

- [54] **PEDICURE PROSTHESIS FOR THE METATARSAL ARCH OF THE FOOT**
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- [73] Assignee: **Amos N. Johnson**, Garland, N.C.
- [22] Filed: **Oct. 30, 1973**
- [21] Appl. No.: **411,099**

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 165,610, July 23, 1971, Pat. No. 3,782,390.
- [52] U.S. Cl. **128/595; 128/90; 264/45; 264/222; 264/DIG. 30**
- [51] Int. Cl.² **A61F 5/14**
- [58] Field of Search **128/595, 90, 89; 264/222, 264/45, DIG. 30**

[56] References Cited

UNITED STATES PATENTS

2,119,590	6/1938	MacDonald	128/595
2,616,418	11/1952	Eberl	128/90
2,952,082	9/1960	Murray	128/595
3,089,486	5/1963	Pike	128/90
3,121,430	2/1964	O'Reilly	128/595
3,257,742	6/1966	Feinberg	36/44
3,373,741	3/1968	Hill et al.	128/90

3,572,330	3/1971	Gander	128/90
3,613,675	10/1971	Larsen et al.	128/90

Primary Examiner—Richard A. Gaudet
Assistant Examiner—J. Yasko
Attorney, Agent, or Firm—Christen & Sabol

[57] ABSTRACT

A support for the metatarsal arch of the foot is formed by injection of a self-curing non-foamable fluid material into the arch support enclosure. This fluid material automatically cures into a rigid support or prosthesis for the arch of the foot. This polymerizable material is normally contained in either a insert under the foot or by a balloon-like material, in either case the polymerizable material is pumped or injected into the resulting enclosure. The same method can be used to form in situ prosthesis casts for any part of the body, that is, to form splints, braces, etc., contoured directly to the portion of the human body for which it is designed to lend support. The self-curing material is preferably a cross-linkable prepolymerized material which includes an initiator, and the self-curing is achieved by the application of mild temperatures, i.e., not greater than 120°F. Also, the self-curing can be achieved by the application of actinic radiation.

21 Claims, 5 Drawing Figures

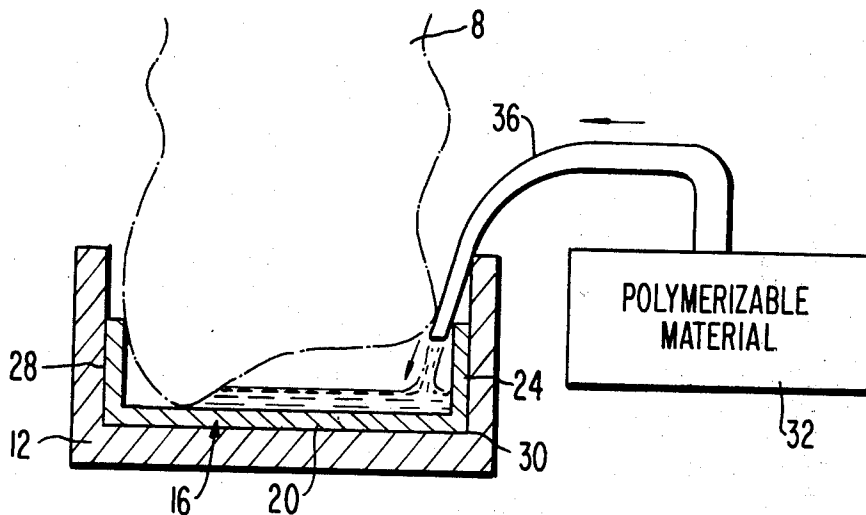


FIG. 1

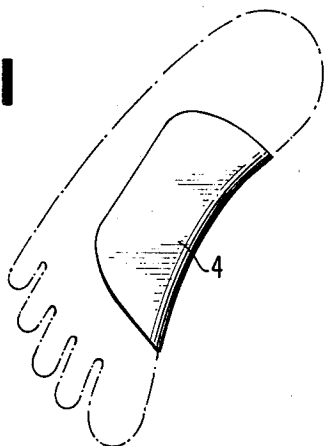


FIG. 2

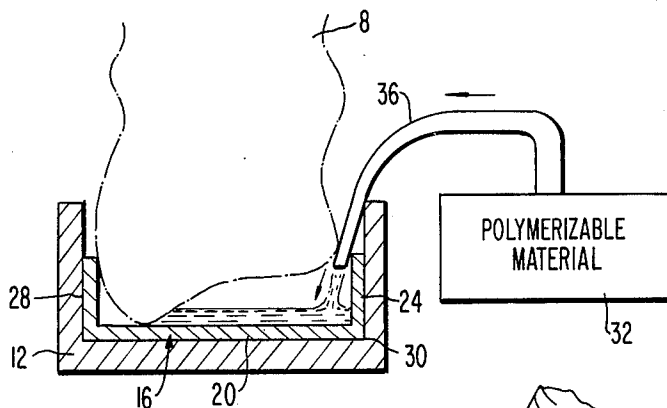


FIG. 3

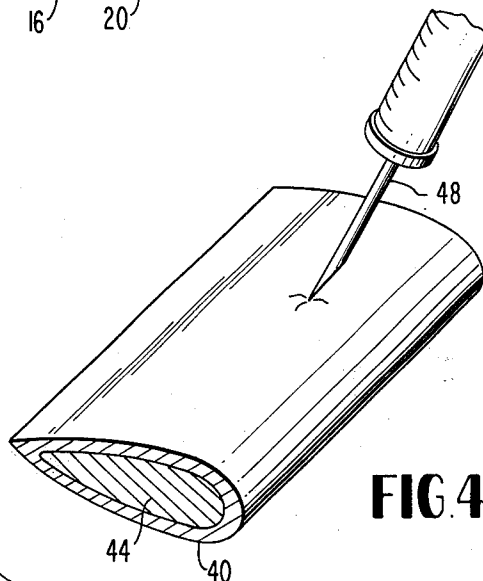
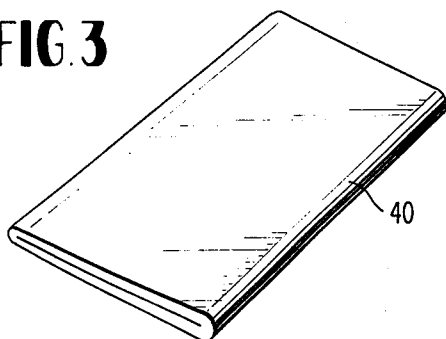


FIG. 4

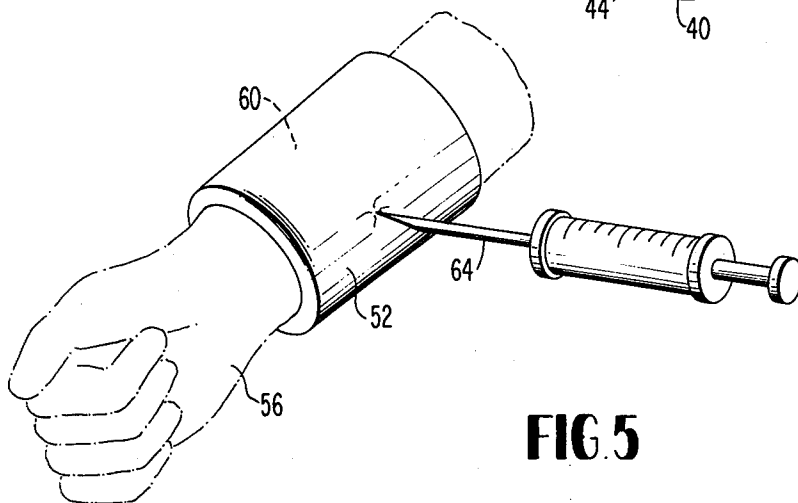


FIG. 5

PEDICURE PROSTHESIS FOR THE METATARSAL ARCH OF THE FOOT

This is a continuation-in-part of U.S. Ser. No. 165,610, filed on July 23, 1971 now U.S. Pat. No. 3,782,390.

