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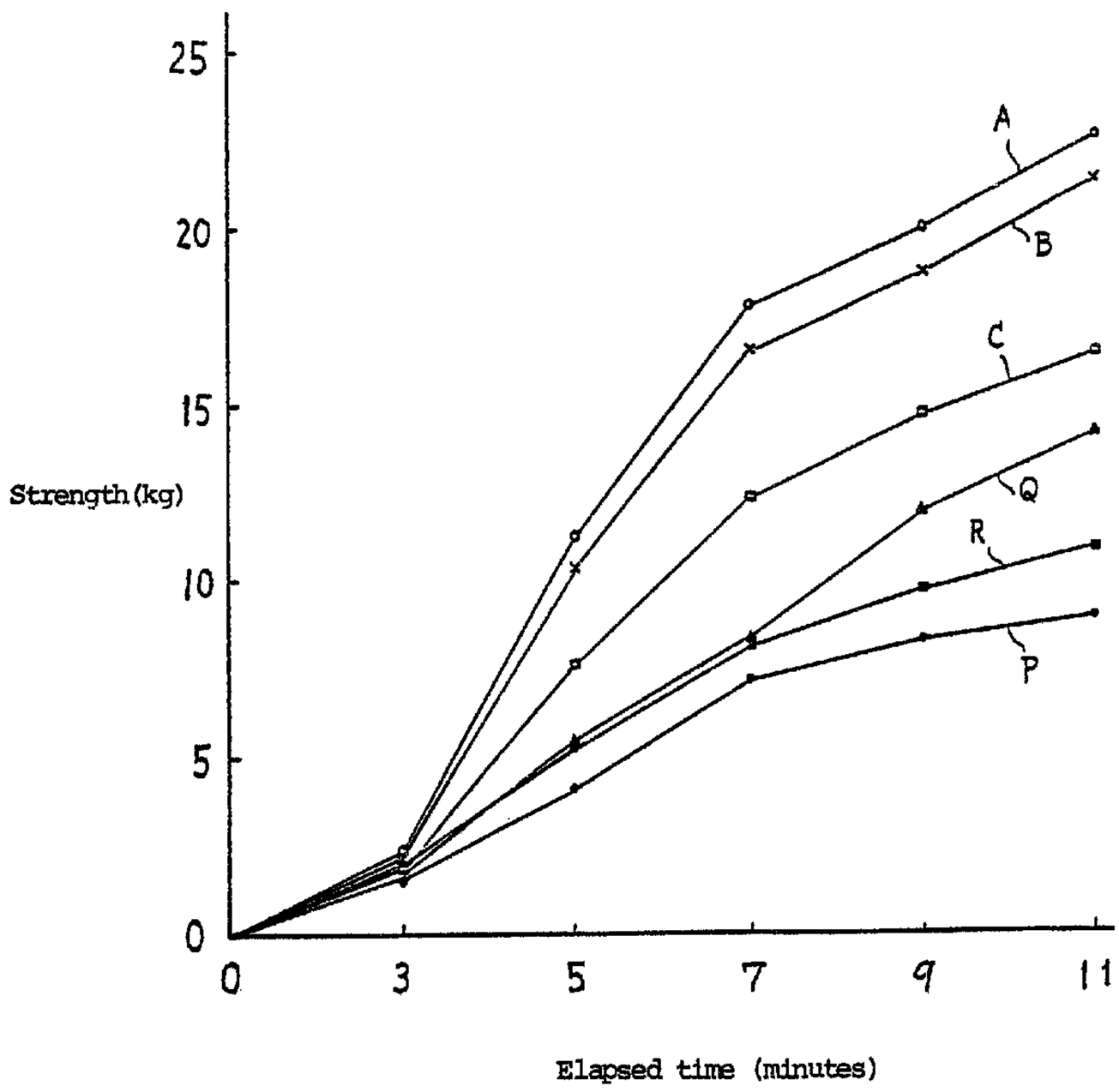

(57) Abrégé/Abstract:
(Purpose) To obtain a water-curable supporting bandage constituted in such a manner that its storage stability is retained over a long period of time, and said supporting bandage has the characteristic that, while it is being applied to the diseased part of a patient's body, the curing thereof proceeds slowly, but thereafter, said supporting bandage rapidly cures. (Constitution) A flexible fabric is coated with a water-curable polyurethane resin composition containing a polyurethane prepolymer consisting of a polyol and a polyisocyanate, a catalyst and a stabilizer, wherein said polyol contains a polyetylene glycol and a bisphenol system diol.

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ABSTRACT

(Purpose) To obtain a water-curable supporting bandage constituted in such a manner that its storage stability is retained over a long period of time, and said supporting bandage has the characteristic that, while it is being applied to the diseased part of a patient's body, the curing thereof proceeds slowly, but thereafter, said supporting bandage rapidly cures.

(Constitution) A flexible fabric is coated with a water-curable polyurethane resin composition containing a polyurethane prepolymer consisting of a polyol and a polyisocyanate, a catalyst and a stabilizer, wherein said polyol contains a polyetylene glycol and a bisphenol system diol.

(Selected Drawing) None

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SPECIFICATION

TITLE OF THE INVENTION: Water-curable supporting bandage

(Industrial Field of Utilization)

The present invention relates to a water-curable supporting bandage used for fixing and treating the diseased parts of surgical and orthopedic patients.

(Prior Art)

A water-curable supporting bandage used in such a manner that a tape-

shaped or a sheet-shaped fabric coated with a water-curable polyurethane resin composition is contacted with water and applied to the diseased part of a patient, so that the water-curable polyurethane resin composition applied onto the fabric is reacted with the water to cure or harden has many advantages as compared with conventional plaster bandages using plaster of Paris and thus is being generally used, taking the place of the conventional plaster bandages. Since the polyurethane resin composition used for said water-curable supporting bandage particularly largely sways the physical properties of the water-curable supporting bandage, various researches and developments have so far been made on polyurethane resin compositions, as a result of which various kinds of compositions are known at present.

The polyurethane resin composition used for a water-curable supporting bandage starts, upon contact with water, to perform a curing reaction, so that the flexible water-curable supporting bandage gradually cures, as a result of which, at the time of applying the water-curable supporting bandage to the diseased part of a patient, it cannot be rewound if said water-curable supporting bandage is in the form of a roll, and its shape cannot be changed for adjustment if said supporting bandage is in the form of a sheet. As the curing reaction further proceeds, the supporting bandage comes to have such a strength that the shape of said supporting bandage is not changed even if some load is applied to it; and when said reaction is completed, said supporting bandage comes to possess a still higher strength. A water-curable supporting bandage for orthopedic treatment is required to cure in a short time, so that, in turn, the polyurethane resin composition is required to have a very high activity to moisture. On the other hand, the water-curable supporting bandage is required to possess a storage stability over a long period, that is, while it is preserved or stored in a hermetically sealed container, its curing must not proceed.

