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(54) Curable resin coated sheet having reduced tack.

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Description

This invention relates to an orthopedic article comprising a prelubricated, flexible casting material, and a method for preparing it.

Current synthetic orthopedic casting tapes are produced using curable resins coated on a substrate (fiberglass, polyester, or other synthetic or natural fabric). U.S. Patent No. 4,411,262 (von Bonin) and U.S. Patent No. 4,502,279 (Garwood) disclose the use of water-curable isocyanate-functional prepolymer in orthopedic casting tapes. After removal of the casting material from the storage pouch, especially after exposure to water used to initiate curing of the prepolymer, these resins are quite tacky until cured. This tackiness makes it difficult to mold the cast to the patient's limb as the resin tends to stick to the protective gloves worn by the cast applier. For example, after the rolls are wrapped but before they harden, some working time is necessary in order to mold the casts to fit the limb. This is accomplished by smoothing the cast with a gloved hand as well as holding the cast at certain points until it hardens. When a roll of tape coated with a tacky resin is used, molding the cast is difficult. The reason for this difficulty is that the glove sticks to the resin and when attempts are made to smooth the cast and form it, the layers of tape pull apart from each other thus requiring reforming of part of the cast.

It is believed that all curable resin coated orthopedic casting materials currently available commercially suffer from the above-noted problems.

U.S. Patent No. 3,089,486 (Pike) discloses the use of beeswax as a release agent in the formation of an immobilizing orthopedic structure reinforced with a methacrylate polymer.

U.S. Patent No. 4,100,122 (Kent) discloses the addition of crystalline wax to a mixture of transpolyisoprene and glass fibers to improve the flow characteristics of the composition during preparation, and the use of such compositions in moldable orthopedic devices.

U.S. Patent No. 3,043,298 (Brickman et al.) discloses the addition of hydroxypropylmethyl-cellulose to a plaster of Paris bandage to be used as an orthopedic cast which gives the plaster of Paris a creamy consistency or texture when wet with water just prior to application.

U.S. Patent No. 3,763,858 (Buese) discloses a composite material, useful as a surgical, medical, or orthopedic wrapping, which will adhere or cohere to another surface or to itself by the application of moderate pressure either at room temperature or at an elevated temperature and will be substantially nontacky to the touch until the application of such moderate pressure. The composite material comprises a cementitious core having bonded thereto a flexible, open cellular, resilient polymeric protective covering, the core having sufficient softness at the conditions of use to extend through the cells of the protective covering and become available at the outer surface thereof upon application of moderate pressure.

U.S. Patent No. 3,830,194 (Boardman) discloses an orthopedic bandage comprising a flexible carrier supporting a solid water-soluble vinyl monomer selected from the group consisting of diacetone acrylamide and an isopropyl diacrylamide and mixtures thereof. The bandage is prepared for use by dipping in water in the presence of a catalyst for initiating polymerization of the vinyl monomer and then wrapping the body portion to be immobilized. The patent also discloses the use of inorganic fillers such as calcium sulfate, calcium carbonate, bentonite, or silica, to render the bandage less sticky and moderate any temperature rise during curing.

U.S. Patent No. 4,454,873 (Laufenburg et al.) discloses an orthopedic cast material having a thermoplastic material and a quantity of polyethylene oxide applied thereto as an anti-block agent to prevent adherence of adjacent convolutions of the cast material when it is in the form of a roll and is immersed in hot water prior to being wrapped on a limb or body part of a patient. The polyethylene oxide can be in the form of a coating on the outer surface of the cast material or in the resin of the cast material. The patent implies that most, if not all of the polyethylene oxide is removed from the casting material when the casting material is removed from the hot water and that talc can be added to the resin to reduce tack.

U.K. Patent Application No. 2,092,606 (Potter et al.) discloses water hardenable splinting bandages comprising a flexible fabric carrying an isocyanate terminated prepolymer having a reaction functionality of two and a catalyst, which bandage is characterised in that the prepolymer is a water absorbing isocyanate terminated prepolymer and the catalyst is water soluble but insoluble in the prepolymer, wherein the prepolymer is derived from an ethylene oxide adduct. The application discloses that the catalyst is preferably an inorganic material which has an alkaline reaction in water, preferably a carbonate or bicarbonate.

A glove lubricant comprised of water, sorbitol, mineral oil and silicone fluid has been sold by 3M Co., St. Paul under the tradename Cast Cream with instructions to apply the lubricant to the gloves of one applying an isocyanate-functional prepolymer coated cast after wrapping of the cast but before molding of the cast to avoid having the exposed casting material adhere to the gloves of the one applying the cast.

EP-A-0 094 222 discloses an orthopedic bandage which comprises a support carrying a vinyl compound, which compound polymerizes when exposed to a water-activated vinyl polymerization catalyst, characterized in that the vinyl compound is a hydrophilic prepolymer which contains not less than two polymerizable vinyl groups and the use of a hydrophilic prepolymer which contains not less than two polymerizable vinylic groups results in a storage stable bandage which on exposure to a water activated polymerization catalyst produces a cast of good strength.

This invention relates to an orthopedic article comprising a prelubricated, flexible, casting material, said casting material comprising:

(1) a porous sheet;

(2) a water curable resin coated on said porous sheet, said resin being selected from isocyanate-functional prepolymers formed by reaction of an isocyanate with a polyol; and

(3) a lubricant additive comprising a polysiloxane, an ionic surfactant, a nonionic surfactant, a polyethoxylated surfactant, a polyethoxylated polymer, or a polymer comprised of a plurality of hydrophilic groups selected from the monomers acrylamide, vinylpyrrolidone, vinylacetate and its hydrolyzed derivatives, and hydroxy and amino functional lower alkyl acrylates;

whereby the kinetic coefficient of friction of a major surface of the coated sheet is less than 1.2.

As discussed hereinafter, the tack exhibited by a surface of a sheet correlates with the kinetic coefficient of friction of the surface such that a reduction in the tack results in reduction of kinetic coefficient of friction.

This invention also relates to a method of forming an orthopedic article comprising the step of depositing on a major surface of a flexible sheet which has been coated with a resin or mixing with the resin before applying the resin to the sheet, a lubricant additive comprising a polysiloxane, an ionic surfactant, a nonionic surfactant, a polyethoxylated surfactant, a polyethoxylated polymer, or a polymer comprised of a plurality of hydrophilic groups selected from the monomers: acrylamide, vinylpyrrolidone, vinylacetate and its hydrolyzed derivatives, and hydroxy and amino functional lower alkyl acrylates; whereby the kinetic coefficient of friction of said major surface is less than 1.2, said resin being water-curable and comprising an isocyanate-functional prepolymer.

The layer may be deposited onto the surface of the sheet by spraying, by roll coating, or by dipping the sheet into a composition containing the lubricant, e.g., the lubricants that are compatible with water can be added to the water in which the sheet is dipped to effect cure.

The prelubricated sheet used for the orthopedic article of this invention exhibits reduced tack prior to and/or during cure of the prepolymer and yet forms a cast which exhibits acceptable strength and lamination of the wrapped layers. As used herein, a pre-lubricated sheet is a sheet which has the lubricant at the surface of the coated sheet prior to wrapping of the sheet about a substrate, including when used as an orthopedic bandage.

The embodiments of this invention may be classified into one or more of three classes. In one class, a lubricant is an additive which is chemically unreactive with the curable resin, e.g., a polydialkylsiloxane or an alkyl ionic surfactant as described below. In a second class, the additive is reactive with the resin such that at least a portion of the amount of lubricant may become chemically bonded to the resin, e.g., a hydroxyl-functional surfactant. In a third class, the lubricant is a combination of at least one of the foregoing with hydrophilic groups covalently bonded to the resin. Further, these classes are not mutually exclusive in that a single embodiment of this invention may be comprised of a lubricant from all three classes, i.e., a combined lubricant. Indeed, the best mode of this invention is a combined lubricant.

The reactive lubricant additives will vary in the degree to which they react with the resin based on 1) their inherent reactivity, e.g., primary hydroxyl additive lubricants may react faster than secondary hydroxyl lubricants, 2) the length of the period of time from the addition of the reactive additive to the initiation of curing by exposure to water, e.g., the longer the period, the greater the amount of reactive lubricant which will have reacted with the prepolymer to become chemically bonded thereto, and 3) in the case of reactive lubricant additives which are deposited on a curable resin coated sheet the greater the rate of mixing of the reactive lubricant and the curable resin, the greater the amount of lubricant reacted with the resin.

Because of these various factors, it is not convenient to determine precisely to what extent a given reactive lubricant additive applied in a given manner at a given time is chemically bonded to the resin. Accordingly, the disclosure below will not deal with the question of the extent to which a reactive lubricant additive may, in fact, be chemically bonded to the resin. Moreover, because the determination of the extent to which a given reactive lubricant additive is chemically bonded to the resin is unnecessary insofar as the utility of the lubricant in reducing tack is concerned, no distinction will be made below between unreactive and reactive lubricant additives, i.e., the unreactive and reactive lubricant additives will be disclosed together in Section I, below, apart from the bound lubricants disclosed in Section II, below.

The embodiments of the invention which employ a polysiloxane as a lubricant exhibit reduced tack both prior to and after exposure of the prepolymer to water.

The kinetic coefficient of friction of the articles of this invention generally range from 0.2 to 1.2, more preferably less than 0.75 and most preferably less than 0.4.

One element of this invention is a semi-rigid or flexible sheet upon which a curable resin can be coated to reinforce the sheet when the resin is cured thereon. The sheet is preferably porous such that the sheet is at least partially impregnated with the resin. Examples of suitable sheets are non-woven, woven, or knit fabrics comprised of natural or synthetic fibers. Preferred sheets are knit fiberglass fabrics, and particularly preferred sheets of this type are extensible, heat-set fabrics as disclosed in U.S. Patent 4 609 578 which corresponds to EP-A- 0 181 731.

The curable resins useful in this invention are resins which can be used to coat a sheet material and which can then be cured to reinforce the sheet material. The resin is curable to a crosslinked thermoset state. The preferred curable resins are fluids, i.e., composition having viscosities between 5,000 cps and 500,000 cps, preferably 10,000 cps to 100,000 cps.

The resin used in the casting material of the invention is a curable resin which will satisfy the functional requirements of an orthopedic cast. Obviously, the resin must be nontoxic in the sense that it does not give off significant amounts of toxic vapors during curing which may be harmful to either the patient or the person applying the cast and also that it does not cause skin irritation either by chemical irritation or the generation of excessive heat during cure. Furthermore, the resin must be sufficiently reactive with the curing agent to insure rapid hardening of the cast once it is applied but not so reactive that it does not allow sufficient working time to apply and shape the cast. Initially, the casting material must be pliable and formable and should adhere to itself. Then in a short time following completion of cast application, it should become rigid or, at least, semi-rigid, and strong to support loads and stresses to which the cast is subjected by the activities of the wearer. Thus, the material must undergo a change of state from a fluid-like condition to a solid condition in a matter of minutes.

The resins are cured with water.

The resins for use in the present invention are water-curable, isocyanate-functional prepolymers. Suitable systems of this type are disclosed, for example in U.S. Pat. No. 4,411,262, and in 4,502,479. The following disclosure relates primarily to the preferred embodiment of the invention wherein water-curable isocyanate-functional prepolymers are employed as the curable resin.