PRIOR ART

Foamed thermoplastic material used as prosthesis are known.

U.S. Pat. No. 3,257,742 shows a soft readily deformable foot support for shoes. The support has a plastic or putty-like consistency and is a foot support that is readily impressionable in response to pressure exerted thereon by the foot. After the foot pressure is removed, the support returns to its original shape. The support is essentially a cured epoxy resin or linear polybutadiene that has these characteristics, and an outer encompassing layer, such as, leather, at col. 3, lines 73 to 74, the uncured resins are stated to be flowable so that they take the shape of the container into which they are poured. This patent does not disclose in situ curing in a shoe to set up a permanent foot support that is tailor molded in effect to aid each foot problem. The patent further discloses the use of a hard non-foamed prosthesis.

Likewise with U.S. Pat. No. 3,402,411 which is drawn to a ski-boot ankle support and the use of polymers which lend themselves to ready molding when pressure is applied with slow shape recovery.

U.S. Pat. No. 3,407,406 is directed essentially to a ski-boot and it uses a flexible, hollow material filled with a substance which holds its shape a lone time or until an outside pressure is exerted. The patent does not disclose a non-foamable prosthesis which is prepared from a self-curing polymerizable material.

U.S. Pat. No. 3,089,486 discloses using a flexible bandage impregnated with a curable, monomer-treated, polymer to form a cast. The monomer can be a methacrylate monomer, i.e., methyl methacrylate monomer. The polymer can be a methacrylate polymer, such as, polymerized methyl methacrylate. The monomer that is added also contains a promoter; and the polymer is plasticized and contains a polymerization catalyst. The polymer is plasticized with "honey" — it can also contain a secondary plasticizer (to stabilize the honey, etc.). High percentages of honey are used. The patent calls the honey an "essential constituent" and is credited with enabling the curing to take place at room temperature. The patent states that there have been prior attempts to use methacrylate polymers and methacrylate monomers, but such attempts have been unacceptable to the art. In the patent system, the methacrylate polymer is placed on the flexible bandage and dried and then the liquefied admixture of methacrylate monomer, promoter, etc., are added to the methacrylate monomer. The patent states that the methacrylate polymer and methacrylate monomer cure at low temperatures. Maximum curing temperatures of 101° to 108°C. are shown — see Table III. Curing can be accelerated by applying heat with an infra-red element. The patent states that a protective barrier is first applied to the injured body member "in order to protect the member from skin irritating fumes and/or seepage from the monomer component." The protective barrier normally would involve the unsatisfactory procedure of wrapping a strip of material several times

around the arm, with the constant danger of skin damage from fumes or seepage. A tubular sheath can be used but such involves the possibility of irritating folds developing as the curable resin impregnated webbing is wrapped around the body member. The patent speaks of removal of the protective layer by cutting the cast and then bending the cast back together. The patent states that a cushion layer can be used between the cast and the skin. Application of the curable resin impregnated bandage is also unsatisfactory. It is wet, messy and gloves must be used to handle it. If it touches anyone's skin, there can be skin irritation or damage.

U.S. Pat. No. 3,215,137 involves a cast bandage scheme that cures at a low temperature, but it suffers from many of the above disadvantages. The patent bases its invention on the use of certain special acetate diluents, the purpose being to reduce the heat let off by the polymerizations (which are strongly exothermic). The monomers are certain polyhydric alcohol esters of specific dimethyl acrylates. A powdered polymer or other filler is used. The curable resin composition is impregnated on gauze, with the numerous problems therewith arising when the impregnated gauze is used to form a cast.

U.S. Pat. No. 3,032,033 uses an air- or non-cured liquid resin, but does not specify what it is. Such resin is used on fiber glass cloth; an inner sponge rubber liner is used.

U.S. Pat. No. 3,630,194 discloses an orthopedic cast which starts with a flexible fabric carrier supporting a dry cast-forming composition comprised of at least 9 percent of particular solid, water-soluble vinyl monomers. The fabric is immersed in water containing a polymerization initiator for the vinyl monomer. The water should be at least 110°F., and preferably is 120° to 130°F. Care has to be taken in order to avoid contact with the skin or else buffers may have to be used. The requirement of using a wet fabric is messy and dangerous to one's skin and health. Also, there is the problem of removal of the water after hardening of the vinyl monomer.

Cast have been made from web wrappings which are impregnated with a photocurable resin. The curing is done by exposure to actinic radiation, to produce a rigid cast. Such systems are essentially impossible to use in preparing shoe prosthesis. Such impregnated web wrappings generally contain soft underlying layer, and other protective and cushion-type layers. The impregnated web wrappings are used to allow dispersion of heat during the curing step and air circulation during use of the cast. In one particular system, a polypropylene stockinette is placed over the skin, then a polypropylene web wrap is placed over the polypropylene stockinette to cushion bony prominences; a webbed fiber glass impregnated with a specific UV sensitive plastic resin is applied over the web wrap, and the resin is hardened by a 3-minute cure under a UV lamp. This system is marketed under the tradename "Lightcast II."

Ultrasonic curable resins have also been used.

The various references cited in this prior art section have a number of disadvantages and negative teachings which are not dealt with herein due to space conditions.

Attention is drawn to U.S. Pat. Nos. 3,674,021, 3,375,822, 3,373,741, 2,952,082, 2,119,590, 3,048,169, 3,325,919, 3,293,663, 3,067,431,

3,121,430, 3,631,854, 3,585,639, 3,477,968,
2,086,242, 3,613,675, 3,669,708, 3,618,599,
3,421,501, 3,566,487, 3,415,243 and 3,656,475.

BROAD DESCRIPTION OF THIS INVENTION

The invention involves a process for preparing a prosthesis for supporting or restraining a part of the body. The process, broadly, involves placing a prosthesis enclosure on the affected portion of the body; placing a fluid, curable, non-foamable material in the prosthesis enclosure; and curing in situ the fluid curable material to form a rigid cured non-foamed material which conforms to the shape of the affected portion of the body.

Preferably a self-curing material is used, and preferably such utilizes a prepolymer scheme. The most preferred fluid self-curing material is polymethyl methacrylate dissolved in monomeric methyl methacrylate (1:1 weight ratio), and the material contains about 0.1 percent of an acyl peroxide as a catalyst (initiator).

In one embodiment, the prosthesis enclosure is first placed in a shoe, wherein the affected part of the body is the metatarsal arch of a foot and wherein the prosthesis enclosure is placed on the affected portion of the body by placing the foot in the shoe. Preferably, pressure is placed on or applied to the fluid self-curing material before it completely cures so that the fluid self-curing material takes the shape of the metatarsal arch. The pressure can be applied by the weight of the body being shifted onto the foot. One sub-embodiment involves a prosthesis enclosure which is a sealed envelope with at least its top surface being elastic. In that sub-embodiment the fluid self-curing material is placed in the prosthesis enclosure by piercing a side of the prosthesis enclosure with an elongated hollow tube device and force injecting the fluid self-curing material through the elongated hollow tube device into the prosthesis enclosure. The hollow tube device is removed after the fluid self-curing material is placed in the prosthesis enclosure and the side of the prosthesis enclosure is rapidly sealed. Preferably the region of the side of the prosthesis enclosure, which is pierced by the hollow tube device, is self-sealing when the hollow tube device is removed.