The process of applying the water-curable supporting bandage to the

diseased part of a patient comprises the following steps:

(1) The step of applying to the diseased part the water-curable supporting bandage which is already contacted with water. (This time zone will hereinafter be referred to as working time.)

(2) The step of partially correcting, in other words, modelling, the water-curable supporting bandage which has thus been applied to the diseased part. (This time zone will hereinafter be referred to as modelling time.)

(3) The step of maintaining or keeping the thus modelled water-curable supporting bandage until its curing proceeds into the state in which a load can be applied to said supporting bandage. (This time zone will hereinafter be referred to as weight-bearing time.)

(4) The step in which the curing of the water-curable supporting bandage further proceeds into a perfectly cured state.

To examine the relationship between the strength of the water-curable supporting bandage which has undergone the abovementioned steps and the time, the following becomes clear: The step (1) is the step of wrapping the water-curable supporting bandage to the diseased part, in which case, if the diseased part is a part having a particularly complicated shape, a certain length of time is required for the application of the water-curable supporting bandage. If, during this period, the curing of the water-curable polyurethane resin composition proceeds too fast and, thus, the water-curable supporting bandage cures too fast, then it becomes impossible for the water-curable supporting bandage to be correctly applied to the predetermined position; and therefore, during the shortest possible length of time which is considered to be necessary for applying the water-curable supporting bandage, the strength of the water-curable supporting bandage should desirably be kept as

low as possible. The working time required should desirably be about 2.5 minutes to 3.5 minutes though it varies with the degree of skill of the operating doctor and the part of the patient's body to which the water-curable supporting bandage is applied. Next, in the step (2), the water-curable supporting bandage applied to approximately the correct position in the step (1) is only partially corrected, so that, if the strength of the water-curable supporting bandage is maintained at a low value for an excessively long time, then it follows that, even if, in an attempt to make a shape correction, a force is applied to the water-curable supporting bandage to thereby model it into the accurately correct shape, said water-curable supporting bandage is restored to its original shape before the correction thereof was made, when the application of the force is stopped, due to its restoring force of the water-soluble supporting bandage and/or the elasticity of the patient's body. Thus, too much time and labor are required for finishing the final modelling of the water-curable supporting bandage. Therefore, it is desirable that, after the application of the water-curable supporting bandage is over, the strength of said water-curable supporting bandage should be greatly increased. In the step (3), the modelling is already over, and the water-curable supporting bandage is disposed at the correct position as a whole, so that it is necessary to keep the diseased part of the patient immovable until the water-curable supporting bandage cures into such a state that an ordinary load can be applied thereto. Therefore, the strength of the water-curable supporting bandage should desirably increase as fast as possible. Further, in the step (4), in order to shorten the time during which both the patient and the doctor must be engaged or involved in the medical treatment, it is desirable for the water-curable supporting bandage to perfectly cure or harden as soon as possible and for the strength of the thus cured supporting bandage to reach the highest possible value. That is, it is ideal for the water-curable supporting bandage to possess such a curing reaction characteristic that the strength of the water-curable supporting bandage can be kept at a low value during the manipulation

period during which the water-curable supporting bandage is applied to the diseased part, and then, during the subsequent modelling period, said strength can abruptly increase and keep sharply increasing thereafter on to bring the water-curable supporting bandage into a perfectly cured state, thus finally reaching a high value.

In connection with the abovementioned requirements, the following can be pointed out concerning the typical polyurethane resin compositions used in conventional water-curable supporting bandages: In Japanese Laid-Open Patent Publication No. S54-100181, there is disclosed a resin composition consisting of 10 to 70 weight % of a -NCO group-containing prepolymer which is obtained by reacting a polymer compound containing a hydroxyl group or an active methylene group or a primary or secondary amino group with an oxycarbonyl isocyanate-free multifunctional isocyanate and of 90 to 30 weight % of a low-viscosity isocyanate monomer or oligomer containing two or more -NCO groups within molecule. This resin composition, which contains no catalyst, has the drawback that said resin composition is slow in curing though said resin composition has an excellent storage stability. In Japanese Laid-Open Patent Publication No. S57-148951, there is disclosed a polyurethane resin composition which contains a prepolymer having isocyanate groups at the terminals thereof and two or more functional groups and a catalyst, wherein said prepolymer is a water-absorbing prepolymer, and said catalyst is soluble in water but insoluble in said prepolymer. This polyurethane resin composition is improved but still insufficient in respect of the curability or curing characteristics, and moreover, said polyurethane resin composition is inferior in storage stability, which is another disadvantage. In Japanese Laid-Open Patent Publication No. S54-100181, there is disclosed a resin which comprises an aromatic polyisocyanate and a polyol at an equivalent ratio of 2 : 1 to 15 : 1 and contains, as a catalyst, dimolpholinodiethylether of 0.1 to 10 weight % based

on the prepolymer. This polyurethane resin composition is excellent in respect of storage stability and curability, but said resin composition has the drawback that it cures very fast, allowing only a short working time. Japanese Laid-Open Patent Publication No. S62-87162 discloses the fact that, in a curable resin, a hydrophilic group covalently bonded to the curable resin or a lubricant such as an additive which is not compatible with the curable resin is contained, so that the dynamic friction coefficient of the surface of the curable resin is set at to 1.2 or less. This curable resin is directed to preventing the resin composition from tackily sticking at the time of performing a medical treatment. Since the prepolymer in this case is a prepolymer which is composed mainly of polypropylene glycol, a large amount of catalyst must be used in order to enhance the curability, and the working time is relatively short, which is the drawback of this resin composition. Japanese Laid-Open Patent Publication No. S62-172008 proposes a polyurethane prepolymer composition containing a polyurethane prepolymer and a tertiary amine catalyst and, in addition, methanesulfonic acid as a stabilizer. This composition is improved in respect of the storage stability but has the drawback that said composition sticks to the operator's gloves and needs to contain a relatively large amount of the catalyst. In Japanese Laid-Open Patent Publication No. H3-41116, there is proposed a polyurethane resin composition which comprises a polyurethane prepolymer consisting of a polyol and a polyisocyanate, a catalyst, a stabilizer and an ester compound of a polyethylene glycol. This composition is lessened in the degree of tackily sticking to the operator's gloves but not satisfactory in respect of the curing characteristics. In Japanese Laid-Open Patent Publication No. H3-503611, there is proposed an isocyanate functional resin which contains the respective residues of (a) a polyethylene glycol, (b) a triol or a tetrol having a molecular weight of 200 or less, and (c) an aromatic isocyanate, wherein the weight ratio between (a + b) and (c) is 1:1 or less. This resin has a low adhesion and an excellent curing

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characteristics, but, since a low-molecular and tri- or higher-functional polyol is used, said resin has the drawback that the storage stability and the working time thereof are inferior. In Japanese Laid-Open Patent Publication No. H4-120117, there is proposed a polyurethane resin composition which comprises a polyol and a polyisocyanate, wherein, as the polyol, there is used a specific bisphenol system diol of at least 1 weight % based on the components of the polyol. This polyurethane resin composition is further improved in respect of the storage stability but remains unsatisfactory in respect of the curing characteristics.

