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(54) **Cultured onyx products and methods therefor.**

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US-A-3 396 067
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Description

This invention relates to a method of manufacturing a shaped structure having a cultured onyx, cultured marble or other mineral appearing surface. In the ensuing description, cultured onyx will be primarily referred to as an ideal illustrative embodiment of the practice of the invention.

A large market exists for tubs, pullmans, tile, tub enclosures, plaques, sculptures, and other shaped products having the uniquely attractive, nearly nacreous layered translucent depth of onyx, an optical effect heightened by the presence of subtly or strongly contrasting, diffuse striations of visually differentiable localized zones of concentration of contrastant having indistinct mergence with the surrounding matrix in three dimensions. In general this market has been supplied with products based on a polyester resin matrix extended and optically modified with a filler comprising tiny glass particles, referred to as frit.

In United States Patent 3,396,067 to K. A. Schafer the simulation of naturally occurring oynx in a wide variety of useful products is taught to be achievable by blending polyester resins filled with one or another fillers, e.g. silicas and more particularly glass frit in a specific manner to interdistribute essentially alike polyester phases and thereafter simultaneously curing all the polyester to hardness with one phase frozen in another. The disadvantages of the technique taught include obtention of a nonpolishable surface and excess weight since glass is more than twice as heavy as polyester resin and so hard relative to the polyester that surface polishing produces a multiplicity of discrete islands too small to really be seen and too numerous to count but which in the aggregate appear as a surface dullness which increases with polishing rather than diminishing. Thus those in the art having only the Schafer process and product have resorted to gel coats, surface coverings of clear resin, which are polished appearing, to conceal the true surface and thus beautify the product. Unfortunately, this expedient brings its own problems, since gel coats may be rubbed through by too vigorous cleaning, which may occur in a washbasin, for example. Too they are typically water vapor pervious, and over time, in use, they permit water seepage into the underlying structure which is manifested by a separation of the gel coat from the substrate, and the resultant appearance of an air pocket or bubble behind the gel coat which is disruptive of the light reflection and spoils the product aesthetics.

A further example of a synthetic onyx material is disclosed in U.S. 4343752. In that patent a manufactured article such as a sink is prepared by spraying a mold with a gel coat, drying the coat, applying a mixture of clear, liquid casting resin with a dual promotion catalyst mixture and then mixing the resin-catalyst mixture with a filler of fine and coarse alumina particles. A colouring material is then applied to the top surface of the matrix and depressed into the matrix so that on vibration within the mould the hardening decorative veins are formed in the article.

In U.S. 2761176 there is disclosed a method and composition for the production of speckled plastic ware. One powder is added to another and then the combined powders are compression molded. In that patent neither powder is first cured to final hardness, but since both are powders and neither is soluble in the other, patterns can be obtained. Therefore, according to the present invention there is provided a method of manufacturing a shaped structure having a cultured onyx, cultured marble, or other mineral appearing surface including preparing a liquid first hardenable synthetic organic resin, preparing a solid, particulate second visually distinguishable resin by prehardening the resin to its final desired hardness so as to be insoluble in said liquid resin and grinding to a desired particle size, combining said liquid first resin and said second solid particulate resin together in distributively commingled relation while said liquid resin is liquid and in such relative proportions as to provide an onyx, marble or other mineral simulative surface appearance, and hardening said first resin to the same hardness as said second resin to form said shaped structure. The shaped articles of the present invention preferably have the requisite surface appearance; lighter weight for reduced shipping costs; tougher surfaces against in-use degradation; uniform polishability deriving from chemical and physical property homogeneity at the surface; freedom from costly gel coats which are likely to wear or lift off from water vapor permeation; ease of shape forming into conventional as well as non conventional, artistic and aesthetic products; increased variety of visual effects through limitless variation in colour, size, uniformity of size, concentration, distribution, and patterning of the filler, colorants, and matrix relative one to the other, as compared with previously known cultured mineral products, such as cultured onyx. The shaped articles may be products such as tubs, tub enclosures, lavabos, pullmans, basins and vases, fixtures, fountains and the like which are free of internal hygroscopicity inducing agents such as glass and which thereby are impervious to humid environments or water contact and able to be free of gel coats whereby unsightly lifting of film at the product surface is avoided and the aesthetic and practical use life of the product greatly extended.

The second visually distinguishable resin typically comprises particles of resin hardened to the predetermined hardness prior to intimate combination with the continuous resin portion and which are less than about 300 μm (50 U.S. mesh) in mean average particle size diameter. The discontinuous resin portion particles preferably comprise polyester resin.