In another sub-embodiment, the preferred embodiment of the invention, the prosthesis enclosure is a rigid insert that is placed on or affixed to the insole of the shoe. The insert comprises: a flat plate that extends across the width of the insole and extends lengthwise at least across the metatarsal arch of the foot; a low side wall on the side away from the metatarsal arch; and a high side wall which completely covers the arch when the foot is inserted into the shoe. The foot serves as the top of the prosthesis enclosure. The fluid self-curing material is placed in the prosthesis enclosure by means of a tube inserted between the high side wall and the foot. The tube is rapidly removed after the fluid-curing material is placed in the prosthesis enclosure.

In still another sub-embodiment of the invention, a cast is placed over the prosthesis enclosure before the fluid self-curing material is placed in the prosthesis enclosure. This sub-embodiment can be used whenever a cast is used, for example, with broken limbs.

The invention also involves the prosthesis for supporting or restraining a part of the body. The prosthesis includes a prosthesis enclosure on the affected part of the body and a rigid, polymerized, non-foamed mate-

rial, within the prosthesis enclosure, which conforms to the shape of the effected portion of the body. The prosthesis can be one where the prosthesis enclosure is located between the affected part of the body and a cast.

The prosthesis can be one where the prosthesis enclosure is located on the insole of a shoe where the metatarsal arch of a foot is located. This latter prosthesis can be one where the prosthesis enclosure is a sealed enclosure. Or, preferably, this latter prosthesis can be one where the prosthesis enclosure is a rigid insert that is placed on or affixed to the insole of the shoe. The insert comprises a flat plate that extends across the width of the insole and extends lengthwise at least across the metatarsal arch of the foot; a low side wall on the side away from the metatarsal arch; and a high side wall on the side of the metatarsal arch which completely covers the arch when the foot is inserted in the shoe. The foot serves as the top of the prosthesis enclosure.

This invention also involves the use of resins or polymers which are cured or polymerized by exposure to actinic radiation.

One advantage of actinic radiation (e.g., U.V. light) curing systems is that it does not require the use of heat. Also, a catalyst does not have to be added to the curable resin material before it is placed in the prosthesis enclosure (although accelerators and/or catalysts can be used).

This invention also involves the use of resins or polymers which are cured or polymerized by exposure to ultrasonic energy.

This invention forms rigid, physiologically inert, integral devices.

The prosthesis, when used as a cast for broken bones, must be rigid (once cured) in order to maintain the bones in proper position throughout the healing process. In other instances, it is also crucial that the prosthesis (once cured) must be rigid, and not have any significant cold flow.

When using this invention, the surgeon, too, can begin at once to fix the limb in the set position, and does not have to work with a slippery, pastey, or generally messy material such as plaster-of-paris or wet curable-resin impregnated web bandages. This invention generally uses an enclosed prosthesis into which the curable-resin is placed. This keeps the monomers, prepolymers, etc., from touching the skin, thereby preventing skin irritation, skin burns, skin allergy reactions and sensitization. As curable-resin materials are used which do not give off gas or fumes, there is no pressure build up problem.

The use of resins as the prosthesis material generally means a reduction of the weight, when compared to such prosthesis materials as plaster of paris. This allows the patient to be more mobile. Most of the cured prosthesis materials of this invention have excellent X-ray transmitting properties.

A crucial feature of this invention is the use of resins or polymers which do not exceed a physiologically acceptable temperature (120°F or below) during the curing or hardening of the resin or polymer. The use of such a temperature prevents unpleasant burns and allows the patient to keep on the prosthesis during curing.

This invention can be used for casts for deformed hands (arthritis) or back braces (it is essentially impossible to properly contour steel or aluminium).

As used herein, unless otherwise specifically stated, an alkyl group contains 1 to 6 carbon atoms, an aryl group contains 6 to 18 atoms, and an alkaryl group or an aralkyl group, wherein alkyl and aryl are defined as above.

DETAILED DESCRIPTION OF THE INVENTION

The objects and advantages of the invention become apparent to those ordinarily skilled in the art in the following description of the invention as illustrated in the accompanying drawings in which:

FIG. 1 is a top view of the prosthesis of this invention; FIG. 2 is a cross sectional view of one embodiment of preparing the prosthesis;

FIG. 3 is a partial perspective view of another embodiment of this invention, namely, the balloon-like enclosure;

FIG. 4 is a partial perspective view illustrating the injection of the polymerized material into the balloon-like enclosure; and

FIG. 5 is a partial perspective view illustrating the preparation of a prosthesis which in effect is an arm cast.

FIG. 1 illustrates a rigid non-foamed arch support 4 and the transverse or metatarsal arch of the foot. FIG. 2 illustrates the embodiment of the invention where the prosthesis is produced in situ. Foot 8 is inserted into shoe 12. Shoe 12 contains prosthesis enclosure 16 which consists of base plate 20, side plates 24 and 28. Prosthesis enclosure 16 fits into the bottom of shoe 12 so that when foot 8 is inserted into shoe 12 the metatarsal arch is completely enclosed by prosthesis enclosure 16. Base plate 20 must be wide enough and long enough so that the circumference areas of the arch are in contact therewith so that a seal is formed between foot 8 and base plate 20. The bottom surface of base plate 20 can contain an adhesive to allow prosthesis enclosure 16 to adhere to the inner sole and remain in the desired position. Side plate 28 is located on the outer extremity on the foot, forming a seal by contacting the side surface of the sole. Side wall 24 is located at the inner extremity of the foot, contacts the side of the foot, and is so shaped as to form a seal with the side of the foot. Self curing material 32 is injected into the area enclosed by prosthesis enclosure 20 and foot 8. Material 32 is injected by means of tube 36, the tip of which is inserted into the enclosure between side wall 24 and foot 8 as shown in FIG. 2. Material 32 is pumped into the enclosure between foot 8 and piece 16 as shown in FIG. 2. The entire enclosure is filled up with material 32 and the tip of tube 36 is removed. Material 32 is then self polymerizable, forming in situ a non-foamable rigid prosthesis which conforms to the metatarsal arch and gives excellent support thereof. The form and shape of the metatarsal arch support prosthesis is determined by the contours of the foot of the wearer who is exerting pressure on the prosthesis as, or immediately after, the self-curing fluid system is injected (before complete curing).

Another embodiment of the invention is illustrated in FIGS. 3 and 4. Prosthesis enclosure 40 is illustrated in a deflated condition in FIG. 3. Prosthesis enclosure 40 is a completely sealed unit and is placed in the shoe in a manner so that it is under the entire metatarsal arch and surrounding foot portion. Enclosure 40 is made of a deformable material at least part of which is self-sealing after puncture by a sharp object. Any self-

sealing material may be used which is compatible with the foot and the self-curing material. While the self-sealing portion is preferred, the puncture area can be sealed by known methods such as those given in U.S.

Pat. Nos. 2,646,707 and 2,803,284 which provide means for injecting self-curing material 44 into the internal space of enclosure 40 by means of a hollow sharp pointed instrument 48. Any sharp hollow pointed instrument, such as, a hypodermic needle, can be used for puncturing enclosure 40 and force injecting self-curing material 44 into the internal space of enclosure 40 so that it may cure to form a rigid non-foamable prosthesis. The bottom surface of the arch support prosthesis may be coated with an adhesive to allow the device to be attached to the inner sole securely enough to remain in the desired position in the footwear.