(Problems that the Invention is to solve)

The many polyurethane resin compositions which have so far been proposed have both merits and demerits of their own as pointed out above; and thus, there have not been yet obtained a polyurethane resin composition which is satisfactory in respect of both the storage stability and the curing characteristics.

It is the object of the present invention to provide a water-curable supporting bandage which retains its storage stability over a long period of time and has such an ideal curing characteristics that, when the supporting bandage is applied, the curing reaction is effected as mentioned above.

(Means of Solving the Problems)

In order to achieve the abovementioned object, the water-curable supporting bandage according to the present invention is constituted in such a manner that a flexible fabric is coated with a water-curable polyurethane resin composition which contains a polyurethane prepolymer consisting of a polyol and a polyisocyanate, a catalyst, and a stabilizer, wherein the polyol cotnains a polyethylene glycol and a bisphenol system diol.

The content of the polyethylene glycol and the bisphenol system diol in

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the components of the polyol is desirably at least 50 weight % or higher based on the components of the polyol. It is because, if said content is less than 50 weight %, the abovementioned curing characteristics cannot be obtained.

The compounding proportion between the polyethylene glycol and the bisphenol system diol in the components of the polyol varies with the kind of the bisphenol system diol used but should desirably lie within the range of from 1 : 0.2 to 1 : 5. If said compounding ratio is outside of this range, the strength of the water-curable supporting bandage, the storage stability thereof are lowered and the amount of heat produced during the curing thereof is large.

As the flexible fabric used in the present invention, there can be used a knitted fabric, a woven fabric or an unwoven fabric composed of a material which has a low moisture regain and a high tensile strength and is unreactive and wettable with the polyurethane resin composition. As an example of such a knitted fabric, a woven fabric and an unwoven fabric, there can be pointed out a knitted fabric, a woven fabric or an unwoven fabric which is composed of, for instance, glass fibers, alamide fibers, polyester fibers, polyolefin fibers, polyamide fibers, polyacryl fibers, rayon fibers, or cotton fibers. Of these material fabrics, a particularly suitable one is the fabric made in such a manner that aggregates (threads) of glass fibers or polyester fibers are raschel-knitted into a fabric with a thickness of 0.08 to 5.0 mm and a mesh size of 3 to 30 meshes/cm^2. More concretely, the base fabrics proposed by the present applicant in Japanese Laid-Open Patent Publication Nos. H6-277249, S60-242851, H2-71746, etc. can be used.

The polyurethane prepolymers usable in the present invention are those

which are each obtained by reacting a polyol with a polyisocyanate and have isocyanate groups at the terminals.

The polyols usable in the present invention each comprise a polyethylene glycol and a bisphenol system diol as indispensable components, but other polyols such as for instance polypropylene glycols, random or block copolymers of ethylene oxides and propylene oxides can also be used.

The polyethylene glycol is obtained by adding an ethylene oxide to an ethylene glycol at a temperature of from 100 to 180 ℃ in the presence at a catalyst. The average molecular weight of the polyethylene glycol is normally 200 or higher, but a water-curable supporting bandage using a polyethylene glycol with a molecular weight smaller than 1000 tends to produce, when it cures, a heat higher than a water-curable supporting bandage using a polyethylene glycol with a molecular weight larger than 1000. Thus, a polyethylene glycol with a molecular weight less than 1000 should desirably be used in as small an amount as possible. On the other hand, in the case of a water-curable supporting bandage using a polyethylene glycol with a molecular weight higher than 1000, the rigidity thereof after it has cured is low. Therefore, the use of such a polyethylene glycol with a molecular weight higher than 1000 should also desirably be avoided in view of the rigidity. As a result, it becomes necessary to select a suitable mixture of a low-molecular PEG and a high-molecular PEG in view of the generated heat and the rigidity. The polyethylene glycols ordinarily sold at the market often contain the catalyst which was used for the synthesis thereof. Therefore, it is necessary to previously remove such a catalyst or neutralize it by adding a mineral acid such as for instance sulfuric acid or hydrochloric acid or a stabilizer to be described later.

As for the bisphenol series diol, it is obtained in such a manner that, to a bisphenol such as bisphenol A, bisphenol F, bisphenol B or the like, an

alkylene oxide is added in the presence of a catalyst at a temperature of 100 to 180 ℃. As said alkylene oxide, there can be pointed out an ethylene oxide, a propylene oxide, a butylene oxide or the like. A suitable or desirable bisphenol system diol is the ethylene and/or propylene oxide adducts of bisphenol A. The number of mol addition of the alkylene oxide to the bisphenol system diol is 2 or more. The adduct of 2 to 3 mol of ehylene oxide and the adduct of 2 to 30 mol of propylene oxide are effective for an improvement in the storage stability of the polyurethane prepolymer. The amount of the bisphenol in the bisphenol system diol which is required for improving the storage stability of the urethane prepolymer composition is ordinarily 2.5% or higher and, more preferably 5% or higher, based on the polyurethane resin composition. If the amount of the bisphenol system diol is less than 2.5%, the storage stability cannot be sufficiently improved. In the case of using the bisphenol system diol for purposes other than the improvement of the storage stability, bisphenol system diols with the mol addition numbers outside of the range mentioned above can also be used.

The usable average molecular weight of the polyol obtained by blending a polyethylene glycol with a bisphenol system diol is 400 to 2000 and, more preferably 500 to 800. A polyurethane resin composition using a polyol with an average molecular weight less than 400 is hard yet brittle when it is cured, and thus, it cannot be used for a supporting bandage. On the other hand, a polyurethane resin composition using a polyol with an average molecular weight of 2000 or higher is too soft when it is cured and thus not suited in use for a supporting bandage, either.

As the polyisocyanate, a hitherto known aromatic polyisocyanate can be used. As more desirable polyisocyanates, there can be pointed out 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, polymethylene polyphenylene polyisocynate, and such polyisocyanates modified by carbodiimide, etc. They can be used

singly or as a combination of two or more of them. Particularly desirable are 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, and such polyisocyanates modified by carbodiimide.

The compounding ratio of the polyol and the polyisocynate for obtaining a polyurethane prepolymer having isocyanate groups at the terminals thereof is normally 2 to 5 equivalents, and more preferably 2.5 to 5 equivalents, of the polyisocyanate per one equivalent of the polyol. The reaction between the two substances is achieved by stirring under heating, normally at 30 to 100℃ and more preferably 50 to 80℃. The viscosity of the polyurethane prepolymer is normally 10000 to 50000 cps and, more preferably 15000 to 40000 cps, at room temperature.