The continuous resin portion also preferably comprises polyester resin and embeds the discontinuous portion in local discontinuity and distribution defining relation. The locally discontinuous resin portion pwrticles of hardened resin may have a mean average particle size diameter less than about 180 µm (80 U.S. mesh).

Typically, the discontinuous resin portion particles comprise from about 5% to 55% of the weight of the structure.

In particularly preferred embodiments, the continuous resin portion and the discontinuous portion are each polymers of the same monomer, e.g. each polyester resin.

The structure typically also includes a colorant distinguishable within the continuous phase, e.g. dispersed nonuniformly in continuous phase. Further the discontinuous phase is typically particulate, uniformly distributed in the continuous phase, and the structure also includes a colorant nonuniformly dispersed in the continuous phase.

The invention contemplates provision of a moldable mixture hardenable into the foregoing product, i.e., a resinous mass for the production of cultured onyx, cultured marble, or like mineral product comprising visually distinguishable portions of synthetic organic resin, including a first, major weight portion defining a continuous, moldable and hardenable resin matrix, a second, minor weight portion defining a particulate, prehardened resin filler of less than about 300 µm (50 U.S. mesh) in mean average particle diameter, the second resin portion particles having discontinuous distribution in the first resin portion matrix, and a colorant visually distinguishably marking the product with randomly localized zones of distributed filler concentration, the zones having indistinct mergence with the surrounding matrix in three dimensions after mold-shaping and hardening of the matrix portion simulatively of the surface appearance of onyx, cultured marble, or like mineral.

The second resin portion typically constitues from 25% to 50% by weight of the resinous mass, and the first portion or matrix is hardenable with the filler in situ to the hardness of the filler to have both filler and matrix portions which may be polymers of the same monomer substantially equally wear resistant to polishing on the product surface.

It is a signal feature of the present invention that by virtue of the like hardness of the resin portion phases it is possible to polish the surface of the structure to a uniform gloss, without use of an overlayer of gelling resin, i.e. in gel coat free relation.

Brief description of the drawing

The invention will be further described as to an illustrative embodiment thereof in conjunction with the attached drawing, in which:

Figure 1 is a perspective view of a shaped product, namely a faucet produced in accordance with the methods of the invention, using the compositions of the invention;

Figure 2 is a view in horizontal section thereof; and

Figure 3 is a view in vertical section of a faucet handle shaped product according to the invention.

Description of the preferred embodiments

The present invention uses a resin portion as filler. The resin filler is prepared by hardening a heat or catalytically curable liquid resin, such as polyester, or other resin as described below, in bulk to form a solid body of hardened resin. The degree of hardening is not narrowly critical, with typical resin bodies being nor friable but triturable by application of grinding or abrading force. Thus a body of hardened resin is triturated to a fine powder comprised of discrete particles of generally polygonal shape, by impacting at high centrifugal speed against circularly fixed teeth under temperature conditions conductive to embrittlement of the resin body so as to facilitate erosion of the body and generation of particulate. Crushing of the resin body after freezing is effective, with the resultant lumps being further refined by high speed impact with appropriately arranged teeth, also under lowered temperature conditions where resin gumming may occur. A grind to at least 300 µm (50 U.S. mesh) mean average particle size diameter is usually required for obtaining a cultured onyx product, although other minerals having coarser, even grainy striations may be made with coarser particulate, and grinding will not have to be so fine. A mean average particle size of 180 µm (80 U.S. mesh) and below is preferred for optimum subtlety of transition from accent to background in cultured onyx. Typically the hardened resin body is coarsely divided and the coarse pieces impacted against teeth until a particulate of the desired size distribution is realized.

The particulate filler may be the color of the resin body which in a polyester resin tends to be a water white to gray in the absence of added colorant. A colorant, i.e. a material imparting a color value other than the naturally occurring color, may be added to the resin, e.g. before hardening, for example an organic or inorganic dye and/or pigment, liquid or solid powder, may be added to a slurry of the polygonal chips in uncured resin or other vehicle prior to addition of the particulate to the matrix resin. Advantageously, a masterbatch of chips may be prepared and specific colorants added as need be from time to time for product production purposes, thus to minimize inventory of colors. The use of reactive color formers on the particulate is also practical, the color being developed in situ in the product. The color may be any tone including deepened or lightened aspects of the eventual matrix color. In this connection, it is the presence of visual distinguishability through the presence of a contrast between the phases of the product that is important, not specific color contrasts. The polyester resins for example exhibit contrast between commingled phases regardless of a colorant as an additional contrastant.