FIG. 5 illustrates the universality of using this invention to form a rigid supporting conformed non-foamable prosthesis wherever any cast or similar enclosure is used on a human or animal. FIG. 5 specifically illustrates the use of the prosthesis in conjunction with cast 52 on limb 56. Cast 52 can be made of any conventional cast material, such as, plaster of Paris, or can be a relatively deformable or elastic material, such as, rubber. Between limb 56 and cast material 52, a prosthesis enclosure such as 40 in FIG. 3 is inserted and encompasses all or part of limb to illustrate this variation of this invention. Prosthesis enclosure 60 can be elongated and wrapped around limb 56 before cast 52 is applied or it can be doughnut shaped and inserted over limb 56 before cast 52 is applied. The self-curing material is injected into prosthesis enclosure 60 by means of a hypodermic needle 64. Cast 52, when it is relatively elastic or when it is rigid, acts in effect as a restraining force which causes the formed prosthesis to conform to the outline of the limb. Thus, if the limb has been broken, it is in effect a cast which is superior to any known cast. The self-curing material which is used herein should broadly be a thermoplastic or thermoset material which polymerized or cures in situ after being placed in the prosthesis enclosure, should not give off any gas during curing, should be gaseous or liquid, should have the same volume in the prepolymerized states as in the resulting polymerized state (i.e., as after curing), and which should be nontoxic or nonharmful to human or animals, particularly the effected skin area. The term self-curing material encompasses an admixture of any cross-linkable prepolymerized material and any ethylenically unsaturated monomer which does not cure to any substantial degree until the admixture is placed in the prosthesis enclosure. This encompasses curable systems which are admixed with a catalyst and immediately injected into the prosthesis enclosure.

The self-curing material can be replaced by any actinic radiation-curable material. The term actinic radiation-curable material encompasses an admixture of any cross-linkable prepolymerized material and any ethylenically unsaturated monomer which does not cure to any substantial degree until the admixture is placed in the prosthesis enclosure and exposed to actinic radiation. The curing environment and the curing material should not involve any temperature exceeding 120°F.

At least a portion of the prosthesis enclosures, such as, 40 and 60, need to be transparent or translucent (colored, white, clear or opaque) so that the actinic

radiation-curable material can be exposed to actinic radiation.

The cross-linkable prepolymerized materials are broadly unsaturated polymerizable materials which are generally conventional classes of known resins such as unsaturated polyester resins, acrylic resins and the like which that have unsaturation either in the polymer backbone or in the side groups.

The preferred cross-linkable prepolymerized materials are the poly(esters of methacrylate), and the preferred poly(ester of methacrylate) is poly(methyl methacrylate).

Any of the ethylenically unsaturated monomers listed below [(1) and (6)] can be prepolymerized to be used as the cross-linkable material.

The most preferred polyester resins are prepared by the esterification of alpha, beta-unsaturated polybasic acids, (preferably a dibasic acid) and a polyhydric alcohol (preferably a dihydric alcohols). Certain compounds of this type may be indicated generacally as follows:

—M—G—M—G—M—G, where —M— represents an unsaturated dibasic acid residue and —G— represents a dihydric alcohol residue. Modifying saturated dibasic acids may also be used in the polyester resin compositions. Representative dihydric alcohol and unsaturated polybasic acids are shown below.

In preparing unsaturated polyester which may be employed in the practice of the present invention, the alcohol component may comprise one of the group of solid polyethylene glycols designated as "Carbowax." Polyethylene glycols such as the Carbowaxes are understood to have molecular weights above 300. Those most useful for this invention have weights below 4000 and preferably are in a range of about 1000 to 2000, e.g., 1500.

Examples of dihydric alcohols are propylene glycol, ethylene glycol, trimethylene glycol, 2,2-dimethylpropanediol, 1,2-butanediol, 2,3-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,3-butanediol, pinacol, 2-methyl-2,4-pentanediol, 1,5-hexanediol, 1,8-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-hendecanediol, 1,12-dodecanediol, 1,13-tridecanediol, 1,14-tetradecanediol, 1,15-pentacanediol, 1,16-hexadecanediol, 1,18-octadecanediol, 1,24-tetracosane and 1,30-tricacontanediol. Examples of trihydric alcohols are glycerol, 1,2,3-butanetriol and 1,1,1-trihydroxymethylethane. Examples of higher polyhydric alcohols are 1-1,2,3,4-butanetetrol, tetrahydroxypentane, D-arabitol, adonitol, L-arabitol, xylitol, sorbitol, D-mannitol, o-ioditol, dulcitol, L-tatitol, styracitol, perseitol, volemitol, cellobiitol, lactitol, melibiitol and maltitol.

The acid component usually comprises an alpha, beta-ethylenically unsaturated polycarboxylic acid such as maleic, fumaric or itaconic acid, or the well-known derivatives of these polycarboxylic acids having ethylenic unsaturation in alpha-beta relation to the carboxyl group. Polybasic acids such as aconitic acid, tricarballic acid or citric acid may also be employed. A plurality of such acids may also be mixed with each other, if so desired. In many instances, it may be desirable to include a dicarboxylic acid free of ethylenic unsaturation. Examples of this latter type of dicarboxylic acid include phthalic acid or terephthalic acid, which, although they contain double bonds in the benzene

ring, do not undergo addition reaction with monomer compounds and may, therefore, be considered as being the equivalent of saturated compounds. Likewise, aliphatic dicarboxylic acids such as succinic acid, adipic acid, sebacic acid, or azelaic acid, may be substituted for a part of the alpha, beta-ethylenically unsaturated dicarboxylic acid. The proportion of the non-ethylene acid with respect to the alpha, betaethylenically unsaturated acid is susceptible of wide variation. A molecular proportion of 0.25 to 12 moles of saturation acid per mole of unsaturated acid is usually used for commercial applications. Also acid anhydrides of these dicarboxylic acids can be used instead of the dicarboxylic acids.

The cross-linked prepolymerized materials can be prepared by any conventional method. In preparing the polyester, a small excess (usually 5 or 10 percent) of the dihydric alcohol is usually employed. The conditions of the esterification reaction are those conventionally employed in preparing polyesters. For example, the mixture of the alcohol and the acid is heated in a vented container or under an inert atmosphere until the water of reaction is expelled from the system, which usually occurs in a temperature range of about 150° to 210°C. The reaction is continued until the acid value is reduced to a reasonable low point, e.g., within a range of about 5 to 50, or until the mixture becomes highly viscous or even solid when it is cooled. Usually these conditions are attained in a period of 2 to 20 hours. In any event the reaction is concluded before the product becomes infusible and insoluble because of the advanced stage of polymerization. The product is then blended with the ethylenically unsaturated monomer in such a manner as to maintain the temperature of the blend below 150°F.

The preferred ethylenically unsaturated monomers which can be used as the cross-linking agent are the esters of methacrylate and the most preferred is methyl methacrylate.

The ethylenically unsaturated monomers which can be used as the cross-linking agent may be selected from the following general list:

(1) Monoolefinic hydrocarbons, that is, monomers containing only atoms of hydrogen and carbon, such as styrene, alpha-ethyl styrene, alpha-butyl styrene, vinyl toluene and the like.