As the catalyst, any of those catalysts which are excellent in respect of the storage stability can be used. Such catalysts which have hitherto been well known are catalysts represented by dimolpholinodiethylether, bis(2,6-dimethylmolpholino) dietheylether, the substituted molpholinodiethylethers disclosed in Japanese Laid-Open Patent Publication No. S62-103071, etc.

These catalysts all can be used singly or in the form of a mixture of two or more of them. As for the amount of the catalyst used, the catalyst is added in such an amount that the working time of the water-curable supporting bandage may become about 2 to 3 minutes. Normally, the amount of the catalyst is 0.1 to 5.0 weight %, and more preferably 0.5 to 3 weight %, based on the polyurethane resin composition. If said catalyst amount is less than this value range, the working time becomes too long, while conversely if said catalyst amount is greater than said value range, the working time becomes too short.

As the stabilizer, benzoyl chloride, methanesulfonic acid or the like which has hitherto been known can be used. These stabilizers all can be used singly or in the form of a mixture of two or more of them. The amount

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of the stabilizer used is, though it varies with the amount of the catalyst used, normally 0.005 to 1 weight %, and more preferably 0.01 to 0.5 weight %, based on the polyurethane resin composition. If the amount of the stabilizer is less than 0.005 weight %, no stabilization effect is obtained, while if said stabilizer amount is more than 1 weight %, the activity of the catalyst is spoiled.

To the polyurethane resin composition according to the present invention, various kinds of additives such as an anti-foaming agent, an anti-oxidizing agent, a viscosity modifier, an adhesion inhibitor, an ultraviolet abosorbing agent, a coloring agent such as a pigment or dye, a filler such as calcium carbonate, titanium dioxide, carbon black, clay, etc. can also be added as required.

The manufacture of the polyurethane resin composition can be performed in such a manner that, to the urethane prepolymer obtained from a polyol and a polyisocyanate, a catalyst, a stabilizer, and various other additives are added, or that, when the urethane prepolymer is manufactured, a catalyst, a stabilizer, and various other additives are partially or wholly added beforehand together with a polyol and a polyisocyanate.

The manufacture of the water-curable supporting bandage by coating a flexible fabric with a polyurethane resin composition can be performed by use of a known method such as for instance the method according to which, in a room adjusted to a low humidity, the polyurethane resin composition is applied onto the fabric by means of rolls. The water-curable supporting bandage which can be obtained by coating the fabric with the polyurethane resin composition is preserved in a hermetically sealed state in a container which can be shut off from moisture, so that, when it is to be applied to the diseased part of a patient, the container is opend, and the water-curable supporting bandage is contacted with water and then applied to the diseased

part.

(Operation of the Invention)

The curing reaction mechanism of the water-curable supporting bandage according to the present invention cannot be clearly and accurately elucidated since various factors such as the kind and the amount of the catalyst, the reaction temperature, the hydrophilicity of the polyurethane resin composition, etc. are complicatedly entangled, but concerning this matter, it is possible to consider as follows:

That is, the polyethylene glycol as one component of the polyol in the polyurethane prepolymer is highly hydrophilic, so that, if the supporting bandage is dipped into water, then the amount of water necessary to cure the polyurethane resin composition quickly penetrates into the polyurethane resin composition, and the water uniformly spreads through the whole polyurethane resin composition, as a result of which the reaction of the water with the isocyanate groups takes place. The catalyst in the polyurethane resin composition promotes the reaction between the water and the isocyanate and, also, the curing thereof. Since the temperature of the polyurethane resin composition is raised due to the heat of reaction resulting from the reaction between the water and the isocyanate, the reaction speed or rate is further promoted, so that the water-curable supporting bandage cures in a short time. This process corresponds to the afore-said steps (2) and (3); and thus, it becomes possible to perform a modelling correctly, and a weight-bearingable state is brought about in a short time. Further, since the water necessary for the reaction can be retained in the surface of the supporting bandage, all the reactive groups react at the same time, so that the reaction is completed in a short time, as a result of which a supporting bandage with a high strength can be obtained. This process corresponds to the afore-mentioned step (4).

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On the other hand, a polyurethane prepolymer in which the polyol component thereof comprises only a polyethylene glycol is hydrophilic as compared with the polyurethane prepolymer comprising a polypropylene glycol and; therefore, the former is highly reactive with water, and the amount of the catalyst necessary for adjusting the curing time can be reduced. However, the resulting cured polyurethane resin is also hydrophilic and therefore retains the excess water content for long time, and the water-curable supporting bandage remains in a plasticized state until it is dried, and thus, the manifestation of its strength is delayed. Further, a polyurethane prepolymer comprising a polyethylene glycol is hydrophilic, and therefore, the reaction thereof with water is completed relaltively early, so that there is the tendency that the heat of reaction concentrates, and the temperature rise due to the generated heat increases. In particular, in the case of a polyurethane prepolymer comprising a polyethylene glycol with a molecular weight of 1000 or less, the temperature reached when the prepolymer cures tends to become high. It is considered that the reason therefor is related to the fact that, the lower the molecular weight of the polyetylene glycol used is, the higher the heat of solution is emitted when it dissolves into the water. Further, a polyurethane prepolymer formed from a polyethylene glycol is inferior in respect of the storage stability.

With reference to the abovementioned drawback, the bisphenol system diol used in the present invention can make an improvement without spoiling the advantageous point of the polyethylene glycol. If a (hydrophobic) bisphenol system diol with a molecular weight of 800 or less is used in place of the low-molecular polyethylene glycol, then the temperature reached in curing is lowered, and the manifestation of its strength can be quickened. This is considered to be due to the hydrophobicity resulting from the molecular structure of the bisphenol system diol. Such bisphenol system diol does not dissolve into water and emits scarecely any heat when it is mixed with water. It is considered that the manifestation of the strength is

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due to the fact that said diol is hydrophobic and, at the same time, each have benzene nucleuses within molecule, so that the strength is enhanced. Further, a compound composed in such a manner that a large amount of an ethylene oxide is added to a bisphenol can be used in place of the polyethylene glycol. Moreover, an alkylene oxide adduct with suitable mol number can improve the storage stability of the polyurethane resin composition.

(Working Examples)

Embodiments of the present invention will now be described in detail, referring to Comparative Examples. The materials used for the polyurethane resin compositions according to the embodiments of the present invention and those according to the comparative examples are shown in Table 1, while the recipes therefor are shown in Table 2. Further, the properties of the polyurethane resin compositions obtained in accordance with said recipes and the product evaluations thereof in the form of the water-curable supporting bandages obtained by applying said polyurethane resin compositions to base fabrics are set forth in Table 3 and Table 4.