The hardened filler is then mixed with the matrix material, suitably a further portion of the filler resin. Colorant to form localized concentrations of high contrast, e.g. striations, bursts, veins, whorls, umbras and the like, typical of onyx and marble is added. The mix is controllably agitated or not as desired to achieve the nonuniform, locally randomized, concentration pattern of distribution of colorant in the uniformly comixed filler and matrix. Swirling, agitating, adding from single or multiple points in thick or thin streams all have their effect on the final pattern. It is preferable to slowly combine a first mix of a given background color of liquid, nonhardened matrix and the hardened filler particulate with a second mix of another background color of liquid, nonhardened matrix resin and the hardened filler and to combine these different background color mixes with pigment or other pattern forming colorant, with careful definition of distribution, and then to add the combined mixes and colorant to the mold to be used to shape the product structure using more or less percentage of particulate filler to vary the viscosity of the combined mixes for application to the form and to determine the apparent concentration of pattern in the final product desired, more mixing reducing colorant concentration and less mixing maintaining an initial pattern of distribution. The substantially equivalent specific gravities of the filler and matrix in the invention preferred compositions give a high degree of control over distribution pattern not available where the filler for example is far heavier than the matrix, as in prior art systems.

The relative quantities of filler and matrix for achieving a cultured onyx appearance is between about 5% and 55% of filler on the total weight of the product, with the balance being matrix, colorant and any specific additives employed. Typically, colorant is added at the rate of about 0.1 to 1.5% of the total weight of the product. The term "product" herein refers to the combination of two resin phases, without regard to colorants, contrastants, extenders, and nonresin components present in a final shaped structure. This ratio again is for achieving the best appearing cultured onyx product, other mineral simulations can use other ratios, e.g. from as little as 0.5% filler to as much as 75% filler by weight, based on the weight of the product, the matrix conversely comprising from 99.5% to as little as 25% by weight of the product.

After the combined resins are placed in a suitable mold, the matrix resin is cured, by heat and/or catalysis with the filler resin in situ therein. A signal feature of the present invention is the cohardening of the matrix to the hardness of the filler or approximately so, to a degree affording a polishability to the filler and matrix phases at the product surface which is uniform across the phases. The result is that upon polishing, by sanding, buffing and/or light grinding, both phases wear, or do not wear, but do so evenly and uniformly, so that islands of relatively harder filler do not protrude, as happens with glass frit fillers, as polishing progresses. In the present products, the filler and matrix wear at the same rate, i.e. without phase differentiation where the filler and matrix are hardened to the same degree.

Molding of the combined resin phases is accomplished simultaneously with the hardening of the matrix about the prehardened filler. The final shape of the product is determined by the mold as in other molding processes.

The mold may typically define a tub or wash basin, or countertop or the like. Advantageously with the present method and products, shaped articles of increased value relative to their resin content can be formed reliable and easily. For example, faucets and handles for operating water control valves can be readily molded of the present moldable combination of hardened and unhardened resin.

With reference now to the accompanying drawing, a faucet is depicted in Figs. 1 and 2. The faucet F is shown to comprise a neck portion 16 and a base 24, the base being centrally recessed to receive a brass fitting 22 with the fitting annular shoulder 22a being embedded within the molded faucet for security of fit. A conventional threaded conduit 28 extending from household plumbing (not otherwise shown) is threaded into the faucet fitting 22 at 26. A preformed element in the form of a conduit 20 of plastic or brass extends through the faucet neck 16 defining a water passage 18 therethrough. The conduit 20 is sweated to the fitting 22 at one end and to the fitting 32 at the faucet nozzle 30. Nozzle fitting 32 is suitably molded in place and interiorly threaded at 36 to receive a conventional aerator.

The received preformed element can be any structure which leads a particular utility to the final molded product. In a faucet handle, for example, and with particular reference to Fig. 3, the knob 10 defines the handle and is provided with a central top recess 12 which receives for subsequent concealment under a hot/cold tab, a valve stem 14 through bushing 15 which is fitted in the central bore 17 of the handle.