It is preferred to coat the resin onto the fabric as a polyisocyanate prepolymer formed by the reaction of an isocyanate and a polyol. It is preferred to use an isocyanate which has low volatility such as diphenylmethane diisocyanate (MDI) rather than a more volatile material such as toluene diisocyanate (TDI). Suitable isocyanates include 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, mixtures of these isomers, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, mixtures of these isomers together with possible small quantities of 2,2'-diphenylmethane diisocyanate (typical of commercially available diphenylmethane diisocyanate), and aromatic polyisocyanates and their mixtures such as are derived from phosgenation of the condensation product of aniline and formaldehyde. Typical polyols for use in the prepolymer system include polypropylene ether glycols (available from Union Carbide under the tradename Niox™ PPG and from BASF Wyandotte under the tradename Pluracol™), polytetramethylene ether glycols (Polymeg™ from the Quaker Oats Co.), polycaprolactone diols (Niox™ PCP series of polyols from Union Carbide), and polyester polyols (hydroxyl terminated polyesters obtained from esterification of dicarboxylic acids and diols such as the Rucoflex™ polyols available from Ruco division, Hooker Chemicals Co.). By using high molecular weight polyols, the rigidity of the cured resin can be reduced.

An example of a resin useful in the casting material of the invention uses an isocyanate known as Isonate™ 143L available from the Upjohn Company (a mixture containing about 73% of MDI) and a polypropylene oxide polyol from Union Carbide as Niox™ PPG725. To prolong the shelflife of the material, it is preferred to include from 0.01 to 1.0 percent by weight of benzoyl chloride or another suitable stabilizer.

The reactivity of the resin once it is exposed to the water curing agent can be controlled by the use of a proper catalyst. The reactivity must not be so great that: (1) a hard film quickly forms on the resin surface preventing further penetration of the water into the bulk of the resin; or (2) the cast becomes rigid before the application and shaping is complete. Good results have been achieved using 4-[2-[1-methyl-2-(4-morpholinyl)ethoxy]ethyl]-morpholine (MEMPE) at a concentration of 0.05 to 5 percent by weight.

Foaming of the resin should be minimized since it reduces the porosity of the cast and its overall strength. Foaming occurs because carbon dioxide is released when water reacts with isocyanate groups. One way to minimize foaming is to reduce the concentration of isocyanate groups in the prepolymer. However, to have reactivity, workability, and ultimate strength, an adequate concentration of isocyanate

groups is necessary. Although foaming is less at low resin contents, adequate resin content is required for desirable cast characteristics such as strength and resistance to peeling. The most satisfactory method of minimizing foaming is to add a foam suppressor such as silicone Antifoam A (Dow Corning), DB-100 silicone fluid (Dow Corning) to the resin. It is especially preferred to use a silicone liquid such a Dow Corning DB-100 at a concentration of 0.05 to 1.0 percent by weight.

A water-curable isocyanate-functional prepolymer as used herein means a prepolymer derived from polyisocyanate, preferably aromatic, and a reactive hydrogen compound or oligomer. The prepolymer has sufficient isocyanate-functionality to cure upon exposure to water, e.g., moisture vapor or, preferably liquid water.

I. ADDITIVE LUBRICANTS

In another aspect of this invention, the lubricant is an additive. The additive is incompatible with the curable resin such that the additive forms a shear layer on the surface of the curable resin. Accordingly, the term "incompatible" as used herein shall mean the ability of any composition to form a shear layer on the surface of a curable resin. Some additives, e.g., the ionic alkyl surfactants form a shear layer when wetted with water. These additives can be mixed with the resin before application of the resin to the sheet, but is preferably deposited on the surfaces of a curable resin coated sheet in an amount sufficient to reduce the kinetic coefficient of friction of the coated sheet during cure.

The additive is deposited on the surface of the casting material prior to wrapping about a substrate in any manner which will deposit the amount necessary to reduce the kinetic coefficient of friction to the desired level. The additive is preferably coated on the surfaces of the casting material prior to the packaging thereof but it may be applied just prior to the wrapping of the casting material. In particular, some additives may be added to a water bath in which the casting material may be immersed to activate the curing of the prepolymer in an amount sufficient to deposit the desired amount of lubricant on the surfaces of the casting material.

The additive lubricants will be discussed herein below as follows:

A. Polysiloxanes

B. Surfactants and Polymers Consisting of Hydrophilic Groups

1. Ionic Alkyl, Aryl, Aralkyl Surfactants

2. Polyethoxylated Surfactants

a. Polyethoxylated Alcohols

b. Block Copolymers of Propylene Oxide and Ethylene Oxide

3. Ionic Derivatives of Polyethoxylated Alcohols.

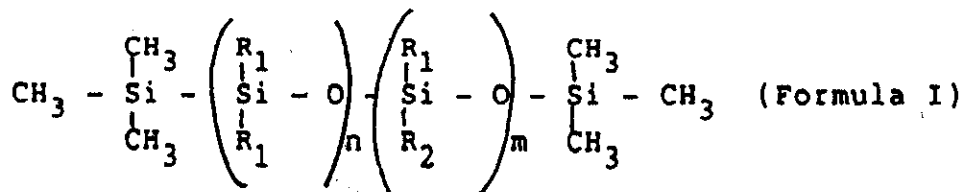
A. Polysiloxanes

Two classes of hydrophobic materials were initially evaluated as lubricants: organic based oils and waxes and silicone based fluids. Of those materials evaluated only those compounds which are essentially immiscible with the resin maintained a lubricating feel after being stored for longer than a few days. Materials such as corn oil; mineral oil; and hydrocarbons such as hexadecane and motor oil did give a non-tacky and even slippery feeling surface which allowed easy application and moldability of the casting tape to the patient, but the effect was transient. On the average, the slippery effect induced by these materials lasted only a day to a week apparently due to dissolution of the lubricant into the resin. Compounds such as lanolin, when applied to the surface of the coated tape in the molten state did remain on the surface of the resin for an extended period of time and did reduce the tackiness of the resin but also affected the cast detrimentally by reducing the lamination of the casting material.

Unlike the materials discussed above, the silicone based fluids dramatically reduced the tackiness of the resin and surprisingly did not affect the other properties of the cast and even at elevated temperatures remained on the surface of the resin and remained slippery.

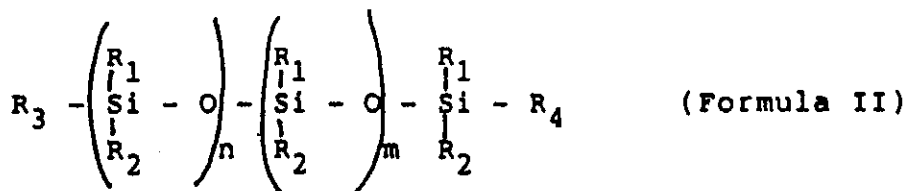
Accordingly, this aspect of the invention relates to the use of lubricating silicone fluids which are generally non-irritating to skin in order to reduce the tackiness of curable liquid resin coated casting tapes. The fluids are preferably applied to both major surfaces at 0.9-9.0 g/m² resulting in a casting tape which is easy to apply and mold to a patient's limb. The silicone fluids in the amounts stated above do not adversely affect the physical properties of the cast and many are safe for use on the skin.

Specifically, the use of the following silicone based compounds is contemplated:



R_1 and R_2 may independently be: alkyl ($\text{C}_1 - \text{C}_{16}$) chosen independently from: optionally substituted alkyl, optionally substituted aryl, optionally substituted aralkyl, unsaturated, alkyl, alkoxy, provided that R_1 and R_2 are of short enough chain length relative to n and to prevent dissolution of the silicone compound in the resin, m and n are integers, the sum of which range from about 15-800. This value depends on the exact nature of R_1 and R_2 and the range given is reflective of current commercially available compounds.

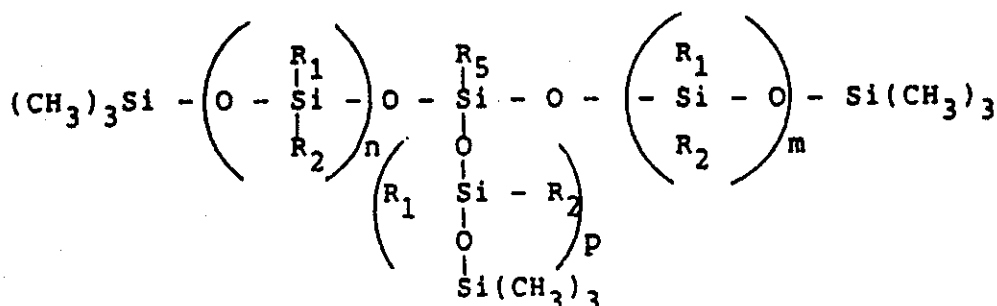
Alternatively, the polysiloxane may be terminated with a nonsiloxane moiety. Such polysiloxanes have the following structure:



where, R_1 and R_2 are as given above, preferably methyl, and R_3 , R_4 may be chosen from: aminoalkyl dimethylsilyl, hydroxyalkyl dimethylsilyl, polyethylene oxide dimethylsilyl, carboxyalkyl dimethylsilyl, chloromethyl dimethylsilyl, methacryloxyalkyl dimethylsilyl, m and n are integers the sum of which is such that the viscosity is in the range of 50 - 10,000 cs.

This value is reflective of the presently available compounds.

Finally, the polysiloxane may also be of a tertiary structure as follows:



where R_1 , R_2 are as given above, preferably methyl, and R_5 may be chosen from: optionally substituted alkyl, optionally substituted aryl, optionally substituted aralkyl. It should also be noted that tertiary siloxane structures such as this could also be terminated in non-siloxane moieties such as those of structure B, m , n and p are integers the sum of which is sufficient such that the viscosity is in the range of 25 - 10,000 cs.

Some examples of the modified silicones described above include: Aminopropyldimethyl terminated polydimethylsiloxanes, ethylene-dimethylsiloxane oxide ABA block copolymers (approximately 1-20% polyoxyethylene), dimethylsiloxane-vinylmethyl siloxane copolymers, tertiary structured polydimethylsiloxanes with phenethylsulfonate or carboxypropyl functionalities at the branch points, methyldecylaryloxymethylsiloxane copolymer, polymethyl-3,3,3-trifluoropropylsiloxane, dimethyldiphenylsiloxane copolymer poly(acetoxypentyl)methylsiloxane, polybis(cyanopropyl)siloxane, polydiethoxysiloxane, polydiethylsiloxane, and poly(chlorophenyl)-methylsiloxane.

The preferred polysiloxanes are commercially available polydimethylsiloxanes of viscosities ranging from 50-500 centistokes (cs) which are applied to the casting tape at 0.9 to 9.0 g/m², preferably 1.8 to 5.4

g/m² roll of casting tape. The higher viscosity fluids up to 350 cs tend to require less material per unit length of tape in order to achieve the desired slippery feel. No significant advantage is apparent in increasing the viscosity from 350 to 500 cs. To these fluids have also been added both ionic and nonionic surfactants. In all cases casting tape which exhibited reduced tack and dramatically improved moldability resulted with no adverse effect on strength or lamination of the cast.

Ionic and non-ionic surfactants can be added to the silicone fluids in order to further reduce the kinetic coefficient of friction when wet. These include dioctylsulfosuccinate (Aerosol OT), nonionic polyethoxylated room temperature waxy surfactants such as BrijTM, TergitolTM, EthospenseTM, GenerolTM, and PluronicTM. In addition, polymeric and clay-type water activated materials have also been added to the silicone fluids to enhance the slippery feel of the casting tape. These materials include polyacrylamides, bentonite, and KeloidTM O.