The polyurethane resin compositions were all alike synthesized as follows in the cases of both the embodiments and the comparative examples:

In a reaction vessel which had the atmosphere inside thereof substituted with a nitrogen gas, a polyol component and a anti-foaming agent and an antioxidant agent were put; the water content was removed at a temperature of 80 to 120 ℃ ; a portion of the stabilizer was added; thereafter, a polyisocyanate component was added to effect a reaction at a temperature of 50 to 90 ℃ .; further, a catalyst and the remainder of the stabilizer were added; and the whole was stirred for about one hour, whereby a polyurethane resin composition was obtained. This polyurethane resin composition was put into a hermetically sealed vessel which had its internal

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atmosphere previously substituted with a nitrogen gas. As for the formation of water-curable supporting bandages, in the cases of both the embodiments of the present invention and the comparative examples, the water-curable supporting bandages were formed all alike by applying the respective polyurethane resin compositions to the same base fabric. More concretely, in each case, a glass fiber specified as EC751/01.0Z by JIS R3413 (1999) was raschel-knitted into a fabric with a width of 10 cm under the condition that the density was 14 warps/inch and 15 wefts/inch, and the weight per unit area of the fabric was 310 g/m^2, and the thus obtained tape-shaped raschel-knitted fabric was subjected to a heat cleaning. This sheet-shaped fabric was used as a flexible fabric. The application of the polyrethane resin composition to this fabric was carried out in a workroom maintained under a low-temperature environment in such a manner that the polyurethane resin composition was applied to about 210 g/m^2 by use of the roll coater method. The fabric to which the resin was thus applied was wound up over a length of 1.8 m, whereby a water-curable supporting bandage was made and enclosed into a moisture-impermeable bag which previously had the atmosphere within substituted with a nitrogen gas.

The properties of the above-mentioned polyurethane resin compositions and the water-curable supporting bandages were evaluated as follows in each case:

* Viscosity

A sample of the polyurethane resin composition with its temperature adjusted to 20℃ was measured by a B type viscometer using a No. 4 rotor at a velocity of 12 rpm.

* Storage stability

About 50 ml of the polyurethane resin composition was collected into a polypropylene bottle of 100 ml in a nitrogen gas atmosphere, and then, the

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bottle was heremetically sealed, kept in a constant-temperature dryer with the temperature of 130℃; and the time spent until the fluidability of the polyurethane resin composition became zero was measured.

* Working time

In a measuring room with its temperature adjusted to 25℃, a water-curable supporting bandage with the width of 10 cm was taken out from the moisture-impermeable bag, dipped into a water with a temperature of 20℃ for 10 seconds and then, after the water was lightly swished off from the supporting bandage, the supporting bandage was wound or rolled around a cylinder, and the time when the rolling of the thus wound or rolled bandage could not be done any more was measured.

* Heat generation temperature

In the measuring room with its room temperature adjsuted to 25℃, a water-curable supporting bandage with a width of 10 cm was taken out from the moisture-impermeable bag and dipped into a water with a temperature of 20℃, and then, the water was lightly swished off from the supporting bandage. Around a polyethylene container into which water was previously put and warmed to 36℃, the above-mentioned water-curable supporting bandage was wound, and, on the third turn or layer of the thus wound bandage, a thermocouple was placed, and then, on said third turn or layer, the bandage was further wound so as to form three more turns or layers. Then, the highest heat generation temperature then was measured.

* Variation in strength due to the lapse of time

The water-curable supporting bandage was taken out from the bag, and the water-curable supporting bandage roll thus taken out was unrolled without applying any tention to it and cut to 60 cm. Six such cut pieces of the supporting bandage were prepared and laid one on the top of another, taking care to ensure that the six bandage pieces would not shifted in the

width direction thereof and that the front surface of each piece would be opposed to the rear surface of the other adjacent piece. Then they were, in this state, enclosed into the bag which preveiously had the atmosphere therein substituted with a nitrogen gas. By use of the thus formed product as a specimen, the subsequent operations were performed. Since it was considered that, in the operation carried out so far, the water component in the air might have reacted with the resin, it was determined that the operation was to be finished within 2 minutes 30 seconds after the bag was opened under the condition that the room temperature was 20℃, and the humidity was 20% RH or lower. By use of the above-mentioned specimen, the measurement was carried out in a measuring room in which the temperature was adjusted to 20℃ and the humidity was adjusted to 50 to 70 % RH. The temperature of the specimen used was adjusted to 20℃. The specimen was placed on a metal net made of stainless steel and dipped, without stirring, into running water which was adjusted to 20℃. After 10 seconds, the specimen was calmly drawn out from the water, and the speciment was shaken to swish off the extra water therefrom. A release paper was laid down on a testing stand (manufactured by EISSHIN Corporation) with its temperature adjusted to 30℃, and, on the release paper thus laid down, the specimen was placed and spread flat, taking care not to apply a pressure higher than necessary. In this case, care should also be taken to ensure that, between the respective adjacent laminated pieces of bandage constituting the specimen, no gap or clearance would be formed. On the specimen thus spread, a further release paper was laid, and a weight which was adjusted in such a manner that, after 60 seconds, a load of 500 g per 100 cm^2 might be applied was put and left in this state for 2 minutes. After 3, 5, 7, 9, and 11 minutes respectively, measurements were made by use of an autographic recorder AG-D (a computer measurement and control type universal testing machine) manufactured Shimadzu Corporation. As for the measuring method, the measurement was carried out in accordance with JIS K7203. As testing condtions, the inter-fulcrum distance was set at 5 cm,

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the area of each test piece was 100 cm^2, the testing speed or rate was set at 25 mm/min, and the chart speed or rate was set at 25 mm/min.

* Compression strength exhibited after one day

The water-curable supporting bandage was dipped into water with a temperature of 20℃ at a room temperature of 20℃ for 10 seconds; and then the water-curable supporting bandage was lightly grasped and shaken three times to swish water off and wound, into three turns or layers, around a stainless steel pipe with a diameter of 60.5 mm around which a release paper was previously wound. After the winding of the bandage was completed, the operator rotated the thus wound bandage by holding it with both hands and further rubbed the surface of the bandage. After 15 minutes, the bandage was drawn out from the stainless steel pipe, taking care to ensure that the bandage might not be deformed. After being left to stand in a constant-temperature device of 20 ℃ for one day, said bandage was compressed in the radial direction by a compression test machine (the crosshead speed: 25 mm/min), and the stress when the bandage was deformed by 5 mm was measured.