Resins useful herein for formation of one or both of the two phases, i.e. the locally discontinuous phase and/or the continuous phase are those resins which harden to useful rigidities for use as structural products. First among such resins for onyx simulation is the polyester resin. Polyester resins are well known and amply described for example in the 1979—1980 Modern Plastics Encyclopedia. Such resins are the reaction product of a dibasic acid and a glycol, e.g. phthalic anhydride, isophthalic acid and adipic acid with one or more of propylene glycol, ethylene glycol, diethylene glycol and dipropylene glycol. Crosslinking monomers used include styrene, vinyl toluene, methyl methylmethacrylate, methyl styrene, and diallyl phthalate. Inhibitors such as quinone, hydroquinone and butyl catechol may be used. Typical catalysts for the reaction are free radial precursors, e.g. the peroxides which decompose at elevated or ambient temperatures, e.g. methyl ethyl ketone peroxide, cyclohexanone peroxide, and benzoyl peroxide, or cumene hydroperoxide, t-butyl perbenzoate, and peroctoate. Resins of less intrinsic clarity will be useful where the ultimate in translucency is not required. Accordingly such thermosetting (including room temperature cure) resins as allyls, ureas, phenolics, polyimides, epoxy, and polyurethanes, may be used in particular cases.

It is particularly preferred herein to employ different portions of the same resin as the raw material for the two distinct phases, one to be hardened and triturated, then distributed in the other portion, whereupon the second portion is the hardened, giving a two phase composite with the difference being not chemical or physical but related to from (continuous or discontinuous) and derived from the time of cure or hardening.

Example

A polyester resin was hardened by the application of moderate temperature, ca. 80°C (175 degrees F) for a period of 60 minutes in a simple rectangular mold to provide a body of hardened resin weighing about 2.3 kg (5 pounds). The body was frozen instantly in liquid nitrogen and crushed in an impact mill into pieces approximatley 6.4×6.4 mm (1/4 by 1/4 inches) on a side, and these pieces fed centrifugally against a series of teeth in a circular path to reduce the pieces in after sufficient passes to polyhedras chips of nonsymmetrical shape and of a mean average particle size of 180 µm (80 U.S. mesh) screen. The particles were combined with a color pigment in a quantity of liquid uncured resin of the same type. A further portion of this polyester resin was combined with particulate, and without the addition of any colorant. These mixtures were then combined to achieve a ratio of 48% particulate by weight relative to the nonhardened resin. Colorant in the form of liquid pigment was distributively added to the combined resins, and a swirl pattern established. The combined resin portions and swirled colorant therein were cast in a faucet mold and the resin matrix as had been the particulate to achieve like hardness. The preformed element, e.g. the conduit and fittings is inserted in the mold in suitably supported relation prior to cure if it is desired to have the element embedded. The part was removed from the mold and lightly buffed to a high gloss. The onyx like translucent striation and veining was striking, both in depth and diffusion below the article surface and in its feathering off into indistinct mergence with the surrounding matrix beyond its locus of concentration, the interposition of solid filler through the matrix liquid serving to give the localized concentrations of striation defining colorant an imperfection of line and edge definition which heightens the comparability to naturally occurring striated, color marked minerals.

Water vapor exposure did not affect the product surface on testing. The absence of a gel coat on the product is to be noted. Heretofore high gloss was dependent on application of a glossy film former onto the molded product, because buffing highlighted the harder filler as it eroded the softer matrix. With the present product, however, the filler and matrix phases are of substantially coequal hardness. The problems of film lift off and poor abrasion resistance, formerly tolerated because of the need for a high gloss on the cultured onyx or cultured marble product, have been obviated.

Accordingly, the invention provides a novel product overcoming the disadvantages of previous products and opening new opportunities for the manufacture of highly attractive cultured onyx and marble products, such as the traditional tubs, pullmans, basins, water closets, lavabos, and additionally fountains, sculptures, tiles, wall decorations, faucets and handles, soap dishes and statuary.

Claims

1. A method of manufacturing a shaped structure having a cultured onyx, cultured marble, or other mineral appearing surface including preparing a liquid first hardenable synthetic organic resin, preparing a solid, particulate second visually distinguishable resin by pre-hardening the resin to its final desired hardness so as to be insoluble in said liquid resin and grinding to a desired particle size, combining said liquid first resin and said second solid particulate resin together in distributively commingled relation while said liquid resin is liquid and in such relative proportions as to provide an onyx, marble or other mineral simulative surface appearance, and hardening said first resin to the same hardness as said second resin to form said shaped structure.