Examples of the polysiloxane embodiments of this invention are shown in Examples 1-8.

B. Surfactants and Polymers Comprised of Hydrophilic Groups

Another aspect of this invention is a modification of the casting tape used in orthopedic casts in which the coated rolls of tape are rendered non-tacky after immersion in water by the addition of surfactants or polymers comprised of hydrophilic functional groups to the composition.

As has been suggested, a variety of polymeric materials consisting essentially of hydrophilic groups are suitable for use as lubricants. Examples of such polymers include, but are not limited to water soluble polymers based on ethylenically unsaturated monomers such as acrylamide, vinylpyrrolidone, vinylacetate and its polymeric hydrolyzed derivatives, hydroxy and amino functional lower alkyl acrylates such as 2-hydroxyethyl acrylate and various specialty monomers containing ionic species.

The preferred surfactants and polymers comprised of hydrophilic groups are discussed in Sections 1-3 below.

1. Ionic Alkyl, Aryl or Aralkyl Surfactants

This aspect of the invention relates to the use of particular lubricants added to polymers used on orthopedic casting tapes which render them non-tacky. In these embodiments, the lubricant consists of ionic alkyl, ionic aryl, or ionic aralkyl compounds. The alkyl compounds generally contain more than about eight contiguous methylene units per molecule which give the compound fatty characteristics. The ionic alkyl compounds can be anionic, cationic or zwitterionic in nature, for example, sodium hexadecyl sulfate and cetyl trimethyl ammonium bromide and lecithin derivatives. Examples of the aryl and aralkyl ionic compounds are the naphthalene sulfonates and alkylbenzene sulfonates, respectively. In practice the ionic compounds may be added to the isocyanate-functional prepolymer during formulation generally at a level of from about 1.0% to about 5.0% by weight of the total. The curable resin is coated on a sheet in the standard fashion to give rolls of tape. Alternatively, and preferably, the ionic compound can be deposited on the surface of a curable resin coated sheet.

When immersed in water, the tapes quickly become very slippery. The rolls unwind easily and do not stick to gloves. After the roll is wrapped around the limb, molding of the cast becomes easy due to the non-tacky nature of the resin. The cast can be rubbed over its entire length without sticking to the gloves and the layers of tape do not separate from each other. This pre-lubricating resin approaches the handling characteristics of plaster of Paris bandages very closely.

In summary, the addition of ionic compound surfactants to an isocyanate-functional prepolymer used in orthopedic casting tapes results in a tape which becomes non-tacky after immersion in water. This is advantageous in that the resulting coating material mimics the properties of a plaster bandage in its ease of application and handling. The rolls unwind easily and molding of the cast is facilitated. Despite its slipperiness, the layers of tape laminate well to each other.

2. Polyoxyethylated Surfactants

This aspect of the invention relates to use of polyoxyethylated surfactants which, when applied to the surface of curable liquid resin coated casting materials or incorporated into the resin produce a casting product which is slippery and easy to mold to a patient's limb. These materials are of relatively high molecular weight and are generally waxy at room temperature. In addition, the skin permeability and general toxicity of these materials is very low making them well suited for addition to an orthopedic bandage. These compounds may be combined with the silicones described above in order to yield a casting material which

is non-tacky when dry and very slippery when wet. In addition, these compounds are active as lubricants even when hard water is used to cure the prepolymer.

The following chemical classes of materials when applied to the surface of a casting tape as previously described have been found to yield the desired non-tacky or slippery casting materials.

5

a. Polyethoxylated Fatty Alcohols

The general structural formula of this class of compounds is represented by the following:



wherein

- 15 R is a group having a functionality of a and is a saturated or unsaturated alkyl group, optionally halogenated (e.g., chain length C_8-C_{20}), an aryl group such as an alkylphenyl, or a polyalicyclic group (e.g., a sterol derivative);
- n is an integer from 3-200, preferably about 20 to about 100; and
- a is from 2 to about 10.

The Hydrophile-Lipophile balance (HLB) is greater than 11 and more preferably greater than 15. Examples of these compounds include: Brij™ series, Tergitol™ 15-S series, Generol™ 122E series, 20 Ethospense™ series, etc. as described below.

It is believed that only those compounds of this class which are solids at room temperature will be effective in producing a slippery casting material with commercially acceptable shelf life for use as an orthopedic bandage.

25 b. Block Copolymers of Propylene Oxide and Ethylene Oxide

The general structure of this class of compounds may be represented by the following:



where

- a and c are independently about 3-150 and
- b ranges from 0 to about 150 such that the resulting HLB of the compound is greater than about 11.

35 It has been found that a high molecular weight polyethylene oxide (available from Union Carbide as Carbowax™) applied to the surface does yield a non-tacky casting material, however, the material was not as slippery as that of the polymeric materials described in 2 a. and b. above of similar molecular weight.

Many surfactants, detergents, and emulsifiers may be useful as slip agents but are unsuitable for use with an isocyanate-functional prepolymer because they adversely affect the shelf-life of that prepolymer and, more importantly for medical uses, are deleterious to skin. Non-ionic surfactants, especially those of 40 higher molecular weight described herein, are known to have extremely low or nondetectable skin permeability and are often reported as additives to cosmetic and pharmaceutical formulations as a means of reducing skin permeability to detergents and other more toxic substances. The nonionic surfactants of this invention, for the most part, are not skin irritants and usually contain functionalities which allow them to react 45 with the resin thus minimizing the possibility of direct or prolonged skin contact.

The surfactants useful in this invention are commercially available from many suppliers. The following have been shown to be useful:

ICI Americas Inc.:

- 50 Brij™ 58 - 20 mole polyoxyethylene cetyl ether,
Brij™ 78 - 20 mole polyoxyethylene stearyl ether
Brij™ 99 - 20 mole polyoxyethylene oleyl ether,
Brij™ 700 - 100 mole polyoxyethylene stearyl ether;

Glyco Chemicals Inc. (Williamsport Pa.):

- Ethospense™ CA-20 - 20 mole polyoxyethylene stearyl ether
55 Pegospense™ CO-200 - 200 mole polyoxyethylene castor oil
Henkel-Speciality Chemicals Div. Teaneck, N.J.:

Generol™ 122E-16 - 16 mole polyethylene glycol soya sterol
Generol™ 122E-25 - 25 mole polyethylene glycol soya sterol

Eumulgin™ B2 - fatty alcohol polyglycol ether;

Union Carbide:

Tergitol™ 15-S-40 - Alkoxy (C₁₂-C₁₄) polyethyleneoxyethanol avg. molecular weight (M.W.) 1960

Tergitol™ NP-40 - Nonylphenol polyethylene glycol ether avg. molecular weight 1980;

5 BASF Wyandote:

Pluronic™ F-68 Polyethylene oxide terminated polypropylene oxide, 80 mole % EO, avg. M.W. = 8350,

Pluronic™ F108 Polyethylene oxide terminated polypropylene oxide, 80 mole % EO, avg. M.W. = 14,500,

Pluronic™ F127 Polyethylene oxide terminated polypropylene oxide, 70 mole % EO, avg. M.W. = 12,500,

Pluronic™ P65 Polyethylene oxide terminated polypropylene oxide, 50 mole % EO, avg. M.W. = 3400.

10 other suppliers are available for these types of surfactants. In order to achieve a non-tacky feel both dry and wet, these surfactants are usually combined with the silicone fluids described above.

3. Ionic Derivatives of Polyethoxylated Alcohols

15 This aspect of the invention relates to the use of ionic derivatives of polyethoxylated alcohols (IPEA) which when applied to the surface of isocyanate-functional prepolymer casting resins effectively reduce or eliminate the tack without significantly affecting other properties of the casting material. This effectively increases the ease of application of the casting tape as well as the moldability to the patient's limb. The IPEA class of materials is useful in synthetic casting resins for several reasons: IPEA's have very low or no

20 skin permeability and in most cases no skin irritation; many yield little or no foaming; IPEA's are active in hard water (e.g., in water used for plaster casts); and in most cases, the IPEA surfactants are waxy and therefore, can be applied to the surface of the casting tape in a molten state and subsequently solidify. This latter property allows the surfactant to remain on the surface of the tape where it is most active as well as making the roll easier to unwind.

25 Specifically, the following surfactant structures will yield the desired properties:



30 where

R₁ may be a straight or branched chain hydrocarbon and n is at least 3. The length of the hydrocarbon must be in balance with that of the polyethylene oxide chain to give the ethoxylated nonionic primary alcohol a HLB in the range of 11-35 and more preferably in the range of 15-25. R₁ may be selected from saturated or unsaturated optionally halogenated alkyl (preferably C₁-C₂₀, more preferably C₈-C₁₈), aryl or optionally substituted aryl, aralkyl (preferably C₇-C₂₄).

Y is a derivative of the alcohol and is an organic or inorganic salt of a group selected from -OSO₃H, -SO₃H, -OPO₃H, -PO₃H, N(R₁)₃⁺.

40 R₂ is hydrogen or is selected from the same group as R₁.

It has been found that the IPEA's described herein can either be added directly to the resin at concentrations ranging from 0.5-7% or preferably, applied to the surface of the tape at coating weights of 0.45 to 6.3 g/m² (preferably 0.9 to 3.6 g/m²). The higher melting compounds may be suspended in a carrier fluid such as silicones, organic oils, or suitable solvents in order to be sprayed. Silicone fluids or nonionic

45 polyethoxylated waxes, such as those described above may be used in conjunction with the IPEA in order to augment the slippery feel. Furthermore, it is possible that other surfactants which may be more skins irritating than some of those of the IPEA may be added in reduced amounts in order to increase the slipperiness of the casting material without compromising the skin biocompatibility. In addition, bactericidal surfactants may also be added in order to effectively kill bacteria between the skin and cast for better

50 hygiene (e.g. benzalkonium chloride or Cetrimide B.P.).

IPEA type surfactants are commercially available from several chemical suppliers including Shell Chemical (Neodol™ 3S and 3A) Henkel™ (Standopol series), DuPont Zonyl™ UR (polyfluoroaliphatic ethoxylated phosphonate).

The additive lubricants can further be combined with bound lubricants.

II. BOUND LUBRICANTS

One aspect of this invention is a sheet, e.g., a scrim, coated with a curable resin wherein one or more hydrophilic groups are chemically bound to the resin. When this orthopedic casting material is brought into contact with water, the hydrophilic group causes the resin to become slippery. This allows for easy application and molding of the cast for the most efficacious fit without the casting material sticking to the gloved hands of the person applying the cast. As noted above, this is advantageous because if the casting material is sticky, application and molding of the cast is difficult. Further, because the hydrophilic groups are chemically bonded to the curable resin, they cannot be leached out by contact with water subsequent to curing. Accordingly, any potential for skin irritation is reduced.

The curable resin containing bound hydrophilic groups can be prepared by a variety of methods. One method relates to the introduction of hydrophilic groups into a curable resin. For example, an aromatic isocyanate-functional prepolymer can be sulfonated with sulfonic acid or its derivatives to obtain a sulfonated isocyanate-functional prepolymer.

