insure surface roughness providing interstices to trap microscopic pockets of gas, which serve as nuclei for the formation of bubbles. For this reason, if polytetrafluoroethylene sheet stock is used as the degassing medium abrasion with emery paper or similar abrading material is necessary. Usually, if polytetrafluoroethylene is deposited as a coating on an inert base, the necessary porous, low surface energy surface is readily provided for degassing.

The larger the ratio of surface area of degassing medium to volume of liquid being degassed, the shorter will be the time required for degassing. Combining agitation with the use of the degassing agents of this invention helps still more to decrease degassing time by bringing fresh gas-containing liquid in contact with the degassing agent and mechanically removing bubbles adhering to the degassing material. Such bubbles are then free to be transported to the free surface of the liquid and removed through the vacuum system.

Another factor found to be important is the size of the individual pieces of degassing agent. In the degassing of water, for example, it was found that polytetrafluoroethylene powder functions very poorly as a degassing agent, whereas pieces of polytetrafluoroethylene larger than about 1/16 inch in diameter perform quite well. Apparently the very finely divided degassing medium does not possess suitable porosity.

The particular manner in which the degassing material is immersed in the liquid being degassed is not critical so long as a large amount of surface area of degassing agent is provided. Pellets of the material can be strung on a wire like beads or can be contained in a wire basket possess suitable porosity.

Non-wettability of the surface of the degassing material is another way of describing the material as having low

¹ As described in U.S. 2,643,964. Other organopolysiloxanes, as for instance those mentioned in U.S. 2,258,218-2,258,222 and U.S. 2,448,756 may also be employed.

² As described in U.S. 1,605,180 and 1,744,880.

surface energy and this behavior is important so that the microscopic pores do not fill with liquid wheerupon the surface would become deactivated.

Tests have established that the use of the process of this invention does not deleteriously effect the mechanical and electrical properties of the liquid being degassed or of solids cast therefrom (in the case of potting compounds or resin castings).

Where necessary, even more conventional liquids, as for example water, are more effectively degassed by the application of the teachings of this invention. One example of such a useful application is illustrated in FIG. 3, wherein a domestic hot water heating system is schematically represented. Therein make-up water being charged into a hot water heating system enters degassing tank 26 from a source of domestic water via line 27 and automatic charging valve 28. In tank 26 the incoming makeup water is heated with heat transfer coil 29 through which hot water circulates from furnace 31 to radiators 32. Within tank 26 a concentration of degassing agent is disposed as in basket 33. As air bubbles nucleate and grow in tank 26 on the surfaces of the degassing material, these bubbles rise through the water to accumulate at the top of the tank 26. This accumulated air leaves tank 26 via the automatic vent 34 and the degassed make-up water enters the system via pipe 36 leading into the cold water return line 37. In this manner the collection of air in pockets in the heating system by liberation from the water in the system is greatly reduced or eliminated and the noise and decreased heat transfer occasioned by such air accumulations are avoided.

The principle of this invention and the advantages secured thereby have been described using exemplary degassing (or bubble nucleation) agents and fluids to be degassed. Obvious modifications of these parameters and of the means for exposing fluids to the degassing agents may be made without departing from the spirit and scope of the invention as set forth in the appended claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. In a process for degassing liquids contained in bulk by the application of a pressure below atmospheric to the free surface of the bulk liquid, the improvement comprising the step of exposing the bulk liquid during degassing

to contact with a concentration of solid inert bubble nucleation material, said bubble nucleation material having surface area of a low surface energy penetrated by pores of microscopic dimension.

2. The improvement substantially as recited in claim 1 wherein the bubble nucleation material has extensive surface area of microscopically porous polytetrafluoroethylene.

3. The improvement substantially as recited in claim 2 wherein the bubble nucleation material is in particulate form larger than about $\frac{1}{16}$ inch in diameter.

4. In a hot water heating system wherein hot water circulates to at least one radiator from a boiler for distribution of heat therefrom to the ambient atmosphere and wherein make-up water is supplied to the system as required from a supply tank, the improvement comprising a perforated container containing a concentration of solid inert bubble nucleation material located in the supply tank in contact with the make-up water, the surface area of which material has a low surface energy and is penetrated by pores of microscopic dimension.

5. The improvement substantially as recited in claim 4 wherein the inert material has extensive surface area of microscopically porous polytetrafluoroethylene.

6. The improvement substantially as recited in claim 5 wherein the inert material is in particulate form larger than about $\frac{1}{16}$ inch in diameter.

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