2. A method according to Claim 1, including grinding said solid particulate resin to a particle size of less than about 300 micron (50 U.S. mesh) in mean average particle diameter.

3. A method according to Claim 1, including selecting polyester resin as said first resin, said second resin or as both first and second resins.

4. A method according to Claim 1, 2 or 3, including also proportioning the weight amounts of said first and second resins so that said second resin constitutes from 25% to 50% by weight of said shaped structure.

5. A method according to Claim 1, 2, 3 or 4, including also depositing said combined first and second resins into a structure defining form prior to hardening of said first resin, and thereafter hardening said first resin with said second resin distributively disposed therein.

6. The method according to Claim 1, 2, 3, 4 or 5, including selecting a polyester resin as said first and second resin.

Patentansprüche

1. Verfahren zum Herstellen eines Formgebildes, welches das äußere Erscheinungsbild von gewachsenem Onyx, gewachsenem Marmor oder einem anderen Mineral vermittelt, bei welchem ein flüssiger, erster, härtbarer, synthetischer, organischer Harz zubereitet wird, ein feststofförmiger, partikelförmiger, zweiter, visuell unterscheidbarer Harz dadurch zubereitet wird, daß der Harz zu seiner endgültig gewünschten Härte der-

art vorgehärtet wird, daß er in dem flüssigen Harz unlösbar ist und daß er auf eine gewünschte Teilchengröße zerkleinert wird, bei dem der flüssige, erste Harz und der zweite, feststofförmige, partikelförmige Harz mit einer Vermischungsverteilungszuordnung und in solchen relativen Anteilen kombiniert werden, daß man das äußere Erscheinungsbild von Onyx, Marmor oder einem anderen Mineral nachbildet, und bei dem der erste Harz auf die gleiche Härte wie der zweite Harz zur Bildung des Formgebildes ausgehärtet wird.

2. Verfahren nach Anspruch 1, bei welchem der feststofförmige, partikelförmige Harz auf eine Teilchengröße von kleiner als etwa 300 µm (50 US mesh) als mittlerer Teilchendurchmesser zerkleinert wird.

3. Verfahren nach Anspruch 1, bei dem Polyesterharz als erster Harz oder als zweiter Harz oder als erster und zweiter Harz gewählt wird.

4. Verfahren nach Anspruch 1, 2 oder 3, bei welchem die Gewichtsmengen der ersten und zweiten Harze derart zugemessen werden, daß der zweite Harz 25 Gew.-% bis 50 Gew.-% des Formgebildes ausmacht.

5. Verfahren nach Anspruch 1, 2, 3 oder 4, dadurch gekennzeichnet, daß die kombinierten ersten und zweiten Harze auch in ein die Form bestimmendes Gebilde vor dem Härten des ersten Harzes eingelagert wird und daß dann anschließend der erste Harz mit dem zweiten Harz in darin verteilt vorliegender Form gehärtet wird.

6. Verfahren nach Anspruch 1, 2, 3, 4 oder 5, bei dem ein Polyesterharz als erster und zweiter Harz gewählt wird.

Revendications

1. Procédé de fabrication d'une structure profilée munie d'une surface présentant un aspect d'onyx de marbre ou autre minéral procédé caractérisé en ce qu'il consiste à préparer une première résine organique synthétique liquide durcissable, à préparer une seconde résine en particules solides pouvant se distinguer visuellement, en faisant pré-durcir cette résine jusqu'à sa dureté finale voulue de façon qu'elle soit insoluble dans la résine liquide et en la broyant pour obtenir la taille de particules voulue, à combiner la première résine liquide et la seconde résine en particules en les mélangeant distributivement pendant que la résine liquide est encore liquide, et dans des proportions relatives permettant d'obtenir un aspect de surface simulant l'onyx, le marbre ou autre minéral, et à faire durcir la première résine jusqu'à la même dureté que la seconde résine pour former la structure profilée.

2. Procédé selon la revendication 1, caractérisé en ce qu'il comprend le broyage de la seconde résine en particules jusqu'à une taille de particules de moins d'environ 300 micromètres de diamètre moyen (maille USA 50).

3. Procédé selon la revendication 1, caractérisé en ce qu'il comprend le choix d'une résine polyester pour constituer la première résine, la seconde résine ou à la fois la première résine et la seconde résine.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce qu'il comprend en outre le dosage des proportions en poids des première et seconde résine de façon que la seconde résine constitue de 25% à 50% en poids de la structure profilée.