(2) Halogenated monoolefinic hydrocarbons, that is, monomers containing carbon, hydrogen and one or more halogen atoms such as alpha-chlorostyrene, alpha-bromostyrene, 2,5-dichlorostyrene, 2,5-dibromostyrene, 3,4-dichlorostyrene, 3,4-difluorostyrene, ortho-, meta and para- fluorostyrenes, 2,6-dichlorostyrene, 2,6-difluorostyrene, 3-fluoro-4-chlorostyrene, 2,4,5-trichlorostyrene, dichloromono-fluorostyrene, chloroethylene (vinyl chloride), 1,1-dichloroethylene (vinylidene chloride), bromoethylene, fluorethylene, iodoethylene, 1,1-dibromoethylene, 1,1-difluoroethylene, 1,1-diiodoethylene and the like.

(3) Esters of organic and inorganic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl caproate, vinyl enanthate, vinyl benzoate, vinyl toluate, vinyl p-chlorobenzoate, vinyl o-chlorobenzoate, vinyl m-chlorobenzoate, and similar vinyl halobenzoates, vinyl p-methoxybenzoate, vinyl o-methoxybenzoate, vinyl p-ethoxybenzoate, methyl methacrylate, ethyl methac-

rylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, heptyl methacrylate, octyl methacrylate, decyl methacrylate, methyl crotonate, ethyl crotonate, and ethyl tiglate, methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, heptyl acrylate, octyl acrylate, 3,5,5-trimethylhexyl acrylate, decyl acrylate and dodecyl acrylate, isopropenyl acetate, isopropenyl propionate, isopropenyl butyrate, isopropenyl valerate, isopropenyl caproate, isopropenyl enanthate, isopropenyl benzoate, isopropenyl p-chlorobenzoate, isopropenyl o-bromobenzoate, isopropenyl m-chlorobenzoate, isopropenyl toluene, isopropenyl alpha-chloroacetate and isopropenyl alpha-bromopropionate;

Vinyl alpha-chloroacetate, vinyl alpha-bromoacetate, vinyl alpha-chloropropionate, vinyl alpha-bromopropionate, vinyl alpha-iodopropionate, vinyl alpha-chlorobutyrate, vinyl alpha-chlorovalerate and vinyl alpha-bromovalerate;

Allyl chlorocarbonate, allyl formate, allyl acetate, allyl propionate, allyl butyrate, allyl valerate, allyl caproate, diallyl phthalate, diallyl succinate, diethylene glycol bis (allyl-carbonate) allyl 3,5,5-trimethylhexoate, allyl benzoate, allyl acrylate, allyl crotonate, allyl oleate, allyl chloroacetate, allyl trichloroacetate, allyl chloropropionate, allyl chlorovalerate, allyl lactate, allyl pyruvate, allyl aminoacetate, allyl aminoacetate, allyl acetoacetate, allyl thioacetate, diallyl-3,4,5,6,7,7-hexachloro-4-endomethylene tetrahydrophthalate, as well as methallyl ester corresponding to the above allyl esters, as well as esters from such alkenyl alcohols as beta-ethyl allyl alcohol, beta-propyl allyl alcohol, 1-buten-4-ol, 2-methyl-buten-1-ol-4, 2(2,2-dimethylpropyl)-1-buten-4-ol and 1-penten-4-ol;

Methyl alpha-chloroacrylate methyl alpha-bromoacrylate, methyl-alpha-fluoroacrylate, methyl alpha-iodoacrylate, ethyl alpha-chloroacrylate, propyl alpha-chloroacrylate, isopropyl alpha-bromoacrylate, amyl alpha-chloroacrylate, octyl alpha-chloroacrylate, 3,5,5-trimethylhexyl alpha-chloroacrylate, decyl alpha-chloroacrylate, methyl alpha-cyano acrylate, ethyl alpha-cyano acrylate, amyl alpha-cyano acrylate, amyl alpha-cyano acrylate and decyl alpha-cyano acrylate;

Dimethyl maleate, diethyl maleate, diallyl maleate, dimethyl fumarate, dimethallyl fumarate and diethyl glutaconate;

(4) Organic nitriles such as acrylonitrile, methacrylonitrile, ethacrylonitrile, crotonitrile, and the like;

(5) Acid monomers such as acrylic acid, methacrylic acid, crotonic acid, 3-butenic acid, angelic acid, tiglic acid itaconic acid, fumaric acid and the like; and

(6) Amides such as acrylamide, alpha-methyl acrylamide, N-phenyl acrylamide, N-methyl-N-phenyl acrylamide, N-methyl acrylamide and the like.

The total mols of acid constituents of the unsaturated polybasic acid (and any saturated polybasic acid) are preferably balanced stoichiometrically with the polyfunctional alcohol.

The heat curable composition of U.S. Pat. No. 3,215,137 (the pertinent portions thereof which are incorporated herein by reference) can be used in this invention.

Because of the nature of the invention, the preferred monomers are liquid compounds soluble in the cross-linkable prepolymerized material. This means that the cross-linkable prepolymerized material is a homopoly-

mer and the monomer is the same monomer from which the cross-linkable prepolymerized material is formed, because the liquid monomer is then most likely soluble in the prepolymerized material and vice versa.

Solvents can be used, but very little if any solvent should be used because of the enclosed curing (cross-linking) area used in this invention. Examples of useful solvents and diluents are: alcohols, such as, methanol (b.p. = 64°C.), ethanol (b.p. = 78°C.) isopropanol (b.p. = 80°C.), propanol (b.p. = 95°C.), n-butyl alcohol (b.p. = 118°C.), secondary butyl alcohol (b.p. = 99°C.), isobutyl alcohol (b.p. = 107°C.), and methyl isobutyl carbinol (b.p. = 131°C.); glycol ethers, such as, ethylene glycol monomethyl ether (b.p. = 125°C.), ethylene glycol monoethyl ether (b.p. = 136°C.), ethylene glycol monobutyl ether (b.p. = 171°C.), diethylene glycol monomethyl ether (b.p. = 194°C.), diethylene glycol monoethyl ether (b.p. = 195°C.) and diethylene glycol monobutyl ether (b.p. = 230°C.) ketones such as acetone (b.p. = 56°C.), methyl ethyl ketone (b.p. = 79°C.), methyl isobutyl ketone (b.p. = 115°C.) and isophones (b.p. = 207°C.); aliphatic hydrocarbons, such as hexane (b.p. = 69°C.), and heptane (b.p. = 98°C.), esters such as, ethyl acetate, amyl acetate and butyl acetate; aromatic hydrocarbons such as, benzene (b.p. = 80°C.), toluene (b.p. = 110°C.) and mixed xylene (b.p. = 275°C.); and halogenated hydrocarbons such as, chloroform, perchloroethylene, carbon tetrachloride (b.p. = 76°C.), and trichloroethylene (b.p. = 86°C.). Water, and water plus another diluent (water is usually not a solvent for organic materials) can be used, but neither is preferred. A diluent means that the carrier is not a solvent for the polymeric constituents, catalyst, etc., being used.

In general, the monomer component or components may be employed over a relatively broad range, but usually, the amount thereof upon a weight basis will be less than that of the prepolymerized material. Usually, the percentage of monomer will fall within a range of about 10 to 45 percent by weight of the total mixture of the prepolymerized material and monomer. The preferred range of monomer is about 20 to 40 percent in most instances.

The curing time of the systems varies between about 1 minute and about 24 hours. This time span depends, in part, upon the type of prepolymerized material, the monomer, the amount of catalyst, the amount of inhibitor, and so forth. The curing temperature of the resin systems varies, and preferably the resin system can be cured at room temperature (15° to 30°C.).

The curing temperature should not be so high that the wearer cannot keep his foot, etc., in the shoe when the rigid form of the prosthesis is being prepared by the curing. Also the curing time should be two hours or less for the comfort of the wearer.

As the scope of useful resin systems is extensive, the type of promoter which can be used in those systems is also extensive. A few exemplary promoters are given in the following paragraphs.