A second method relates to the polymerization of monomers comprised of hydrophilic groups to form a curable resin. For example, the preferred resin is an isocyanate-functional prepolymer that is, at least in part, the reaction product of an active hydrogen compound or oligomer with an isocyanate-functional compound or oligomer wherein at least one of the reactants is comprised of at least one hydrophilic group such that the reaction product retains sufficient hydrophilicity to give the prepolymer the desired kinetic coefficient of friction when contacted with water. Preferred prepolymers are prepared from hydroxyl-functional oligomers comprised of hydrophilic groups having repeating units derived from ethylene oxide.

Many hydrophilic functional group prepolymers are suitable for making moldable orthopedic casting materials within the scope of this invention. Preferred isocyanate-functional prepolymers are prepared by reacting a polyisocyanate compound or oligomer, e.g., diphenylmethanediisocyanate, (MDI), with an active hydrogen compound or oligomer comprised of groups selected from the following:

- 1) alkali metal salts of sulfated or sulfonated polyesters or polyethers,
- 2) quaternary ammonium salts containing carbamates derived from polyesters or polyethers,
- 3) alkali metal salts of phosphonated or phosphated polyesters or polyethers,
- 4) polyethylene oxide.

The curing of an isocyanate-functional prepolymer coated sheet is generally initiated by immersion of the sheet in water. Accordingly, the hydrophilicity of the water-curable isocyanate-functional prepolymer should not be so great that the resin composition is very dispersible in water which would allow the resin composition to leach out into the water bath in which the sheet is immersed. Therefore the hydrophilicity of the prepolymer should be such that the prepolymer is not appreciably dispersible, if at all, in water at ambient temperatures. By not appreciably dispersible, it is meant that a roll of curable resin coated sheet when immersed in water and squeezed several times while immersed will retain at least 70%, more preferably at least 85%, and most preferably at least 95% by weight of the resin composition on the sheet. Further, water retained in or absorbed into the cured resin may adversely affect the rigidity of the cured resin and thereby, reduce its wet strength. Accordingly, the hydrophilic functionality of the cured resin should be controlled such that excess amounts of water are not retained in, or absorbed into the cured resin. The hydrophilicity of the resin composition can be controlled by choosing prepolymer-forming reactants having sufficiently low hydrophilic group functionality that the reactants are not appreciably dispersible in water or by using amounts of dispersible reactants that are minor compared to the amounts of reactants that are not appreciably dispersible in water. For example, when the prepolymer is prepared from a mixture of an aromatic isocyanate, e.g., 2,2-diphenylmethane diisocyanate (MDI) and one or more polyether polyols having only polyethylene oxide as a hydrophilic group, the amount of polyethylene oxide by weight of the prepolymer should be less than 15 percent, preferably less than 10 percent, most preferably less than 6 percent, e.g., 3-4 percent.

Reference Examples 1-6 illustrate embodiments of bound lubricants.

III. COMBINED LUBRICANTS

As noted above, the lubricant may be comprised of both hydrophilic groups bound to the prepolymer and one or more additive lubricants. The particular procedures used in obtaining a bound lubricant and the particular procedures used with additive lubricants are used in conjunction with one another, generally without modification. For example, a casting tape coated with a curable liquid resin having bound hydrophilic groups in accordance with Reference Example 1 below can be coated with a polysiloxane lubricant in accordance with Examples 1-8, to obtain an article in accordance with this invention, as in

Example 23.

One advantage of the combined lubricants resides in the pre-wetted reduction in tack provided by a polysiloxane and the great reduction in tack provided by a bound lubricant after initiation of cure by exposure to water.

Examples

Test for Determining the Coefficient of Friction of Synthetic Casting Tapes

Determination of the frictional properties of many materials is often measured in terms of the coefficient of friction. This type of measurement may be made when sliding the material of interest over itself or over another object. The coefficient of friction is a dimensionless term which quantifies the frictional properties and may distinguish between surfaces of varying roughness, tackiness, slipperiness, etc. In the present application, a wide variety of lubricating properties are generated by surfactants or other surface active materials which are added either directly to the casting resins prior to coating the scrim or applied to precoated tape. A test has been developed which measures the tack, i.e., kinetic coefficient of friction of these various materials. This test method is based on ASTM test method D 1894 ("Static and Kinetic Coefficients of Friction of Plastic Film and Sheet") and measures the kinetic coefficient of friction between a horizontal stationary piece of test specimen in low tension and a 200 g 304 stainless steel sled polished to a No. 4 finish. The procedure and apparatus of ASTM test method D 1894 have been modified to accommodate relatively rough and elastic materials such as synthetic casting tapes. This method yields empirical data which, for the most part, correlates with actual performance and thereby offers a quantitative measurement of the lubricating properties of a given casting material.

As used herein, the following terms have the following meanings:

"Kinetic Friction" - the resisting or opposing force that arises when a surface of one object slides over the surface of another object.

"Kinetic Coefficient of Friction" - (KCOF) the ratio of the kinetic frictional force to the force acting perpendicularly to the two surfaces in contact (usually the gravitational force). This dimensionless term is a measure of the relative difficulty with which the two materials will slide across one another i.e., the higher the coefficient of friction the more difficult it is to slide the two materials over one another. The kinetic coefficient of friction, as used herein, is determined from the test described hereinafter and is calculated by the equation:

Kinetic Coefficient

$$\text{of Friction} = \frac{\text{force required to pull the sled(g)}}{200 \text{ (g)}}$$

Test Method

SAMPLE AND MATERIALS CONDITIONING

Sample Conditioning - Test samples should be conditioned at 21-25°C for not less than 24 hours prior to testing.

Water Conditioning - Water for use in this test should be deionized or soft water conditioned to 22-24°C. Fresh water should be used for each set of samples, i.e., for each lot of test samples.

Test Conditions - Testing must be conducted in a controlled temperature and humidity environment of 21-25°C and 45-55% relative humidity.

APPARATUS

A. Sled - A 304 stainless steel half round cylinder 4.92 cm (1 15/16") diameter by 2.54 cm (1.000") wide and 2.54 cm (1.000") high with a 4-40 0.5" thread in one end into which an Instron part no. T53-5 eye screw is fastened. Material is added or removed from the top of the sled so as to adjust the weight to 200 ± 0.5 g. The radiused face of the sled is polished to a No. 4 finish.

B. Test Fixture - The Instron Coefficient of Friction Fixture (Catalog No. 2810-005) was modified to accommodate testing of casting materials. Specifically, the pulley assembly was raised 2.54 cm (1.000") and an additional Teflon™ coated brass tension pulley .953 cm (0.375") in diameter x 13.34 cm (5.25") was fixed to the end of the table opposite the load pulley and positioned such that the top of the pulley was in the plane of the table. In addition, a 12.7 cm (5") x .953 cm (.375") x .953 cm (.375") hold down clamp was positioned 7.62 cm (3.0") from the load pulley in order to fix the test specimen in place. A series of weights fixed to spring clamps were fabricated in order to keep the test specimen in tension. The proper weight is determined by the width of the test sample, 0.045 kg/cm (1/4 lb/inch) (e.g., with a 7.62 cm (3") wide test specimen a 1.65 kg (3/4 lb) weight should be used).

C. Force Measuring Device - An Instron Model No. 1122 Table top measuring instrument equipped with a 50 lb. load cell (Instron assembly No. A-30-39) and connected to an Instron Microcon II microprocessor Model No. MC4100.

PREPARATION OF APPARATUS

1. Assemble the apparatus as described above.
2. Set the drive speed of the sled (i.e. the crosshead speed) to 127 cm (50 inches)/min.
3. Calibrate the 50 lb. load cell using a 500 g weight.
4. The following settings on the control panel of the Instron Model No. 1122 measuring device should be set:

crosshead speed	= 127 cm (50 in)/min
full scale load	= 0-500 g
chart speed	= 12.7 cm (5 in)/min auto
load cell filter	= in
polarity	= up

The Microcon II microprocessor should be set to the following:

area	= 0
gage length	= 2.54 cm (1.0 inch)
speed	= 127 cm (50 in)/min
fail criteria	= 100%
load limit	= 45,360 K grams force
elongation	= 100%
crosshead stop	= off
elongation correction factor	= no correction

5. Set up the Microcon II microprocessor Model No. MC4100 to integrate the tension force for travel between 1.27 cm and 19.0 cm (0.5 and 7.5 inches) and to calculate the average tension force. Be sure the first 1.27 cm (0.5") of travel is not included in this calculation to avoid incorporating the static frictional force.

PROCEDURE

The following procedure is appropriate for water-activated casting materials which set, i.e. resist passive motion in about three to five minute. The water immersion time and subsequent waiting time to initiation of sled movement may require adjustment if the set time of the material to be tested is substantially different from three to five minutes. This procedure is also used to determine coefficient of friction on dry material by eliminating the water immersion and subsequent waiting time.

1. Open the pouch containing the test specimen immediately cut the sample to obtain a length of from 46 cm to 61 cm (18 in. to 24 in.) and immediately immerse the sample into 3.8 liter (1 gallon) of fresh 22-24° C tap water without agitation of any kind. Start a stopwatch immediately upon immersion in the water.
2. After 15 seconds gently remove the test specimen (avoid any agitation) from the water and briskly shake the specimen twice to remove excess water.
3. While avoiding contact with the specimen as much as possible place the sample flat on the testing table and fix one end into the hold down clamp and attach the proper weight (0.045 kg/cm width) (1/4 lb/inch width) of tape to the free end.
4. 15 seconds after the specimen has been removed from the water, gently place the sled on the specimen such that the wire is straight without sagging and under 10-15 g tension.

5. Exactly 3 seconds after the sled has been placed on the specimen start the driving mechanism which was previously adjusted to a crosshead speed of 127 cm (50 inches)/min.
6. Record the average tension force calculated by the Microcon II microprocessor.
7. Remove the sled and immediately clean the polished sliding surface with a soft paper towel and a solution of 50% acetone and 50% ethanol. Allow the sled to dry.
8. Remove the test specimen, dry and clean off the table, tension pulley, and clamp. If necessary use the cleaning solution of step 7.

Reference Examples 1-6

Bound Lubricants

Reference Example 1

A 3.8 liter (one gallon) glass vessel equipped with a 12.7 cm x 2.54 cm x .318 cm (5x1x1/8") Teflon™ impeller, addition funnel, nitrogen purge line, and thermometer was assembled and purged with nitrogen for 30 minutes to ensure the entire apparatus was completely dry. The following chemicals were added to the reactor through the addition funnel in order and at 5 minute intervals:

Chemical	Wt (g)	Wt %
Isonate 143L (Upjohn Co.)	2151.7	58.15
Benzoyl Chloride	2.59	0.07
Pluronic F-108 (BASF)	148.0	4.00
DB-100 (Dow Chemical)	6.66	0.18
butylated hydroxy toluene (BHT)	17.76	0.48
PPG-425 (Union Carbide)	217.45	5.88
PPG-725 (Union Carbide)	1109.56	29.99
MEMPE	46.25	1.25

The agitation rate was gradually increased as the viscosity increased. The vessel was temporarily insulated with glass wool and the temperature of the reaction was allowed to increase (due to reaction exotherm) to 55° C. The glass wool was removed along with the agitator, thermometer, and addition funnel. The vessel was sealed and the resin was allowed to cool for 24 hours.

The resin was coated onto three inch wide knit fiberglass scrim as described in U.S. Serial No. 668,881, filed November 6, 1984, at a resin content of 42.5% by weight. The coated fabric was converted to individual rolls 3.66 m (12 feet) in length. These rolls were packaged individually into moisture proof pouches. Ten days after coating two of the rolls were unpackaged in a 2% relative humidity environment and cut to 61 cm (24 inch) lengths and resealed individually in the moisture-proof pouches.