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(Table 1)

Name	Contents		
Polyol components			
PEG 400	Sanyo Chemical Industries, Ltd.,	PEG 400™	(Average molecular weight 400)
PEG 700	Sanyo Chemical Industries, Ltd.,	PEG 700™	(Average molecular weight 700)
PEG 2000	Sanyo Chemical Industries, Ltd.,	PEG 2000™	(Average molecular weight 2000)
PEG 4000	Sanyo Chemical Industries, Ltd.	PEG 4000S™	(Average molecular weight 3300)
BP-23	Sanyo Chemical Industries, Ltd.,	Newpol BP-23P™	(Average molecular weight 360)
BP-600	Sanyo Chemical Industries, Ltd.,	Newpol BP-600™	(Average molecular weight 600)
BPE-20	Sanyo Chemical Industries, Ltd.,	Newpol BPE-20™	(Average molecular weight 360)
BPE-180	Sanyo Chemical Industries, Ltd.,	Newpol BPE-180™	(Average molecular weight 1000)
PPG-400	Sanyo Chemical Industries, Ltd.,	PPG 400™	(Average molecular weight 400)
Polyisocyanate components			
MDI	Dow Mitsubishikasei Limited	Isonate 125 M™	
Modified MDI	Dow Mitsubishikasei Limited	Isonate 143 L™	
Catalyst			
BDM	Bis-4-(2,6-dimethylmolpholino)ethylether		
Stabilizer			
MSA	Methanesulfonic acid		
Anti-foaming agent			
Byk	BYK-Chemie Japan KK	Byk-A525™	

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(Table 2)

	Embodiments					Comparative Examples			
	1	2	3	4	5	1	2	3	4
Content of the PEG and the bisphenol system diol in the polyol components	100	100	100	100	50	0	33	100	100
Ratio of the bisponel system diol to the PEG	0.63	1.04	0.36	3.1	0.68		0.25	0.0	0.15
Polyol									
PEG 400	53	95		39	26		20	248	120
700	110		218		55		50		155
2000	17	37							
4000S	60	60	59	60	30		20	59	60
BP 23	50		99		25				50
600	100	200			50		50		
BPE 20				80					
180				227					
PPG 400					25	50	30		
700					201	400	250		
Average molecular weight	627	645	622	690	629	646	653	481	567
Polyisocyanate									
MDI	475	472	483	521	500	525	485		479
Modified MDI	119	118	120	58	59	0		680	120
Catalyst BDM	13.5	15.0	12.0	12.0	15.8	18.0	12.7	12.7	12.0
Stabilizer MSA	0.7	0.65	0.65	0.65	0.65	0.65	0.65	0.7	0.65
Anti-foaming agent Byk	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

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(Table 3)

	Embodiments					Comparative Examples			
	1	2	3	4	5	1	2	3	4
Viscosity (cps)	23500	23000	21400	22500	20700	2140	22000	24300	20700
Storage stability (hours)	76	75	74	76	59	52	55	41	42

(Table 4)

	Embodiments					Comparative Examples			
	1	2	3	4	5	1	2	3	4
Working time (minutes, seconds)	2'15"	2'22"	2'25"	2'18"	2'30"	2'25"	2'15"	1'15"	2'30"
Temperature when heat is generated (℃)	38.1	39.8	39.9	38.8	39.8	38.0	38.7	42.5	41.3
Strength after the lapse of time									
3minutes (kg)	2.3	2.1	2.1	2.2	2.0	1.6	1.7	2.0	2.0
5minutes (kg)	11.2	10.3	10.7	10.5	7.7	4.1	5.4	5.3	5.5
7minutes (kg)	17.8	16.5	17.0	16.8	12.3	7.1	8.3	8.2	8.7
9minutes (kg)	20.2	18.8	17.2	19.0	14.8	8.2	12.0	9.8	10.7
11minutes (kg)	22.5	21.3	22.7	20.1	16.4	8.9	14.1	10.9	11.3
Strength afte one day	9.9	8.9	9.0	10.9	9.4	9.5	10.1	7.8	8.5

Fig. 1 shows the relationship between the strength exhibited by the water-curable supporting bandages and the elasped time with reference to Embodiments 1, 2 and 5 of the present invention and Comparative Examples 1, 2 and 3. In Fig. 1, A, B and C stand for the characteristic curves of the Embodiments 1, 2 and 3, while P, Q and R stand for the characteristic curves of the Comparative Examples 1, 2 and 3.

Embodiment 1 was constituted as follows: The respective components of the polyol were blended in such a manner that the sum of the PEG and the bisphenol system diol was 10%, and the compounding ratio between the PEG and the bisphenol system diol lay within the range of 1 : 0.2 to 1 : 5.0. This resin composition and the water-curable supporting bandange have the following advantageous points due to their characteristics: The viscosity was 23500 cps, so that the resin composition could be appplied to the base fabric at room temperature, and the resin thus applied was hard to separate from the fabric. Thus, a stabilized water-curable supporting bandage could be obtained. Further, the storage stability was 76 hours, so that the product, i.e. the water-curable supporting bandage could be preserved for a long time, and any special place was not needed as a place for the preservation thereof. This water-curable supporting bandage had a working time of 2 minutes 15 seconds and could therefore be applied to the diseased part of a patient's body sufficiently. This length of time was sufficiently long to allow the water-curable supporting bandage to be applied even to a complicated part of the patient's body by use of the ordinary casting technique. After the working time elapsed, the strength of the water-curable supporting bandage rapidly increased; and thus, the water-curable supporting bandage rapidly lost its plasticity, so that it became possible for the water-curable supporting bandange to be kept in the modelled shape thereof. That is, while the strength of the water-curable supporting bandage immediately after the laspe of the working time was 2.3 kg, said strength reached 11.2 kg after five

minutes. In addition, in spite of the fact that said strength was thus increased by a rapid curing reaction effected after the lapse of the working time, the heat generation temperature was 38.1℃, so that there was caused no undesirable effect such as for instance the patient being scalded. Further, nine minutes later, said strength became 20.0 kg or higher, and thus, the loading of the body weight became possible.

Embodiments 2, 3 and 4 were constituted as follows: Of the polyol components, the sum of the PEG and the bisphenol system diol was 100 %, and Embodiment 5 was constituted as follows: Of the polyol components, the sum of the PEG and the bisphenol system diol was 50 %. In all of said Embodiments 2, 3, 4 and 5, the compounding ratio of the PEG and the bisphenol system diol lay within the range of 1 : 0.2 to 1 : 5.0. In any of said Embodiments, the viscosity was 20700 to 23500, so that the application of the resin was performed satisfactorily, and the preservation period thereof during which the resin did not separate from the base fabric was also excellent. The storage stability of said Embodiments was 59 to 76 hours, thus providing a sufficient storage or preservation period. Further, the working time was 2 minutes 15 seconds to 2 minutes 30 seconds which was within an ideal range. The curing reaction after the lapse of the working time rapidly took place, as a result of which, in all said Embodiments, the strength of the supporting bandage reached 7.7 kg or higher after 5 minutes, during which period the highest heat generation temperature was 39.9℃, which did not bring about any adverse effect. The strength after nine minutes was higher than 14 kg, and thus, it turned out that all the embodiments constituted water-curable supporting bandages which each could be weight-beared. Moreover, the finished state of the water-curable supporting bandages was such that moisture was only somewhat left, but it was not such as to give a sense of incomfortability to the patient.