On of the promoter type which can be used in the resin system is a cobalt salt which is capable of being dissolved in the resinous composition. Suitable soluble promoters are cobalt octoate or any other higher fatty acid salt of cobalt. The amount of cobalt salt can be varied from about 0.001 to 0.3 percent of the salt calculated as dissolved metallic cobalt based on the total weight of the resin compounds, catalysts and promoter

mixture employed. On the same basis, the preferred amount of cobalt metal ranges from about 0.05 to 0.15 percent.

The vanadium promoters disclosed in U.S. Pat. No. 3,333,021 are useful.

Another promoter type material is a variety of amine-promoters. Suitable amine promoters are disclosed in U.S. Pat. No. 2,480,928. The promoters are described therein as tertiary monoamines which contain attached to hydrocarbons, nitrogen atom two functionally aliphatic radicals selected from the group consisting of alkyl hydrocarbons, hydroxy-substituted alkyl hydrocarbons and aralkyl hydrocarbons and one aromatic radical selected from the group consisting of aryl hydrocarbons, azo-substituted aryl hydrocarbons, amino-substituted aryl hydrocarbons and salts thereof. Specific examples of this class are the following: dimethylaniline, diethylaniline, di-n-propylaniline, dimethyl-p-toluidine, di-methyl-o-toluidine, dimethyl-alpha-naphthylamine, methyl benzyl aniline, p-dimethylaminoazobenzene, N,N-di-methyl-m-aminophenol, p-dimethylaminophenyl oxalate, p-dimethylaminobenzaldehyde, p-dimethylaminophenyl acetate, and p-hydroxy-N,N-di(beta hydroxyethyl)aniline. Additionally, the promoter can be a tertiary alkyl amine, a hydroxy alkyl amine or an acid salt thereof as a promoter. Exemplary of these types of promoters are diethylmethylolamine, triethylamine, triisopropylamine, trimethylamine, triisopropanolamine, ethyl diethanolamine hydrochloride and the like. Tertiary polyamines are also effective for use in the instant manner, such as for example, tetramethylbutanediamine. The amount of amine promoter useful in the practice of this invention varies between about 0.05 to 1.0 percent based on the resin compounds, catalyst and promoter. These amine promoters can be used in conjunction with the above cobalt promoters.

The resin systems of this invention (containing the monomer and the prepolymerized material) are readily cured by any conventional catalyst. The preferred catalysts are organic peroxides most preferably diacyl peroxides, and the preferred organic peroxides are acetyl peroxide and benzoyl peroxide. Other useful diacyl peroxides are caprylyl peroxide, lauroyl peroxide, decanoyl peroxide, 2,4-dichlorobenzoyl peroxide, p-chlorobenzoyl peroxide, pelargonyl peroxide and propionyl peroxide. Other useful organic peroxide catalysts include: peroxyesters, such as, tert.-butyl peroxyacetate, tert.-butyl peroxyisobutyrate, tert.-butyl peroxyvalerate, tert.-butyl peroxybenzoate, tert.-butyl peroxy (2-ethylhexanoate), 2,5-dimethyl-2,5-bis(benzoylperoxy) hexane, 2,5-dimethylhexane-2,5-diperoctoate, and di-tert.-butyl diperoxyphthalate; alkyl peroxides, such as, di-tert butyl peroxide, n-butyl-4,4-bis(tert.-butylperoxy) valerate, 2,5-dimethyl-2,5-bis (tert.-butylperoxy) and 2,5-dimethyl-2,5-bis (tert.-butylperoxy) hexyne-3; hydroperoxides, such as, tert.-butyl hydroperoxide, a-cumyl hydroperoxide and 2,3-dimethylhexane-2,5-dihydroperoxide; and ketone peroxides, such as methyl ethyl ketone peroxides, cyclohexane peroxides and bis(1-hydroxycyclohexyl) peroxide.

Preferably the catalyst is used in an amount small enough to get a fast cure without excessive heat production. Usually from 0.01 to 2 percent of catalyst, based on the total weight of the resin components, are used. Preferably about 0.1 percent of catalyst is used.

The resin systems of this invention can also contain other compatible additives, such as, dyes, reinforcing materials (asbestos, chopped glass fibers), etc. The fluid polymerizable composition can also contain compatible plasticizers, such as, di-n-butyl styryl phosphonate and dimethyl phthalate; and compatible fillers, such as, silicon dioxide, titanium dioxide, calcium carbonate, silica and carbon black. The fluid polymerizable composition can also contain a compatible conventional inhibitor.

To add structural body to the cured polymer resins, material such as styrene, vinyl toluene, α -methylstyrene, dimethylstyrene, the methyl α -methylstyrenes, α -bromostyrene, β -bromostyrene, α -chlorostyrene, β -chlorostyrene, and diallylphthalate, vinyl acetate, methyl methacrylate and divinylbenzene, can be added to the uncured polymer resins so that they can be copolymerized with the other monomer components.

By using free-radical initiator systems such as N,N-dimethyl aniline, sulfanilic acid, thiophenol, N,N-dimethyl p-toluidine, in conjunction with benzoyl peroxide, for the polymerization of acrylate esters, principally, methyl methacrylate, nearly 100 percent conversion of monomer to polymer are obtained in less than 20 minutes at temperatures of or below 120°F.

Methyl methacrylate can be polymerized in the presence of polymethyl methacrylate, using one of the above activated initiation systems, at a temperature of or below 120°F, within a reasonable time period. Preferably there is prior polymerization of a portion of the monomer in order to reduce the exotherm during the polymerization. Preferably, these polymerizations are conducted in the presence of plasticizers (e.g. 2-butoxy ethanol, carbowax) to reduce stress crazing of the solid polymer.

Polymethyl methacrylate can be prepared in the presence of a small amount of a cross-linking agent (e.g., ethylene dimethacrylate), with the polymerization being continued to just below the gel point. This polymer is then dissolved in methyl methacrylate (with or without additional cross-linking agent) and the mixture polymerized with the above activated initiation systems. The incorporation of plasticizers is desirable. This is a useful self-curing material.

In another useful self-curing scheme, copolymers of styrene and a carboxylated monomer or copolymer, e.g., methacrylic acid and polymethacrylic are prepared and cured polymers with polyvalent salts curing agents to convert the polymers into tough, rigid solids.

The self-curing resins of U.S. Pat. No. 3,215,137 can be used in this invention.

Types of useful actinic radiation are U.V. radiation, sunlight (visible light), etc.

In many cases, the main polymer component is prepolymerized, so that the curable resin material placed in the prosthesis enclosure contains a prepolymer and a cross-linkable monomer.

The ultraviolet curable resins usable in this invention include those based on the mechanisms of photocatalysts in resinous polymerization such as are obtained by photocatalytic initiation in materials having ethylenic-type unsaturation. In these materials, the initiation is of first order by double bond activation and any terminal double bonds are progressively activated. In general, the initiation is proportional to the concentration of monomer, and to the square root of light intensity.

A part of the U.V. curable resin is a monomeric ethylenically unsaturated component capable of dissolving minor amounts of a photoinitiator which is active under ultraviolet light. The use of a monomeric substance such as styrene alone is not practical because of low viscosity, high shrinkage upon polymerization, etc. For these and other reasons a higher polymeric substance such as a compatible polyester resin is combined to form a solution, which may be a solid or viscous liquid. The monomer preferably has terminal double-bond unsaturation.