Each 60.96 cm (24") sample was then tested according to the KCOF method described above. The samples were found to have an mean kinetic coefficient of friction of 0.29.

Reference Example 2

The following resin was prepared, coated and packaged according to the procedure of Example 1:

Chemical	Wt (g)	Wt%
Isonate™ 143 L (Upjohn Co.)	2183	59.0
Benzoyl Chloride	2.6	.07
Brij™ 700 (ICI Americas Inc.)	148.0	4.0
DB-100 (Dow Chemical)	6.7	.18
BHT	17.8	.48
PPG-425 (union Carbide)	270.1	7.3
PPG-725 (Union Carbide)	1016.4	27.5
MEMPE	55.5	1.5
Note: Brij 700 is a polyoxyethylene (avg. 100) stearyl ether		

This material was tested according to the KCOF method and exhibited a mean kinetic coefficient of friction of 0.28.

Reference Example 3

The following resin was prepared, coated and packaged according to the procedure of Reference Example 1:

Chemical	Wt (g)	Wt %
Isonate 143L	2045	58.4
Benzoyl Chloride	2.5	.07
PEG 8000	157.5	4.5
DB-100	6.3	.18
BHT	16.8	.48
PPG-425	280.9	8.0
PPG-725	947.1	27.1
MEMPE	43.75	1.25
Note: PEG-8000 is a polyethylene glycol, having a molecular weight of approx. 8000.		

This material was tested according to the KCOF method and exhibited a mean kinetic coefficient of friction of 0.27.

Reference Example 4

A hydrophilic oligomeric diol was prepared by reacting dried polyethylene oxide glycol (available from Union Carbide as Carbowax^R 1000) with dried dimethyl sodium sulfoisophthalate in a 4:1 molar ratio at about 220-250 °C in the presence of a catalytic amount of zinc acetate. This diol, in an amount of 15,164 g, was combined with 1920 grams of trimethylol propane and the mixture was dried by azeotroping with toluene. This was then charged directly into a nitrogen purged vessel containing 26,559 grams of Isonate 143L, 218 g of BHT and 25 g of ethanesulfonic acid. After mixing for about 2 hours at about 60-80 °C, the product was transferred to several 3.785 liter (one gallon) glass jars and sealed under a nitrogen blanket.

One jar containing 4222 grams of the above sulfonated urethane resin was heated at 65 °C (150 °F) for about two hours and then 42 grams of 2,2'-dimorpholinodiethyl ether was mixed in. In a dry room with the humidity held at about 2% relative humidity the resin was then coated onto three inch wide knit fiberglass scrim as previously described at a resin content of 39.9% by weight. The coated scrim was converted to twelve foot lengths by rerolling onto polyethylene cores and cutting to length. These rolls were packaged individually in moisture-proof pouches.

Five months after coating samples were tested according to the KCOF method. These samples were found to have a mean kinetic coefficient of friction of 0.46.

Reference Example 5

About one month after coating the scrim in the Example 4 several rolls of this material were sprayed on both sides at a coating weight of 3.4 g/m² of polydimethylsiloxane 200 - 100 cs (Dow Corning) in a dry room with the relative humidity held at about 2%. Each length of material was rerolled and sealed in a moisture-proof pouch.

After about 4 months several samples were tested according to the KCOF method and were found to have an average kinetic coefficient of friction of 0.40. In addition, one sample was tested dry according to the KCOF method, i.e., it was not immersed in water. This sample was found to have a mean kinetic coefficient of friction of 0.32.

Reference Example 6

A hydrophilic, oligomeric diol, was prepared by reacting dried polyethylene oxide glycol (Carbowax^R 600) with dried dimethyl sodium sulfosophthalate in a 2:1 molar ratio, at 220°-250° C, in the presence of a catalytic amount of zinc acetate. This diol, in the amount of 71.0 grams (.11 eq.) was combined with 128.0 grams (.59 eq.) PPG-425 and 49.0 grams (.10 eq.) PPG-1025. To the stirred mixture, under a nitrogen sweep, was added 3.1 grams BHT, .46 grams benzoyl chloride, 13.3 grams 2,2'-dimorpholinodiethyl ether and 403.0 grams (2.80 eq.) Isonate 143L. The reaction mixture was allowed to exotherm and stirring was continued for 2 hours while the resin cooled.

The resin was coated and packaged according to the procedure of Reference Example 1 except that the resin content was 42% by weight. Samples were tested according to the KCOF method and exhibited a mean coefficient of friction of 0.31.

Examples 1-8Polysiloxane Lubricants

In the following Examples, the fluid was sprayed on 7.6 cm (3") casting tape available from 3M as SCOTCHCASTTM 2 comprising a knit fiberglass scrim impregnated with an isocyanate-functional prepolymer resin. Spraying was accomplished using either a modified air-brush or a Spraying Systems, Wheaton, IL., atomizing 1/4 J spray nozzle unless otherwise indicated. Both sides of the tape were sprayed. The amount of fluid per unit length of tape was controlled by the speed at which the tape was drawn past the sprayer as well as by regulating the flow rate of the spraying apparatus.

Example 1

Dow Corning 200-300 cs silicone fluid was sprayed on both surfaces of a casting tape as previously described at a total coating weight of 3.95 g/m². The resulting casting material was very easy to handle both before and after wetting. The sample was then tested according to the KCOF method. The samples exhibited a mean kinetic coefficient of friction of 0.52.

Example 2

Dow Corning 200-500 cs silicone fluid was sprayed on both sides of a casting tape or previously described at a coating weight of 3.2 g/m². The mean kinetic COF was 0.62.

Example 3

Dow Corning 200-100 cs silicone fluid containing 5% wt/wt Aerosol OT (dioctylsulfosuccinate sodium salt) was sprayed on both sides of a casting tape as previously described at a coating weight of 3.2 g/m². The mean kinetic COF was 0.45.

Example 4

Dow Corning 200-50 cs silicone fluid containing 12.3% wt/wt Keloloid O was sprayed on both sides of a casting tape as previously described at a coating weight of 4.3 g/m² roll. The mean kinetic COF was 0.52.

Example 5

A tertiary structured polydimethylsiloxane with carboxypropyl groups at the branch points (avail. from Petrarch Systems Inc. as PS-402) was sprayed onto both sides of a casting tape as previously described at a total coating weight of 3.6 g/sq. meter. This material was tested for its lubricating properties according to the procedure of KCOF method and was found to have a mean kinetic coefficient of friction of 0.49.

Example 6

A (95-98%) methyldecyl (2-5%) aryloxymethylsiloxane copolymer available from Petrarch Systems Inc. as PS136 was sprayed onto both surfaces of casting tape as previously described at a total coating weight of 3.41 g/sq. meter. This material was tested for its lubricating properties according to the KCOF method and was found to have a mean kinetic coefficient of friction of 0.49.

Example 7

A polydimethyl 3,3,3 trifluoropropylsiloxane available from Petrarch Systems as PS181 was sprayed onto both sides of casting tape as previously described at a total coating weight of 2.33 g/sq. meter. This material was tested for its lubricating properties according to the KCOF method and was found to have a mean kinetic coefficient of friction of 0.69.

Example 8

A (83-85%) dimethyl (15-17%) diphenylsiloxane vinyl terminated copolymer available from Petrarch Systems, Inc. as PS782 was sprayed onto both sides of casting tape as previously described at a total coating weight of 3.2 g/sq. meter. This material was tested for its lubricating properties according to the KCOF method and was found to have a mean kinetic coefficient of friction of 0.55.

Examples 9 and 10Polymers Comprised of Hydrophilic GroupsExample 9

Cyanomer™ A370 (a polyacrylamide available from American Cyanamide) was coated onto a casting tape available from 3M as Scotchcast 2 in Examples 1-8 using a vibratory screen at a coating weight of 4.8 g/m². The resulting casting tape was tested according to the KCOF method and found to have a mean kinetic coefficient of friction of 0.32.

Example 10

A 115,000 molecular weight polyvinyl alcohol available from Aldrich Chemicals, (P.N. 18251-6) was coated onto casting tape as previously described in Examples 1-8 according to the procedure of Example 9, below at a coating weight of 4.2 g/m². The resulting casting tape was tested according to the KCOF method and found to have been a mean kinetic coefficient of 0.42.

Examples 11-21Surfactant Lubricants

In the following examples the surfactant(s) or surfactant/silicone fluid combination was sprayed, except as noted, on the surface of a casting tape, which tape was previously described in Examples 1-8. An air brush was used to spray on the material. In most cases it was necessary to spray on the material in a hot molten state in which case the material solidified almost instantaneously upon expansion and exit from the nozzle. Both sides of the casting material were coated with equivalent amounts.

Example 11

Casting tape as previously described in Examples 1-8 was evenly coated with Metarin™ P (a 95% phosphatides lecithin composition available from Lucas Meyer Inc., Decatur, Ill.) at a coating weight of 3.6 g/m². The Metarin P was deposited on the casting tape using a vibratory screen. This resulting casting tape was tested according to the KCOF method and found to have a mean kinetic coefficient of friction of 0.19.

Example 12

Sodium dodecyl sulfate was coated onto a casting tape as previously described in Examples 1-8 according to the procedure of Example 15 at a coating weight of 3.6 g/m². The resulting casting tape was tested according to the KCOF method and found to have a mean kinetic coefficient of friction of 0.23.

Example 13

The following resin was prepared, coated and packaged according to the procedure of Reference Example 1 except that the Standopol™ 125E (available from Henkel Corp.) was first dried to remove water.

Chemical	Wt. (g)	Wt. %
Isonate™ 143L	1435.5	52.5
Benzoyl Chloride	1.9	.07
DMDEE (Texaco)	77.38	2.83
DB-100	5.0	.18
BHT	12.72	0.47
PPG-725	1117.5	40.9
Standopol™ 125E*	82.0	3.0
(Standopol™ 125E is the sodium sulfonate of a 12 mole ethylene oxide lauryl ether available from Henkel Corp.)		

This material was tested according to the KCOF method and exhibited a mean kinetic COF 0.35.

Example 14

Generol™ 122E-25 was sprayed on both surfaces of a casting tape at a coating weight of 3.2-3.6 g/m². The resulting casting material was very slippery when wet. The mean kinetic COF was 0.25.

Example 15

Tergitol™ 15-S-40 dispersed in Dow Corning 200-100 cs silicone oil (1:1 w/w) was sprayed on both surfaces of a casting tape at a coating weight of 3.6 g/m². The product was both non-tacky dry and very slippery when wet. The mean kinetic COF was 0.31.

Example 16

Tergitol™ NP-40 was sprayed on the both surfaces of a casting tape as previously described in Examples 1-8 at a coating weight of 3.6 g/m. The mean kinetic COF was 0.27.

Example 17

Brij 58™ and Brij™ 78 were sprayed on both surfaces of separate rolls of a casting tape as previously described in Examples 1-8 at coating weights of 3.6 and 3.8 g/m². The mean kinetic COF of each were 0.32 and 0.37 respectively.

Example 18

Ethospense™ CA20 was sprayed on both surfaces of a casting tape as previously described in Examples 1-8 at a total coating weight of 3.2-2.6 g/sq. meter. The mean kinetic COF was determined to be 0.26.

