ABSTRACT: A lightweight strong cast for the repair of broken bones is made by impregnating a fibrous felt with a photocurable resin, wrapping the felt in bandage form around the injured member until a sufficient thickness is built up, then curing the resin by exposing the wrapped “cast” to actinic radiation for a time sufficient to convert the impregnated wrapping into a rigid substance.
PHOTOCURABLE RESIN IMPREGNATED BANDAGE FOR FORMING RIGID SURGICAL CASTS

Despite the efficacy and the rigidity which surgeons secure in a well-made plaster cast, its weight is a serious disadvantage. Numerous attempts have been made to secure the same rigidity to maintain the bones in proper position throughout the healing process, and at the same time greatly reduce the weight of the cast. Most of these expedients have made use of some preform of aluminum traylike support, e.g. for a broken forearm or mended fibrous supports.

The proper setting of bones, however, requires a highly individualized cast, and in a considerable number of instances the traylike supports for broken bones cannot be used.

We have discovered that it is possible to produce casts for the repair of broken bones which can be completely molded to fit exactly the arm or leg or other injured member by impregnating a bandage base, which may be an airlaid or water-laid felt or woven textile with a photocurable resin.

The improved mold may have densities which are no greater than that of water, and very considerable stiffness in thin sections. The "cast" can be made tough, mechanically strong, and very much thinner than is the customary plaster cast, with the result that although the site of injury is made completely immobile, the patient may move without dragging or lifting the heavy weight of plaster as formerly was necessary.

An additional advantage is that the cast can be applied to the patient immediately. It requires only that the prepared casting substance be unwrapped and bandaged onto the limb. It requires neither a pall of plaster-of-paris, nor the soaking of prepared plaster-gauze material. It has the advantage, too, that no new equipment is required. Most hospitals have sources of actinic radiation: the cast can be converted into a solid substance in a very few minutes merely by focusing the rays of a sun lamp onto the cast.

In the drawing, FIG. 1 illustrates in perspective and in section the bandage when formed on a felt fibrous base, and FIG. 2 shows in perspective and in section the bandage when formed on a textile base.

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

Operable compositions are disclosed in the copending application of Kehr & Wszolek, Ser. No. 617,801, filed Feb. 23, 1967, now abandoned, and assigned to the assignee of the present invention. The entire disclosure of application Ser. No. 617,801, is herein incorporated by reference. Many of the compositions disclosed in the said application may be used in the present invention, even those which are malodorous are operative, but the odor of some makes their use impossible.

As a general definition, the group of polyenes includes those having molecular weight in the range of 300 to 20,000, a viscosity ranging from 0 to 20 million centipoises at 70°C. of the general formula: \[ A \xrightarrow{} \xrightarrow{} (X) \] wherein X is a member of the group consisting of \[ R \xrightarrow{} R \xrightarrow{} R \xrightarrow{} (O) \] and \( R-O\xrightarrow{} O \xrightarrow{} C \xrightarrow{} \); \( m \) is at least 2; \( R \) is independently selected from the group consisting of hydrogen, halogen aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, arylalkyl, substituted arylalkyl and substituted alkyl groups containing 1 to 16 carbon atoms and A is a polyvalent organic moiety free of (1) reactive carbon to carbon unsaturation and (2) unsaturated groups in conjugation with the reactive eye or yne groups in X. Thus A may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P, O 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, isobutylenesoprene rubber, polychloroprene, styrene-butadiene-acrylonitrile rubber, and the like, unsaturated polyesters, polyamides, and polyurethanes derived from monomers containing reactive unsaturation, e.g. adipic acid-butylen diol, 1,6-hexanediimide, fumaric acid, and 2,4-tolylen disocyanatobutenedioll condensation polymers.

The polythiols useful in this invention may be simple or complex organic compounds having at least 2 pendant or terminally positioned —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 \( R_S \xrightarrow{} (SH) \) where \( n \) is at least 2 and \( R_S \) is a polyvalent organic moiety free from reactive carbon to carbon unsaturation. Thus \( R_S \) 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 polymer "casts" result, are the esters of thiol-containing acids of the general formula \( HS-R_S-COOH \) where \( R_S \) is an organic moiety containing no "reactive" carbon to carbon unsaturation with polyhydroxy compounds of the general structure: \( R_S \xrightarrow{} (OH) \) where \( R_{16} \) is an organic moiety containing no "reactive" carbon to carbon unsaturation and \( n \) is 2 or greater. These components will react under suitable conditions to give a polythiol having the general structure \( R_S \xrightarrow{} (OC-R_S-SH) \) where \( R_S \) and \( R_{16} \) 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 bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol is greater than 4.

As the impregnating base, I prefer to use airlaid felts. They may be made very lofty and will hold substantial amounts of resin impregnant. 200 percent of resin impregnant calculated on the dry weight of the fibers is a practicable and useful degree of impregnation for bandages which are to be converted to rigid structures. Soft, lofty, water-laid felts are useful, and impregnated fabrics also are useful and find particular use as the outer layer of my improved cast.