Suitable polymers would include almost any of the unsaturated non-catalyzed commercial polyesters of a non-aniline type, and the monomer co-reactant of any compatible terminal ethylenic unsaturated monomer including vinyls, acrylics, allyls, and the like, such as styrene, methyl methacrylate and triallyl cyanurate. The monomer is generally used in an amount of from about 5 to 50 percent by weight of the polyester (can be a prepolymer) along with about 0.002 to 5 percent of a photoinitiator.

An example of a useful U.V.-curable resin of the above type is a polyester (prepared from phthalic anhydride, adipic acid, maleic anhydride and diethylene glycol) in admixture with triallyl cyanurate monomer, hydroquinone and azobisisobutyronitrile.

Photocurable compositions which are operable in the instant invention are those obtained by admixing polyenes or poly-enes containing two or more reactive unsaturated carbon to carbon bonds located terminally, more inwardly, or pendant from the main chain with a polythiol containing two or more thiol groups per molecule.

As a general definition, the group of polythenes includes those having a molecular weight as the range of 300 to 20,000 and a viscosity ranging from 0 to 20 million centipoises at 70°C., of the general formula:



wherein X is a member of the group consisting of



(The R groups do not have to be the same) and $\text{R}-\text{C}=\text{C}-$; is at least 2; R is independently selected from the group consisting of hydrogen, halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, aralkyl substituted aralkyl and alkyl and substituted allyl groups containing 1 to 16 carbon atoms and A is a polyvinyl organic moiety free of (1) reactive carbon to carbon unsaturation and (2) unsaturated groups in conjugation with the reactive ene or yne groups in X. Thus A may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P, or O but contains primarily carbon-carbon, carbon-oxygen or silicon-oxygen containing chain linkages without any reactive carbon to carbon unsaturation.

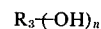
A further group of polyenes which are operable in the instant invention includes unsaturated polymers in which the double or the triple bonds occur also within the main chain of molecules. Examples of these include conventional elastomers derived primarily from diene monomers, i.e., polyisoprene, polybutadiene, styrenebutadiene rubber, isobutyleneisoprene rubber, polychloroprene, styrene-butadiene-acrylonitrile rubber, and the like, unsaturated polyesters, polyamides, and polyurethanes derived from monomers containing

reactive unsaturation, e.g., adipic acid-butene diol, 1,6-hexanediamine fumaric acid, and 2,4-tolylene diisocyanatebutenediol condensation polymers.

The polythiols useful in this invention may be simple or complex organic compounds having at least 2 pendant or terminally positioned $-\text{SH}$ functional groups per average molecule. Useful polythiols may have a viscosity range of 0 to 20 million centipoises at 70°C. as measured by a Brookfield viscometer, and usually have molecular weights in the range of 50 to 20,000, the preferable range being from 100 to 10,000.

A general formula for such compounds is $\text{R}_1-(\text{SH})_n$, where n is at least 2 and R_1 is a polyvalent organic moiety free from reactive carbon to carbon unsaturation. Thus R_1 may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P, or O but primarily contains carbon-hydrogen, carbon-oxygen, or silicon-oxygen containing chain linkages free of any reactive carbon to carbon unsaturation.

One class of polythiols which is particularly useful in connection with this invention because essentially odorless cured polyether "casts" results, are the esters of thiol-containing acids of the general formula $\text{HS}-\text{R}_2-\text{COOH}$ where R_2 is an organic moiety containing no "reactive" carbon to carbon unsaturation with polyhydroxy compounds of the general structure



where R is an organic moiety containing no "reactive carbon to carbon unsaturation" and n is 2 or greater. These compositions will react under suitable conditions to give a polythiol having the general structure $\text{R}_4-(\text{OC}-\text{R}_5-\text{SH})_n$ where R_4 and R_5 are organic moieties containing "no reactive" carbon to carbon unsaturation and n is 2 or greater.

In suitable compositions, the total combined functionality of (a) the unsaturated carbon to carbon to bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol is greater than 4.

Other ultraviolet curable systems suitable for use in the practice of this invention include, for example, the iodoformsensitized hardenable colloids disclosed in U.S. Pat. No. 1,587,274, and the metal carbonylsensitized aliphatic dieneunsaturated long chain oil systems described in U.S. Pat. No. 1,891,203. The pertinent portions of the disclosures of these patents are incorporated herein by reference. Many other ultraviolet curable polymers systems are known and are suitable for use in this invention.

The photocurable compositions have to be kept in the absence of actinic radiation, e.g., in light-impermeable packs or canisters. Many of the photocurable compositions can be stored for weeks or months under such conditions.

Any light with high enough energy per quantum or of short enough wavelength can initiate polymerization directly. For practical reasons concerned with readily available energy sources, and to provide quick polymerization after the invention prosthesis has been placed on the body member, it is desirable to use a photochemical initiator which acts as an absorbent and releases free radicals from ultraviolet light in the region of 3600 Angstroms. Convenient spectral sources containing bands of 3600 Angstrom light energy are mercury vapor discharge lamps, sunlamps, fluorescent lamps with special phosphors and sunlight. Typically, the irradiation is done with source about 12 inches from the prosthesis enclosure. Irradiation is typically done for 5 to 30 minutes.

No specific range of times for exposures to actinic radiation needed to achieve curing can be given, for every cast possesses substantial differences in thickness, etc. The exposure to actinic radiation should continue until substantially all of the resin has been converted to a solid substance in the case of casts, or until the material has become sufficiently rigid so that the patient's foot may be removed from the prosthesis device and then final curing accomplished thermally. (This is necessary because the area available for exposure to u.v. is limited in the case of the foot prosthesis and the depth of penetration by u.v. light is also limited.) As an example, the prosthesis resin may be cured under the light flux of an Ascorlux pulses xenon lamp placed 30 inches from the surface of the cast. Substantial gellation will take place under these conditions through resin coats (polyene-polythiol) of 0.030 of an inch thick with 2 minutes of exposure; thicker casts require longer times of exposure. In all exposures to actinic radiation it is necessary to protect the skin of the patient from burn and damage. This is easily done by covering the patient with sheets or blankets impenetrable to actinic radiation.

The prosthesis enclosure, into which the actinic radiation-curable material is placed, must be actinic radiation-penetrable at least over a portion of its surface. This usually means the use of a transparent or translucent material, e.g., a transparent polyethylene. A colored transparent surface can be used if a more attractive prosthesis is desired. When U.V. is used, it is preferable to use an actinic radiation-impenetrable material next to the skin in order to avoid skin burns, etc. All normal safety precautions should be used when conducting an actinic radiation cure.

The ultrasonic energy-curable systems of this invention can be any curable resin system which is curable, using ultrasonics, at or around room temperature up to about 100°F. Suitable resin systems include many of the unsaturated commercial polyesters of a nonaniline type, and the monomer correagent of any compatible terminal ethylenic unsaturated monomer including vinyls, acrylics, allyls, and the like, such as styrene, methyl methacrylate and triallyl cyanurate. The monomer is generally used in an amount which is very low in relation to the weight of the polyester.

The ultrasonic curing is achieved by exposure for a short time on the order of from a few seconds to one-half hour to ultrasonic energy. The ultrasonic energy is typically supplied by an ultrasonic transducer.

The compositions to be cured, i.e., to be converted into the solid mass of the prosthesis may include materials to increase the rigidity of the prosthesis or resin extruders such as wood flour, talc, etc. Heavier materials which are frequently used as fillers or loaders in resinous compounds, e.g., Barytes, are operative but are useful only if the weight of the prosthesis is of no importance.

The systems of this invention can be stored for long times, either separately or mixed (provided in the latter instance a catalyzed mixture must be heated or exposed to actinic radiation or ultrasonic vibrations to initiate the curing to any significant degree).