Example 19

Anhydrous Neodol™ 3A (ammonium salt of a 3 mol ethoxylated laureth sulfate) was added in a molten state to hot Dow silicone 200-100 cs fluid to 50% wt/wt and the resulting mixture sprayed on both surfaces of a casting tape as previously described in Examples 1-8 at coating weight of 3.6 g/m². The mean kinetic COF was 0.43.

Example 20

Anhydrous Standopol™ 125E (sodium salt of a 12 mole ethoxylated laureth sulfate) was also added in a molten state to hot Dow silicone 200-100 cs fluid to 50% wt/wt both sides of a casting tape as previously described in Examples 1-8 at coating weight of 2.7-3.2 g/m² and sprayed on casting tape. The mean kinetic COF was 0.38.

Example 21

The following resin formulation was prepared and converted according to the procedure of Reference Example 1. The slip additive, Zonyl™ UR available from E.I. duPont de Nemours & Co. Wilmington, Delaware, is a mixture of polyfluoroaliphatic ethoxylated phosphonates having the general structure $(-FCH_2CH_2)_{3-8}(OCH_2CH_2)_{1,2}OP(OH)_{2,1}$.

Chemical	Wt. g	Wt. %
Isonate™ 143L (Upjohn)	1083.3	50.8
Benzoyl Chloride	1.4	.07
Dimorpholinodiethyl ether (DMDEE)	58.4	2.74
DB-100 (Dow Chemical)	3.6	.17
BHT	9.6	.45
PPG-725 (Union Carbide)	843.3	39.5
Zonyl™ UR (DuPont)	134.4	6.3

The resulting casting material was tested according to the KCOF method and found to have a mean kinetic COF of 0.93.

Combination LubricantsExample 22

The casting material was produced according to the procedure of Reference Example 1 except that during the converting operation the coated scrim was sprayed with Dow polydimethylsiloxane 200-100 cs. The spraying was done using an air atomising nozzle at approximately 2.65 g/m² applied to each side of the casting tape. When tested according to the KCOF method the samples were found to have a mean kinetic coefficient of friction of 0.33.

Comparative Examples A and B

The following resin was prepared, coated and packaged according to the procedure of Example 1:

Chemical	Wt (g)	Wt %
Isonate™ 143L (Upjohn Co.)	2046.10	55.30
Benzoyl Chloride	3.68	.10
PPG-725 (Union Carbide)	1582.85	43.05
Dimethyl Ethanolamine	9.28	.25
Niax™ A-99 (Union Carbide)	11.14	.30
LK-221 (Air Products)	36.94	1.00

This material was tested according to the KCOF method and exhibited a mean kinetic COF of 2.06.
The following resin was prepared, coated and packaged according to the procedure of Example 1:

Chemical	Wt (g)	Wt %
Isonate™ 143L (Upjohn Co.)	2046.10	55.30
Benzoyl Chloride	3.70	.10
DB-100 (Dow Chemical)	37.00	1.00
PPG-725 (Union Carbide)	1592.85	43.05
Dimethylethanolamine	9.25	.25
Niax™ A-99 (Union Carbide)	11.10	.30

This material was tested according to the KCOF method and exhibited a mean kinetic COF of 1.76.

It has been found that the tack of a given isocyanate-functional prepolymer tends to peak during cure. Accordingly, prepolymers which have a longer set time than those exemplified herein, may not exhibit kinetic COF as high as those of Comparative Examples A and B because cure has not progressed sufficiently at the time specified in the foregoing test procedure. Therefore, the relative rate of cure of prepolymers tested according to the foregoing method should be considered when comparing results of the test for prepolymer systems having variable rates of cure.

Example 23

The following example illustrates the advantage and synergism between the use of both a topical silicone treatment and a lubricating agent (Pluronic F108) added to the resin system.

The following resin was prepared and converted according to the procedure of Example 1.

Chemical	wt. g	wt (%)
Isonate™ 143L	2162.6	58.5
Benzoyl Chloride	2.6	.07
Pluronic F108	148.1	4.0
DB-100	6.7	0.18
BHT	17.8	.48
PPG-425	270.2	7.3
PPG-725	1045.9	28.3
MEMPE	46.3	1.25

The resulting coating material was tested according to the KCOF method with the omission of the water dip (Procedure step 2), i.e., the casting material was tested in a "dry" state. The mean kinetic coefficient was determined to be 2.18.

A casting material prepared according to the procedure above was sprayed with Dow 200-100 centistoke silicone fluid according to the procedure of Example 28. The resulting orthopedic bandage was tested for its lubricating properties in a "dry" state according to the procedure of Example A. The mean kinetic coefficient of friction was found to be 0.80.

The mean kinetic coefficient of the silicone sprayed material wetted in accordance with the KCOF method was 0.33.

Claims

1. An orthopedic article comprising a prelubricated, flexible, casting material, said casting material comprising:
 - (1) a porous sheet;
 - (2) a water curable resin coated on said porous sheet, said resin being selected from isocyanate-functional prepolymers formed by reaction of an isocyanate with a polyol; and
 - (3) a lubricant additive comprising a polysiloxane, an ionic surfactant, a nonionic surfactant, a polyethoxylated surfactant, a polyethoxylated polymer, or a polymer comprised of a plurality of hydrophilic groups selected from the monomers: acrylamide, vinylpyrrolidone, vinylacetate and its hydrolyzed derivatives, and hydroxy and amino functional lower alkyl acrylates;whereby the kinetic coefficient of friction of a major surface of the coated sheet is less than 1.2.
2. An orthopedic article according to claim 1 wherein the lubricant additive (3) is a mixture of any of a polysiloxane, a surfactant, a polyethoxylated polymer and a polymer comprised of a plurality of hydrophilic groups.
3. An orthopedic article according to claims 1 or 2 wherein additionally the water curable resin (2) contains covalently bonded hydrophilic groups.
4. An orthopedic article according to any one of claims 1 to 3 wherein the porous sheet is a knitted fiberglass fabric.
5. An orthopedic article according to claims 1 or 2 wherein the additive is a surfactant selected from an alkyl, aryl or aralkyl ionic compound.
6. An orthopedic article according to claims 1 or 2 wherein the additive is an alkyl sulfate surfactant.
7. An orthopedic article according to claims 1 or 2 wherein the additive is a polyethoxylated surfactant.
8. An orthopedic article according to claims 1 or 2 wherein the additive is an anionic surfactant.
9. An orthopedic article according to claims 1 or 2 wherein the additive is a polysiloxane having a viscosity of at least about 50 cs.
10. An orthopedic article according to claim 9 wherein the additive is a polydimethylsiloxane.
11. An orthopedic article according to claim 3 wherein polyethyleneoxide groups are covalently bonded to the water-curable resin and the additive is a polysiloxane.
12. An orthopedic article according to claim 11 wherein the polyethylene oxide groups are derived from an ethylene oxide/propylene oxide copolymer which is solid at ambient temperature.
13. An orthopedic article according to claims 1, 3 and 12 wherein the isocyanate-functional prepolymer is derived from
 - a) an aromatic polyisocyanate and b) a mixture of polyether polyols comprised of a copolymer of polypropylene oxide and polyethylene oxide, and an additive comprising a polydimethylsiloxane is deposited on at least one surface of the resin-coated porous sheet.
14. An orthopedic article according to claim 3 wherein sulfonate groups are covalently bonded to the prepolymer.
15. An orthopedic article according to claims 1, 3 and 14 wherein the prepolymer is derived from a polyisocyanate and a poly(ethyleneoxide) glycol ester of a sulfophthalic acid.

16. An orthopedic article according to claim 3 wherein polyethylene oxide groups are covalently bonded to the prepolymer and the amount by weight of polyethylene oxide is less than 15 %, preferably less than 10 % and most preferably less than 6 % by weight of the resin.
- 5 17. An orthopedic article according to claim 3 wherein the hydrophilic groups are derived from a polyethoxylated fatty alcohol.
18. An orthopedic article according to claim 3 wherein the hydrophilic functional groups covalently bonded to the water curable resin are derived from
 - 10 1) alkali metal salts of sulfated or sulfonated polyesters or polyethers,
 - 2) quaternary ammonium salts containing carbamates derived from polyesters or polyethers,
 - 3) alkali metal salts of phosphonated or phosphated polyesters or polyethers, or
 - 4) polyethylene oxide.
- 15 19. An orthopedic article according to claim 7 wherein the surfactant is a polyethoxylated fatty alcohol which is solid at room temperature.
20. An orthopedic article according to claim 3 wherein at least 70 %, more preferably at least 85 %, and most preferably at least 95 % by weight of the curable resin (2) composition is retained on the coated sheet when the sheet is immersed in water and squeezed several times while immersed.
- 20 21. An orthopedic article according to claim 1 or 7 wherein the additive is a nonylphenol polyethylene glycol ether.
- 25 22. A method of forming an orthopedic article comprising the step of depositing on a major surface of a flexible sheet which has been coated with a resin or mixing with the resin before applying the resin to the sheet, a lubricant additive comprising a polysiloxane, an ionic surfactant, a nonionic surfactant, a polyethoxylated surfactant, a polyethoxylated polymer, or a polymer comprised of a plurality of hydrophilic groups selected from the monomers: acrylamide, vinylpyrrolidone, vinylacetate and its hydrolyzed derivatives, and hydroxy and amino functional lower alkyl acrylates; whereby the kinetic coefficient of friction of said major surface is less than 1.2, said resin being water-curable and comprising an isocyanate-functional prepolymer.
- 30 23. A method according to claim 22 wherein the lubricant additive is a mixture of any of a polysiloxane, a surfactant, a polyethoxylated polymer and a polymer comprised of a plurality of hydrophilic groups.
- 35 24. A method according to claims 22 or 23 wherein additionally the water curable resin contains covalently bonded hydrophilic groups.
- 40 25. A method according to any one of claims 22 to 24 wherein the porous sheet is a knitted fiberglass fabric.
26. A method according to claims 22 or 23 wherein the additive is a surfactant selected from an alkyl, aryl or aralkyl ionic compound.
- 45 27. A method according to claims 22 or 23 wherein the additive is an alkyl sulfate surfactant.
28. A method according to claims 22 or 23 wherein the additive is a polyethoxylated surfactant.
- 50 29. A method according to claims 22 or 23 wherein the additive is an anionic surfactant.
30. A method according to claims 22 or 23 wherein the additive is a polysiloxane having a viscosity of at least about 50 cs.
- 55 31. A method according to claim 30 wherein the additive is a polydimethylsiloxane.
32. A method according to claim 24 wherein polyethylenoxide groups are covalently bonded to the water-curable resin and the additive is a polysiloxane.