In the case of textiles, it is somewhat harder to include a very high proportion of resin, but high resin proportions may be secured by first impregnating the sheet with the photocurable composition, allowing the sheet to dry in the dark, and then recoating the sheet with the same photocurable composition under a knife spreader or an accurate calendar.

Example 1

A strip of lofty, air-laid "Dynel" felt, 5 yards long, basis weight 3 oz. per square yard, was impregnated with a diene/tetrathiol blend prepared in the following manner: a solid polyetherdiol having a molecular weight of 3,200 was reacted with allylsiloxaneate to result in a solid diene. The diene then was melted and dissolved in an equal weight of a 50/50 mixture of toluene and ethoxyethylacetate. Pen-
taerythritol tetrakis (β-mercaptopropionate) was then added in the proportion of 1 g. per 13 g. of diene. 1 percent of benzophenone calculated on the weight of the mixture was then added. The “Dynel” fabric was impregnated by passing a web of the fabric through the above solution and then squeezing it sufficiently to permit 90 percent by weight of the resin to remain in the web. The web was then set aside to dry for a period of 12 hours, during which time the toluene and ethoxyethacetae evaporated and the resin crystallized. The web was run through a slitter and cut into 3-inch widths. The slits were rolled up and placed in tin cans to exclude light. Sheets of the material were held in the dark and remained uncured for a period of several weeks.

In building up the cast, the usual techniques of protecting the patient’s skin may be followed: e.g. protective fabrics of medicated gauze or soft padding may first be placed on the skin, or a film of plastic may be applied as a separating medium. The solid polyester composition should be melted at 50° C. and may be cooled to room temperature before application. Thereafter, the bandage is wound on and the cast built up by the usual wrapping techniques. No times for exposures to actinic radiation can be given, for every cast possesses substantial differences in thickness, number of plies, and size. The exposure to actinic radiation should continue until substantially all of the resin in the cast has been converted to a solid substance. As an example, the bandage may be cured under the light flux of an Arcolux pulsed xenon lamp placed 30 inches from the surface of the cast. Substantial gellation will take place under these conditions through resin coats 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. After curing, the polyester composition will recrystallize and impart greater rigidity to the cast.

The compositions to be cured, i.e. to be converted into the solid mass of the “cast” may include materials to increase the rigidity of the cast or resin extenders such as wood flour, talc, etc. Heavier materials which are frequently used as fillers or loaders in resins compounds, e.g. Baryst, are operative but are useful only if the weight of the cast is of no importance. Accelerators of the reaction to actinic radiation are highly desirable, and among the photo-initiators or sensitzers are the benzophenones, acetophenone, acenaphthene-quinoine, acenaphthol-quinone, methylthyl ketone, etc. They greatly increase the rate of hardening. Many of these compositions can be compounded so that they are pastes rather than flowable mixtures, and such paste compositions are highly useful when an already impregnated base must be top coated.

If the bandages are properly packaged in light-impermeable packs or canisters, they may be stored for months without loss of efficacy, but once they are opened and exposed to daylight, they should be used promptly. The speed, ease of application, and the cleanly conditions surrounding the use of these photoactive bandages makes the application of a cast a very much simpler and quicker process than formerly. Their rigidity after cure means that a patient, rather than having to put up with the great weight and clumsiness of a plaster-of-paris cast, has a light, thin, individually created support which permits him to move arms or legs with much less effort. The surgeon, too, can begin at once to bind 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.

The bandages obviously may be put to mechanical use. An interesting use is in conjunction with archaeological artifacts which can be supported and made ready for transportation merely by wrapping the discovery in the field. A high degree of cure is secured by exposing the wrapped article to sunlight, and a few hours exposure in most of the locations where explorations are attempted are sufficient to make a rigid, safe transportation package. Other uses where the convenience of a support that will cure itself in sunlight will readily suggest themselves.

What is claimed is:

1. A strip bandage capable, when exposed to actinic radiation, of forming a rigid cast for bone fractures, comprising a web of fibrous material impregnated with a photocurable composition comprising a polyene containing a polar group selected from the group consisting of oxygen and nitrogen containing functionalities and containing at least two unsaturated carbon to carbon bonds per molecule, and a polyethylene containing at least two thiol groups per molecule, the total combined functionality of (a) the unsaturated carbon to carbon bonds per molecule in the polyene, and (b) the thiol groups per molecule in the polyethylene being greater than 4.

2. A strip bandage as claimed in claim 1 wherein the web of fibrous material is an air-laid felt.

3. A strip bandage as claimed in claim 1 wherein the strip of fibrous material is a woven textile.

4. A strip bandage as claimed in claim 1 wherein the webs of fibrous material is formed of polyester fibers.

5. The strip bandage of claim 1 wherein there is added to the photocurable composition a photosensitizer selected from the group consisting of benzophenone, acetophenone, acenaphthenesquione, acenaphthol-quinone and methylthyl ketone.