5. Procédé selon l'une quelconques des revendications 1 à 4, caractérisé en ce qu'il consiste en outre à placer les première et seconde résine combinée dans une forme de définition de la structure avant de faire durcir la première résine, puis à faire durcir ensuite la première résine contenant la seconde résine dans celle-ci.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce qu'il comprend le choix d'une résine polyester pour constituer les première et seconde résine.

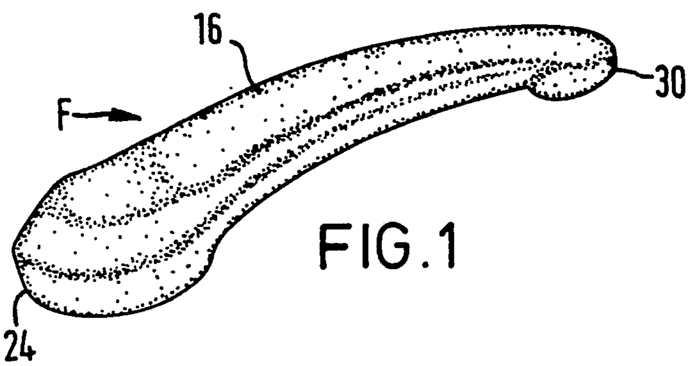

FIG.1

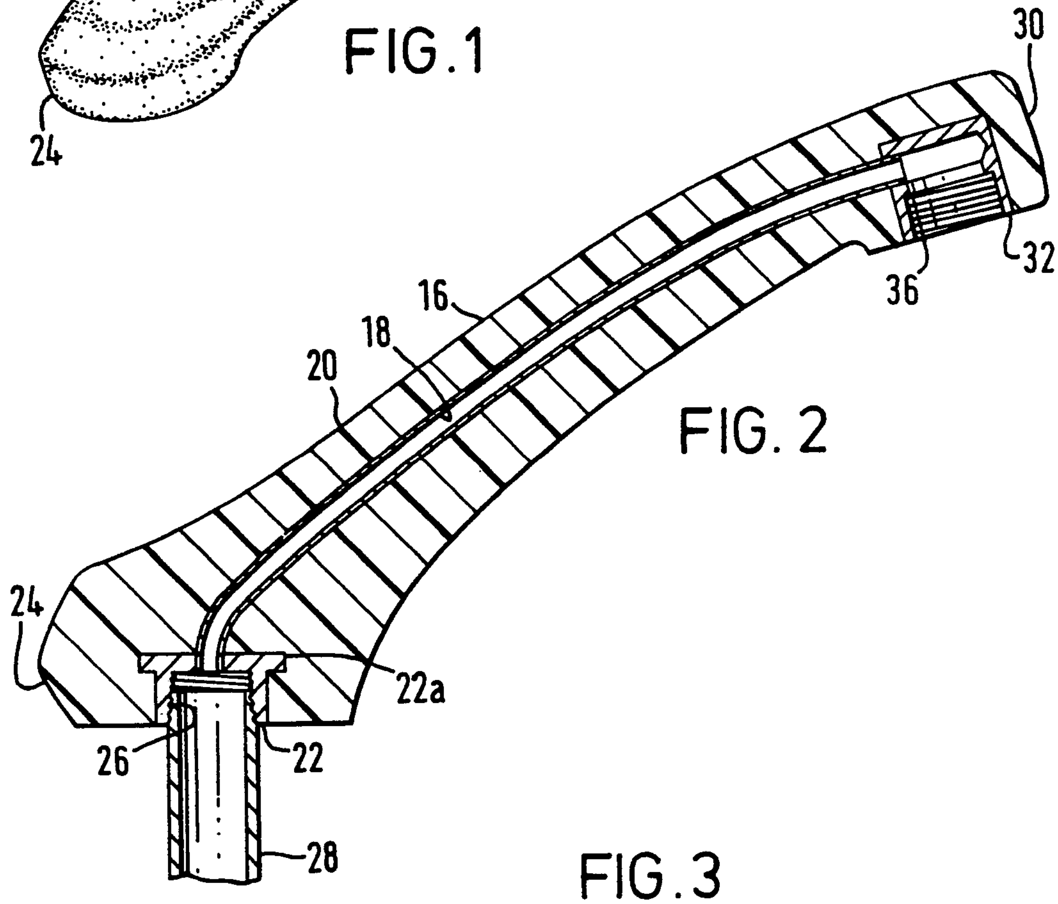

FIG. 2

FIG.3