33. A method according to claim 32 wherein the polyethylene oxide groups are derived from an ethylene oxide/propylene oxide copolymer which is solid at ambient temperature.
- 5 34. A method according to claims 22, 24 and 33 wherein the isocyanate-functional prepolymer is derived from
a) an aromatic polyisocyanate and b) a mixture of polyether polyols comprised of a copolymer of polypropylene oxide and polyethylene oxide, and an additive comprising a polydimethylsiloxane is deposited on at least one surface of the resin-coated porous sheet.
- 10 35. A method according to claim 24 wherein sulfonate groups are covalently bonded to the prepolymer.
36. A method according to claims 22, 24 and 35 wherein the prepolymer is derived from a polyisocyanate and a poly(ethyleneoxide) glycol ester of a sulfophthalic acid.
- 15 37. A method according to claim 24 wherein polyethylene oxide groups are covalently bonded to the prepolymer and the amount by weight of polyethylene oxide is less than 15 %, preferably less than 10 % and most preferably less than 6 % by weight of the resin.
- 20 38. A method according to claim 24 wherein the hydrophilic groups are derived from a polyethoxylated fatty alcohol.
39. A method according to claim 24 wherein the hydrophilic functional groups covalently bonded to the water curable resin are derived from
1) alkali metal salts of sulfated or sulfonated polyesters or polyethers,
25 2) quaternary ammonium salts containing carbamates derived from polyesters or polyethers,
3) alkali metal salts of phosphonated or phosphated polyesters or polyethers, or
4) polyethylene oxide.
- 30 40. A method according to claim 28 wherein the surfactant is a polyethoxylated fatty alcohol which is solid at room temperature.
41. A method according to claim 24 wherein at least 70 %, more preferably at least 85 % and most preferably at least 95 % by weight of the curable resin (2) composition is retained on the coated sheet when the sheet is immersed in water and squeezed several times while immersed.
- 35 42. A method according to claim 28 wherein the additive is a nonylphenol polyethylene glycol ether.

Patentansprüche

- 40 1. Orthopädischer Artikel, umfassend ein vorgeschmiertes, elastisches Gießmaterial, umfassend:
(1) eine poröse Lage;
(2) ein wasserhärtbares Harz, mit dem die poröse Lage beschichtet ist, wobei das Harz ausgewählt ist aus Isocyanat-funktionellen Prepolymeren, gebildet durch Reaktion eines Isocyanats mit einem Polyol; und
45 (3) ein Schmiermitteladditiv, umfassend ein Polysiloxan, ein ionisches Tensid, ein nicht-ionisches Tensid, ein polyethoxyliertes Tensid, ein polyethoxyliertes Polymer, oder ein Polymer, umfassend eine Vielzahl hydrophiler Gruppen, ausgewählt aus den Monomeren Acrylamid, Vinylpyrrolidon, Vinylacetat und dessen hydrolysierten Derivaten und Hydroxy- und Amino-funktionellen Niederalkyl-acrylaten;
50 wobei der kinetische Reibungskoeffizient einer Hauptfläche der beschichteten Lage kleiner als 1,2 ist.
2. Orthopädischer Artikel nach Anspruch 1, wobei das Schmiermitteladditiv (3) eine Mischung aus irgendeinem Polysiloxan, einem Tensid, einem Polyethoxylierten Polymer und einem Polymer, umfassend eine Vielzahl hydrophiler Gruppen ist.
- 55 3. Orthopädischer Artikel nach den Ansprüchen 1 oder 2, wobei zusätzlich das wasserhärtbare Harz (2) covalent gebundene hydrophile Gruppen enthält.

4. Orthopädischer Artikel nach irgendeinem der Ansprüche 1 bis 3, wobei die poröse Lage ein gewirktes Glasfasergewebe ist.
5. Orthopädischer Artikel nach den Ansprüchen 1 oder 2, wobei das Additiv ein Tensid ist, ausgewählt aus einer ionischen Alkyl-, Aryl- oder Aralkyl-Verbindung.
6. Orthopädischer Artikel nach den Ansprüchen 1 oder 2, wobei das Additiv ein Alkylsulfat-Tensid ist.
7. Orthopädischer Artikel nach den Ansprüchen 1 oder 2, wobei das Additiv ein polyethoxyliertes Tensid ist.
8. Orthopädischer Artikel nach den Ansprüchen 1 oder 2, wobei das Additiv ein anionisches Tensid ist.
9. Orthopädischer Artikel nach den Ansprüchen 1 oder 2, wobei das Additiv ein Polysiloxan mit einer Viskosität von wenigstens etwa 50 cs ist.
10. Orthopädischer Artikel nach Anspruch 9, wobei das Additiv ein Polydimethylsiloxan ist.
11. Orthopädischer Artikel nach Anspruch 3, wobei die Polyethylenoxid-Gruppen covalent an das wasserhärtbare Harz gebunden sind und das Additiv ein Polysiloxan ist.
12. Orthopädischer Artikel nach Anspruch 11, wobei die Polyethylenoxid-Gruppen von einem Ethylenoxid/Propylenoxid-Copolymer abgeleitet sind, das bei Umgebungstemperatur fest ist.
13. Orthopädischer Artikel nach den Ansprüchen 1, 3 und 12, wobei das Isocyanat-funktionelle Prepolymer abgeleitet ist von a) einem aromatischen Polyisocyanat und b) einer Mischung aus Polyetherpolyolen, umfassend ein Copolymer von Polypropylenoxid und Polyethylenoxid, und ein Additiv, umfassend ein Polydimethylsiloxan, auf wenigstens einer Oberfläche der harzbeschichteten porösen Lage abgeschieden ist.
14. Orthopädischer Artikel nach Anspruch 3, wobei Sulfonat-Gruppen covalent an das Prepolymer gebunden sind.
15. Orthopädischer Artikel nach den Ansprüchen 1, 3 und 14, wobei das Prepolymer abgeleitet ist von einem Polyisocyanat und einem Poly(ethylenoxid)glycolester einer Sulfophthalsäure.
16. Orthopädischer Artikel nach Anspruch 3, wobei die Polyethylenoxid-Gruppen covalent an das Prepolymer gebunden sind und die Menge Polyethylenoxid sich auf weniger als 15 Gew.-%, vorzugsweise weniger als 10 Gew.-% und meistbevorzugt weniger als 6 Gew.-% des Harzes beläuft.
17. Orthopädischer Artikel nach Anspruch 3, wobei die hydrophilen Gruppen von einem polyethoxylierten Fettalkohol abgeleitet sind.
18. Orthopädischer Artikel nach Anspruch 3, wobei die covalent an das wasserhärtbare Harz gebundenen hydrophilen funktionellen Gruppen abgeleitet sind von
 - 1) Alkalimetall-Salzen sulfatierter oder sulfonierter Polyester oder Polyether,
 - 2) quartären Ammonium-Salzen, enthaltend Carbamate, die von Polyestern oder Polyethern abgeleitet sind,
 - 3) Alkalimetall-Salzen phosphonierter oder phosphatierter Polyester oder Polyether, oder
 - 4) Polyethylenoxid.
19. Orthopädischer Artikel nach Anspruch 7, wobei das Tensid ein polyethoxylierter Fettalkohol ist, der bei Raumtemperatur fest ist.
20. Orthopädischer Artikel nach Anspruch 3 wobei wenigstens 70 Gew.-%, vorzugsweise wenigstens 85 Gew.-% und meistbevorzugt wenigstens 95 Gew.-% der Zusammensetzung des härtbaren Harzes (2) auf der beschichteten Lage zurückgehalten wird, wenn diese in Wasser eingetaucht und während des Eintauchens mehrere Male gedrückt wird.

21. Orthopädischer Artikel nach Anspruch 1 oder 7, wobei das Additiv ein Nonylphenolpolyethylenglycol-ther ist.
22. Verfahren zur Bildung eines orthopädischen Artikels, umfassend den Schritt, daß auf einer Hauptfläche
5 einer elastischen Lage, die mit einem Harz beschichtet wurde, ein Schmiermitteladditiv, umfassend ein Polysiloxan, ein ionisches Tensid, ein nicht-ionisches Tensid, ein polyethoxyliertes Tensid, ein polyet-
hoxyliertes Polymer, oder ein Polymer, umfassend eine Vielzahl hydrophiler Gruppen, ausgewählt aus
den Monomeren Acrylamid, Vinylpyrrolidon, Vinylacetat und dessen hydrolysierten Derivaten und
10 Hydroxy- und Amino-funktionellen Niederalcylacrylaten, abgeschieden oder dieses mit dem Harz vor
dem Auftragen des Harzes auf die Lage gemischt wird, wobei der kinetische Reibungskoeffizient einer
Hauptfläche der beschichteten Lage kleiner als 1,2 ist und das Harz wasserhärtbar ist und ein
Isocyanat-funktionelles Prepolymer umfaßt.
23. Verfahren nach Anspruch 22, wobei das Schmiermitteladditiv eine Mischung aus irgendeinem Polysilo-
15 xan, einem Tensid, einem polyethoxylierten Polymer und einem Polymer, umfassend eine Vielzahl
hydrophiler Gruppen ist.
24. Verfahren nach den Ansprüchen 22 oder 23, wobei zusätzlich das wasserhärtbare Harz covalent
gebundene hydrophile Gruppen enthält.
25. Verfahren nach irgendeinem der Ansprüche 22 bis 24, wobei die poröse Lage ein gewirktes Glasfaser-
20 gewebe ist.
26. Verfahren nach den Ansprüchen 22 oder 23, wobei das Additiv ein Tensid ist, ausgewählt aus einer
25 ionischen Alkyl-, Aryl- oder Aralkyl-Verbindung.
27. Verfahren nach den Ansprüchen 22 oder 23, wobei das Additiv ein Alkylsulfat-Tensid ist.
28. Verfahren nach den Ansprüchen 22 oder 23, wobei das Additiv ein polyethoxyliertes Tensid ist.
29. Verfahren nach den Ansprüchen 22 oder 23, wobei das Additiv ein anionisches Tensid ist.
30. Verfahren nach den Ansprüchen 22 oder 23, wobei das Additiv ein Polysiloxan mit einer Viskosität von
30 wenigstens etwa 50 cs ist.
31. Verfahren nach Anspruch 30, wobei das Additiv ein Polydimethylsiloxan ist.
32. Verfahren nach Anspruch 24, wobei die Polyethylenoxid-Gruppen covalent an das wasserhärtbare Harz
gebunden sind und das Additiv ein Polysiloxan ist.
33. Verfahren nach Anspruch 32, wobei die Polyethylenoxid-Gruppen von einem Ethylenoxid/Propylenoxid-
40 Copolymer abgeleitet sind, das bei Umgebungstemperatur fest ist.
34. Verfahren nach den Ansprüchen 22, 24 und 33, wobei das Isocyanat-funktionelle Prepolymer abgeleitet
45 ist von a) einem aromatischen Polyisocyanat und b) einer Mischung aus Polyetherpolyolen, umfassend
ein Copolymer von Polypropylenoxid und Polyethylenoxid, und ein Additiv, umfassend ein Polydime-
thylsiloxan, auf wenigstens einer Oberfläche der harzbeschichteten porösen Lage abgeschieden ist.
35. Verfahren nach Anspruch 24, wobei Sulfonat-Gruppen covalent an das Prepolymer gebunden sind.
36. Verfahren nach den Ansprüchen 22, 24 und 35, wobei das Prepolymer abgeleitet ist von einem
50 Polyisocyanat und einem Poly(ethylenoxid)glycolester einer Sulfophthalsäure.
37. Verfahren nach Anspruch 24, wobei die Polyethylenoxid-Gruppen covalent an das Prepolymer gebun-
55 den sind und die Menge Polyethylenoxid sich auf weniger als 15 Gew.-%, vorzugsweise weniger als 10
Gew.-% und meistbevorzugt weniger als 6 Gew.-% des Harzes beläuft.