The surface of any prosthesis can be covered with a soft flexible material which makes it soft and comfortable to the skin, but such a coating material must not be of such a thickness as to consist of a cushion or like arrangement or else the rigidity feature of the invention

prosthesis will be defeated, for example, the top of a foot prosthesis may be covered with a very thin layer of leather or simulated leather. The surface of the prosthesis not contacting the skin may be adhered, for example, by gluing, to the cast or shoe to insure that the prosthesis remains securely in the desired portion in relationship to the cast or footwear and the body part.

A package to be purchased by the shoe wearer could contain one prosthesis for each foot, the injection devices and material to be injected, and detailed instructions for the mechanism to be utilized in the injection of the thermoplastic fluid into the hollow interior of the prosthesis. The actual injection of the materials into the cavity of the arch support could be done as a skilled service by the trained footwear salesman or could be done by the purchaser of the articles of footwear. First aid kits or hospital kits could be similarly packaged and sold for use when casts are applied.

One (1.0) mole percent is 0.01 mole per 100 grams of resin. Weight percent or percent by weight as used throughout this application, unless otherwise specifically stated, is defined conventionally as grams per 100 grams of resin.

The following example illustrates this invention. All percentages and parts therein are by weight, unless otherwise stated.

EXAMPLE

A foot was placed in a shoe as shown in FIG. 1, the prosthesis enclosure 16 being made of aluminum. Poly(methyl methacrylate) was dissolved in monomeric methyl methacrylate in a ratio of 1:1 by weight. The solution was then admixed with 0.1 percent by weight, based on that composition, of acetyl peroxide an initiator, and 0.1 percent by weight, based on that composition, as a polymerization promoter. The catalyzed solution was injected into the enclosed area by means of line 36. Line 36 was removed. The catalyzed solution rapidly polymerized at 120°F. and was allowed to self cure to a rigid prosthesis for the metatarsal arch of the foot. A leather covering was placed between the prosthesis and the foot.

What is claimed is:

1. The process for preparing a prosthesis for supporting or restraining a part of the body which comprises: (a) placing a fluid, curable, non-foamable material in a prosthesis enclosure, said fluid self-curable material being comprised of an admixture of a cross-linkable prepolymerized material and an ethylenically unsaturated monomer, and (b) curing in situ said fluid curable material at a temperature between 59° and 120°F. to form a rigid cured material which conforms to the shape of the affected portion of the body and which has essentially the same volume in the pre-cured states as in the cured state, there being no gas given off during the curing.

2. The process of claim 1 wherein said fluid, curable, non-foamable material is a self-curing material, and wherein said self-curing material is permitted to cure in situ.

3. The process of claim 1 wherein said prosthesis enclosure is first placed in a shoe, wherein said affected part of the body is the metatarsal arch of a foot, and wherein said prosthesis enclosure is placed on the affected portion of said body by placing said foot in said shoe.

4. The process of claim 1 wherein pressure is placed on said fluid self-curing material before it completely cures so that said fluid self-curing material takes the shape of metatarsal arch.

5. The process of claim 1 wherein said prosthesis enclosure is a sealed envelope, with at least its top surface being elastic, wherein said fluid self-curing material is placed in said prosthesis enclosure by piercing a side of said prosthesis enclosure with an elongated, hollow tube device and force injecting said fluid self-curing material through said elongated, hollow tube device into said prosthesis enclosure, and wherein said hollow tube device is removed after said fluid self-curing prosthesis enclosure and said side of said prosthesis enclosure is rapidly sealed.

6. The process of claim 5 wherein said region of said shoe of said prosthesis enclosure which is placed by said hollow tube device is self-curing.

7. The process of claim 1 wherein said prosthesis enclosure is a rigid insert that is placed on or affixed to the insole of said shoe, said insert comprising a flat plate that extends across the width of said insole and extends lengthwise at least across the metatarsal arch of said foot, a low side wall on the side away from said metatarsal arch which completely covers said arch when said foot is inserted in said shoe, said foot serving as the top of said prosthesis enclosure, wherein said fluid self-curing material is placed in said prosthesis enclosure by means of a tube inserted between said high side wall and said foot, and wherein said tube is rapidly removed after said fluid self-curing material is placed in said prosthesis enclosure.

8. The process of claim 2 wherein said self-curing material is an admixture of an acrylate ester monomer, an acrylate ester prepolymer and an activated free-radical initiator.

9. The process of claim 8 wherein said admixture also contains a plasticizer.

10. The process of claim 2 wherein the self-curing material is an admixture of (i) polymethyl methacrylate and a cross-linking agent, such having been prepolymerize to just below the gel point, (ii) methyl methacrylate and (iii) an activated free-radical initiator.

11. The process of claim 2 wherein the self-curing material is an admixture of styrene, a carboxylated monomer, a carboxylated bimonomer of prepolymer, and a polyvalent salt curing agent.

12. The process of claim 1 wherein said curing is achieved by means of actinic radiation.

13. The process of claim 1 wherein said curable material contains a filler.

14. The prosthesis for supporting or restraining a part of the body which consists of a prosthesis enclosure adapted to be placed on the affected part of the body and a rigid, cured, non-foamed material, within the

prosthesis enclosure, said rigid, cured, non-foamed material comprising a prepolymerized material cross-linked by an ethylenically unsaturated monomer, said rigid, cured, non-foamed material having been cured at a temperature between 59° and 120°F., said rigid, cured, non-foamed material being adapted to conform to the shape of the affected portion of the body, and said rigid, cured, non-foamed material having essentially the same volume in the cured state it had in the pre-cured state.

15. The prosthesis of claim 14 wherein said prosthesis enclosure is located on the insole of a shoe where the metatarsal arch of a foot is located.

16. The prosthesis of claim 15 wherein said prosthesis enclosure is a sealed enclosure.

17. The prosthesis of claim 16 wherein said prosthesis enclosure is a rigid insert that is placed on or affixed to said insole of said shoe, said insert comprising a flat plate that extends lengthwise across the width of said insole and extends lengthwise at least across the metatarsal arch of said foot and a low side wall on the side away from the metatarsal arch which completely covers said arch when said foot is inserted in said shoe, said foot serving as the top of said prosthesis enclosure.

18. The prosthesis of claim 17 wherein said prosthesis enclosure is comprised of aluminum.

19. The prosthesis of claim 14 wherein said curable material contains a filler.

20. The process for preparing a prosthesis for supporting or restraining a part of the body which consists of: (a) placing a fluid, curable non-foamable material in a prosthesis enclosure, said fluid self-curable material being comprised of an admixture of a cross-linkable prepolymerized material and an ethylenically unsaturated monomer, and (b) curing in situ said fluid curable material at a temperature between 59° and 120°F. to form a rigid cured material which conforms to the shape of the affected portion of the body and which has essentially the same volume in the pre-cured state as in the cured state, there being no gas given off during the curing.

21. The prosthesis for supporting or restraining a part of the body which consists of a prosthesis enclosure adapted to be placed on the affected part of the body and a rigid, cured, non-foamed material, containing a filler or a plasticizer or both, within the prosthesis enclosure, said rigid cured, non-foamed material comprising a prepolymerized material cross-linked by an ethylenically unsaturated monomer, said rigid, cured, non-foamed material having been cured at a temperature between 59° and 120°F., said rigid, cured, non-foamed material being adapted to conform to the shape of the affected portion of the body, and said rigid, cured non-foamed material having essentially the same volume in the cured state it had in the pre-cured state.

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