Comparative Examples 1, 2, 3 and 4 were designed with the utmost

effect so that the viscosity and the working time thereof might fall within the range of 20000 to 25000 cps and within the range of 2 to 3 minutes respectively since, unless they (Comparative Examples) were at least manufacturable as such and applicable to patients, they would be nonsensical in view of their comparison with said embodiments of the present invention.

Comparative Example 1 was the case where no PEG and no bisphenol system diol at all were contained. The viscosity of the composition according to this Comparative Example 1 was 21400 cps, the working time thereof was 2 minutes 25 seconds, and, as for the other properties thereof, it is pointed out that the storage stability was 60 hours, which could be sufficiently realized. However, the drawback of this Comparative Example 1 was that the curing reaction effected after the lapse of the working time was slow, and, after a modelling operation was made, the strength of the supporting bandage hardly reached such a value that its shape thus modelled could be retained. That is, the value of the strength after 5 minutes was 4.1 kg lower than 5.5 kg, and further, even after nine minutes, the value of the strength was 8.2 kg lower than 14.0 kg; and thus, the loading of the body weight to the supporting bandage was impossible.

Comparative Example 2 was the case where, in the components of the polyol, the sum of the PEG and the bisphenol system diol was lower than 50%. In this case, the viscosity was 22000 cps, and the working time was 2 minutes 15 seconds. In these respects, there was no problem, but the curing reaction after the lapse of the working time was slow as in the case of Comparative Example 1, and, after the supporting bandage was modelled, the thus modelled shape could not be retained, and more than 30 minutes was needed for making the weight-bearing possible.

Comparative Example 3 was the case where PEG was used as the sole

component of the polyol, containing no bisphenol system diol at all. In this Example, the viscosity was 24300 cps, and the working time was 1 minute 50 seconds, which did not reach the predetermined range of time. Further, the storage stability was poor, and the heat generation temperature was so high as 42.5℃, and therefore, there was the danger that the patient's body might be scalded. The curing reaction effected after the lapse of the working time was very fast, and, in spite of the fact that the reaction was completed in a short time, the time spent until the final strength was reached was long, and the resulting water-curable supporting bandage was in a wet state, giving a sense of incomfortability to the patient.

Comparative Example 4 was an example in which the proportion of the PEG and the bisphenol system diol in the components of the polyol was smaller than 1 : 0.2. In this example, the viscosity was 20700 cps, and the working time was 2 minutes 30 seconds. These were satisfactory values, but the other properties thereof exhbited approximately the same tendencies as in the case of Comparative Example 3 and thus, in these respects, the Comparative Example 4 was an unsatisfactory one.

(EFFECTS OF THE INVENTION)

The present invention achieves the effects as described below: That is, the storage stability is high in connection with the preservation of the water-curable supporting bandange, so that little restriction is made on the place to preserve it in; it can be preserved even in an ordinary room, and, in a hospital, it can be kept in stock with ease. Further, according to the present invention, a water-curable supporting bandage constituted in such a manner that the working time in the case of applying it to a patient is in a range 2 to 3 minutes can be obtained; such a water-curable supporting bandage can be applied with ease even to such a complicated part of a patient's body to which any conventional supporting bandage could be hardly applied. In addition, after the working time has elapsed, the curing rapidly proceeds,

and the strength of the bandage increases, so that the modelling operation can be performed surely and infallibly. The portion which has once been modelled retains it modelled shape, so that an accurate fixation of the bandage can be realized. Further, even after the modelling operation is completed, the curing keeps proceeding, and thus, a high strength can be obtained in a short time, so that the patient can load the bandage with his body weight after the short time, and therefore, the patient is not required to keep himself in the forced unstable attitude any more, thus lessening his pain. Moreover, in spite of the fact that a high strength is obtained through the rapid curing reaction, the amount of heat produced during this period is relatively small, thus ensuring that the patient is not scalded.

As described above, according to the present invention, a water-curable supporting bandage which can undergo an ideal curing process can be provided.

(BRIEF EXPLANATION OF THE DRAWING)

Fig. 1 is a graph showing the relationship between the strength and the lapse of time pertaining to the water-curable supporting bandages according to the Embodiments of the present invention and the water-curable supporting bandages according to the Comparative Examples.

(Explanation of Reference Symbols)

A .. Characteristic curve of Embodiment 1 of the present invention

B .. Characteristic curve of Embodiment 2 of the present invention.

C .. Characteristic curve of Ebmdodiment 5 of the present invention.

P .. Characteristic curve of Comparative Examaple 1

Q .. Characteristic curve of Comparative Example 2.

R .. Characteristic curve of Comparative Example 3.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A water-curable support bandage characterized in that a flexible fabric is coated with a water-curable polyurethane resin composition containing a polyurethane prepolymer consisting of a polyol and a polyiosocyanate, 0.1 - 5.0 weight %, based on the water-curable polyurethane resin composition, of a catalyst and 0.005 - 1 weight %, based on the water-curable polyurethane resin composition, of a stabilizer, wherein said polyol contains a polyethylene glycol and a bisphenol system diol with a compounding ratio by weight of 1:0.2 - 1:5 in a total amount of at least 50 weight % based on the whole polyol component and has an average molecular weight of at least 400.