38. Verfahren nach Anspruch 24, wobei die hydrophilen Gruppen von einem polyethoxylierten Fettalkohol abgeleitet sind.
39. Verfahren nach Anspruch 24, wobei die covalent an das wasserhärzbare Harz gebundenen hydrophilen funktionellen Gruppen abgeleitet sind von
- 1) Alkalimetall-Salzen sulfatierter oder sulfonierter Polyester oder Polyether,
 - 2) quartären Ammonium-Salzen, enthaltend Carbamate, die von Polyestern oder Polyethern abgeleitet sind,
 - 3) Alkalimetall-Salzen phosphonierter oder phosphatierter Polyester oder Polyether, oder
 - 4) Polyethylenoxid.
40. Verfahren nach Anspruch 28, wobei das Tensid ein polyethoxycierter Fettalkohol ist, der bei Raumtemperatur fest ist.
41. Verfahren nach Anspruch 24, wobei wenigstens 70 Gew.-%, vorzugsweise wenigstens 85 Gew.-% und meistbevorzugt wenigstens 95 Gew.-% der Zusammensetzung des härzbaren Harzes (2) auf der beschichteten Lage zurückgehalten wird, wenn diese in Wasser eingetaucht und während des Eintauchens mehrere Male gedrückt wird.
42. Verfahren nach Anspruch 28, wobei das Additiv ein Nonylphenolpolyethylenglycolether ist.

Revendications

1. Article orthopédique comprenant un matériau de moulage flexible, pré lubrifié, ledit matériau de moulage comprenant :
 - (1) une feuille poreuse ;
 - (2) une résine durcissable à l'eau revêtant ladite feuille poreuse, ladite résine étant choisie parmi les prépolymères à fonctionnalité isocyanate formés par réaction d'un isocyanate avec un polyol ; et
 - (3) un additif lubrifiant comprenant un polysiloxane, un tensio-actif ionique, un tensioactif non ionique, un tensio-actif polyéthoxylé, un polymère polyéthoxylé, ou un polymère comprenant une pluralité de groupes hydrophiles choisis parmi les monomères : acrylamide, vinylpyrrolidone, acétate de vinyle et ses dérivés hydrolysés, et les acrylates d'alkyle inférieur à fonctionnalités hydroxy et amino ;
 tel que le coefficient de friction cinétique d'une majeure partie de la feuille poreuse soit inférieur à 1,2.
2. Article orthopédique suivant la revendication 1, dans lequel l'additif lubrifiant (3) est un mélange d'un polysiloxane, d'un tensio-actif, d'un polymère polyéthoxylé et/ou d'un polymère comprenant une pluralité de groupes hydrophiles.
3. Article orthopédique suivant l'une quelconque des revendications 1 et 2, dans lequel la résine durcissable à l'eau (2) contient en outre des groupes hydrophiles liés par covalence.
4. Article orthopédique suivant l'une quelconque des revendications 1 et 3, dans lequel la feuille poreuse est une étoffe tricotée en fibres de verre.
5. Article orthopédique suivant l'une quelconque des revendications 1 et 2, dans lequel l'additif est un tensio-actif choisi parmi un composé ionique alkyle, aryle ou aralkyle.
6. Article orthopédique suivant l'une quelconque des revendications 1 et 2, dans lequel l'additif est un tensio-actif alkylsulfate.
7. Article orthopédique suivant l'une quelconque des revendications 1 et 2, dans lequel l'additif est un tensio-actif polyéthoxylé.
8. Article orthopédique suivant l'une quelconque des revendications 1 et 2, dans lequel l'additif est un tensio-actif anionique.

9. Article orthopédique suivant l'une quelconque des revendications 1 et 2, dans lequel l'additif est un polysiloxane ayant une viscosité d'au moins 50 cs (i.e. d'au moins $5 \cdot 10^{-5}$ m²/s).
10. Article orthopédique suivant la revendication 9, dans lequel l'additif est un polydiméthylsiloxane.
11. Article orthopédique suivant la revendication 3, dans lequel des groupes poly(oxyde d'éthylène) sont liés par covalence à la résine durcissable à l'eau et l'additif est un polysiloxane.
12. Article orthopédique suivant la revendication 11, dans lequel les groupes poly(oxyde d'éthylène) proviennent d'un copolymère oxyde d'éthylène/oxyde de propylène qui est solide à la température ambiante.
13. Article orthopédique suivant l'une quelconque des revendications 1, 3 et 12, dans lequel le prépolymère à fonctionnalité isocyanate provient a) d'un polyisocyanate aromatique et b) d'un mélange de polyéther-polyols comprenant un copolymère de poly(oxyde de propylène) et de poly(oxyde d'éthylène), et un additif comprenant un polydiméthylsiloxane est déposé sur au moins une surface de la feuille poreuse revêtue de résine.
14. Article orthopédique suivant la revendication 3, dans lequel les groupes sulfonate sont liés par covalence au prépolymère.
15. Article orthopédique suivant l'une quelconque des revendications 1, 3 et 14, dans lequel le prépolymère provient d'un polyisocyanate et d'un ester de poly(oxyde d'éthylène)glycol avec un acide sulfophtalique.
16. Article orthopédique suivant la revendication 3, dans lequel les groupes poly(oxyde d'éthylène) sont liés par covalence au prépolymère et la quantité pondérale de poly(oxyde d'éthylène) est inférieure à 15 %, de préférence inférieure à 10 % et mieux inférieure à 6% en poids de la résine.
17. Article orthopédique suivant la revendication 3, dans lequel les groupes hydrophiles proviennent d'un alcool gras polyéthoxylé.
18. Article orthopédique suivant la revendication 3, dans lequel les groupes fonctionnels hydrophiles liés par covalence à la résine durcissable à l'eau proviennent de
 - 1) sels de métaux alcalins de polyesters ou de polyéthers sulfatés ou sulfonates,
 - 2) sels d'ammonium quaternaire contenant des carbamates et provenant de polyesters ou de polyéthers,
 - 3) sels de métaux alcalins de polyesters ou de polyéthers phosphonates ou phosphates, ou
 - 4) poly(oxyde d'éthylène).
19. Article orthopédique suivant la revendication 7, dans lequel le tensio-actif est un alcool gras polyéthoxylé qui est solide à la température ambiante.
20. Article orthopédique suivant la revendication 3, dans lequel au moins 70 %, de préférence au moins 85 % et mieux au moins 95 % en poids de la composition de résine durcissable (2) est retenue sur la feuille revêtue quand la feuille est immergée dans l'eau et pressée plusieurs fois à l'état immergé.
21. Article orthopédique suivant l'une quelconque des revendications 1 et 7, dans lequel l'additif est un nonylphénol polyéthylèneglycol éther.
22. Procédé pour la préparation d'un article orthopédique comprenant l'étape de déposition sur la majeure partie d'une feuille flexible qui a été revêtue d'une résine ou de mélange avec la résine avant application de la résine sur la feuille, d'un additif lubrifiant comprenant un polysiloxane, un tensio-actif ionique, un tensio-actif non ionique, un tensio-actif polyéthoxylé, un polymère polyéthoxylé, ou un polymère comprenant une pluralité de groupes hydrophiles choisi parmi les monomères : acrylamide, vinylpyrrolidone, acétate de vinyle et ses dérivés hydrolysés, et les acrylates d'alkyle inférieur à fonctionnalités hydroxy et amino ; le coefficient de friction cinétique d'une majeure partie de la feuille poreuse étant inférieur à 1,2 et ladite résine étant durcissable à l'eau et comprenant un prépolymère à

fonctionnalité isocyanate.

23. Procédé suivant la revendication 22, dans lequel l'additif lubrifiant est un mélange d'un polysiloxane, d'un tensio-actif, d'un polymère polyéthoxylé et/ou d'un polymère comprenant une pluralité de groupes hydrophiles.
24. Procédé suivant l'une quelconque des revendications 22 et 23, dans lequel la résine durcissable à l'eau contient en outre des groupes hydrophiles liés par covalence.
25. Procédé suivant l'une quelconque des revendications 22 et 24, dans lequel la feuille poreuse est une étoffe tricotée en fibres de verre.
26. Procédé suivant l'une quelconque des revendications 22 et 23, dans lequel l'additif est un tensio-actif choisi parmi un composé ionique alkyle, aryle ou aralkyle.
27. Procédé suivant l'une quelconque des revendications 22 et 23, dans lequel l'additif est un tensio-actif alkylsulfate.
28. Procédé suivant l'une quelconque des revendications 22 et 23, dans lequel l'additif est un tensio-actif polyéthoxylé.
29. Procédé suivant l'une quelconque des revendications 22 et 23, dans lequel l'additif est un tensio-actif anionique.
30. Procédé suivant l'une quelconque des revendications 22 et 23, dans lequel l'additif est un polysiloxane ayant une viscosité d'au moins 50 cs (i.e. d'au moins $5 \cdot 10^{-5}$ m²/s).
31. Procédé suivant la revendication 30, dans lequel l'additif est un polydiméthylsiloxane.
32. Procédé suivant la revendication 24, dans lequel des groupes poly(oxyde d'éthylène) sont liés par covalence à la résine durcissable à l'eau et l'additif est un polysiloxane.
33. Procédé suivant la revendication 32, dans lequel les groupes poly(oxyde d'éthylène) proviennent d'un copolymère oxyde d'éthylène/oxyde de propylène qui est solide à la température ambiante.
34. Procédé suivant l'une quelconque des revendications 22, 24 et 33, dans lequel le prépolymère à fonctionnalité isocyanate provient a) d'un polyisocyanate aromatique et b) d'un mélange de polyéther-polyols comprenant un copolymère de poly(oxyde de propylène) et de poly(oxyde d'éthylène), et un additif comprenant un polydiméthylsiloxane est déposé sur au moins une surface de la feuille poreuse revêtue de résine.
35. Procédé suivant la revendication 24, dans lequel les groupes sulfonate sont liés par covalence au prépolymère.
36. Procédé suivant l'une quelconque des revendications 22, 24 et 35, dans lequel le prépolymère provient d'un polyisocyanate et d'un ester de poly(oxyde d'éthylène)glycol avec un acide sulfophtalique.
37. Procédé suivant la revendication 24, dans lequel les groupes poly(oxyde d'éthylène) sont liés par covalence au prépolymère et la quantité pondérale de poly(oxyde d'éthylène) est inférieure à 15 %, de préférence inférieure à 10 % et mieux inférieure à 6% en poids de la résine.
38. Procédé suivant la revendication 24, dans lequel les groupes hydrophiles proviennent d'un alcool gras polyéthoxylé.
39. Procédé suivant la revendication 24, dans lequel les groupes fonctionnels hydrophiles liés par covalence à la résine durcissable à l'eau proviennent de
 - 1) sels de métaux alcalins de polyesters ou de polyéthers sulfatés ou sulfonés,

2) sels d'ammonium quaternaire contenant des carbamates et provenant de polyesters ou de polyéthers,

3) sels de métaux alcalins de polyesters ou de polyéthers phosphonates ou phosphates, ou

4) poly(oxyde d'éthylène).

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40. Procédé suivant la revendication 28, dans lequel le tensio-actif est un alcool gras polyéthoxylé qui est solide à la température ambiante.

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41. Procédé suivant la revendication 24, dans lequel au moins 70 %, de préférence au moins 85 % et mieux au moins 95 % en poids de la composition de résine durcissable est retenue sur la feuille revêtue quand la feuille est immergée dans l'eau et pressée plusieurs fois à l'état immergé.

42. Procédé suivant la revendication 28, dans lequel l'additif est un nonylphénol polyéthylèneglycol éther.

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Title CURABLE RESIN COATED SHEET HAVING REDUCED TACK

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