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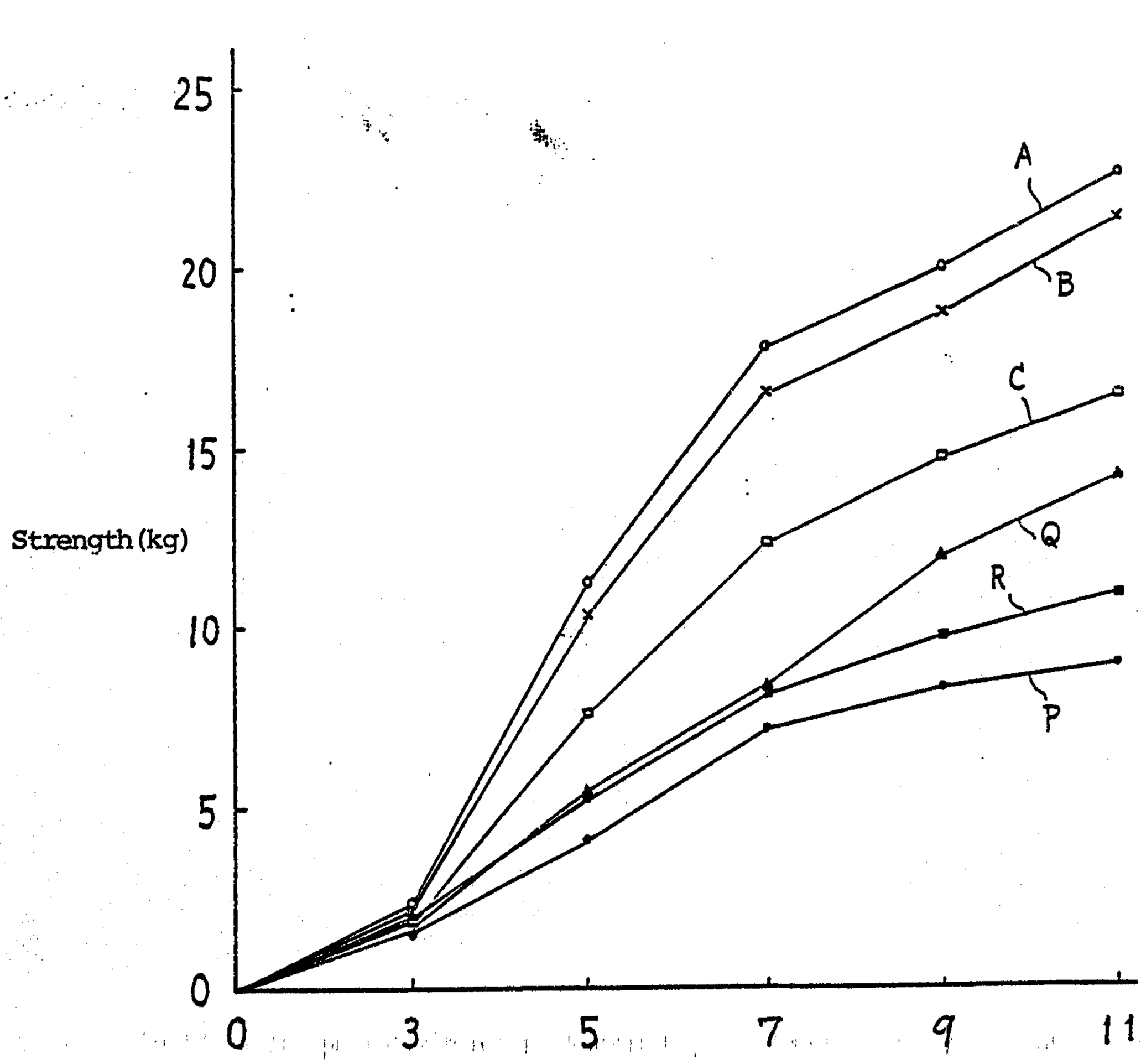

FIG. 1

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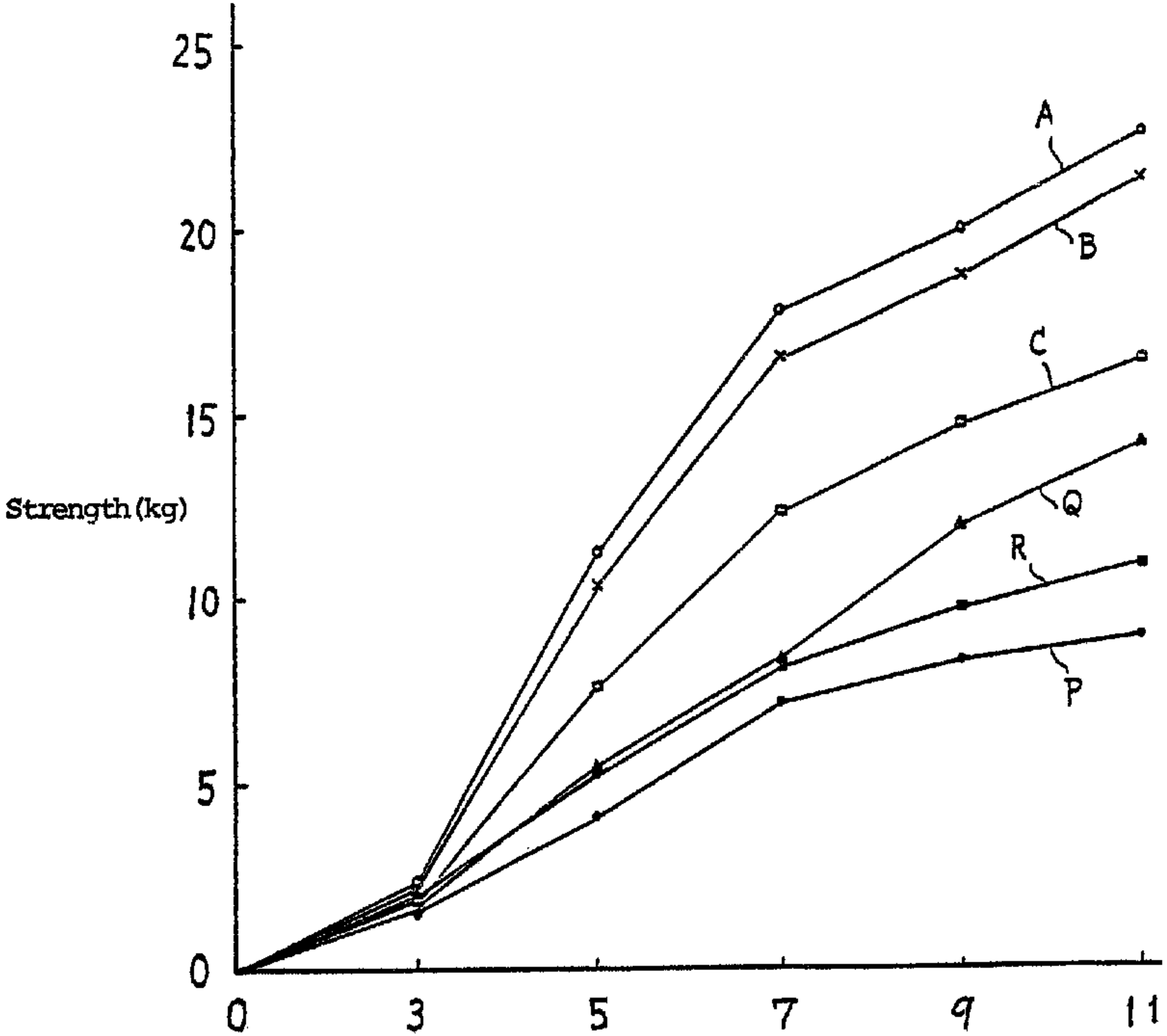
25
20
15
10
5
0
Strength (kg)
A
B
C
Q
R
P
0
3
5
7
9
11
Elapsed time (minutes)