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ORTHOPAEDIC MATERIAL OF ISOCYANATE RESIN

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AU 600333 10633/88 A61L 15/07 C08G 18/10
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(57) Claim

1. An orthopaedic splinting material which comprises a substrate which carries an isocyanate functional resin containing residues of (a) polyethylene glycol, (b) a triol or tetrol of molecular weight less than 200 and (c) an aromatic polyisocyanate in which resin the weight ratio of (a) + (b) to (c) is less than 1:1.

3. An orthopaedic splinting material as claimed in claim 2 wherein the polyethylene glycol has a molecular weight of 700 to 1100 from a mixture of high and low molecular weight polyethylene glycols.

10. A resin when used in an orthopaedic splinting material which comprises components (a), (b) and (c) as set forth in any of claims 1 to 9.

ORTHOPAEDIC MATERIAL OF ISOCYANATE RESIN

The present invention relates to a hardenable material which comprises a substrate which carries an isocyanate functional resin which hardens on contact with water. More specifically, this invention relates to an orthopaedic splint bandage which comprises a substrate which carries low tack isocyanate functional resin which hardens on contact with water to form a strong splint or cast.

UK Patent No 2092606B discloses splinting bandages which comprise a substrate which carries an isocyanate functional resin which hardens on contact with water. The patent points out that hydrophilic components such as polyethyleneoxide condensates, for example polyethylene glycols or polyoxyethylene sorbitan esters, can be employed to make resins. Use of resins incorporating such components leads to a product which has low tack after immersion in water. A difficulty encountered with these products in that they can have a low strength in the period immediately following immersion in water and application although after some time they do form an acceptable splint or cast. A method has now been found by which resins can be made which are intrinsically low tack and which also forms strong splints or casts shortly after immersion in water and application. Thus instead of having to wait until some hours for a major cast to become load bearing the patient has the possibility of walking on a cast in 30 minutes or even less. It has generally been possible to achieve short setting times by increasing the amount of catalyst present in the resins but this then tends to shorten the working time of the splinting material (that is the time after wetting when the material is sufficiently flexible to be moulded about the part of the body to be immobilized) and can lead to a product in which the exotherm is too high.

The present invention provides an orthopaedic splinting material which comprises a substrate which carries an isocyanate functional resin containing residues of (a) polyethylene glycol, (b) a triol or tetrol of molecular weight less than 200 and (c) an aromatic isocyanate in which resin the weight ratio of (a+b) to c is less than 1:1.

The splinting material is preferably a bandage but other forms of sheet materials, for example those to form slabs, are also envisaged.

Suitable triols or tetrols include glycerol, trimethylol propane, triethanolamine, pentaerythritol and the like. Particularly suitable triols or tetrol components are glycerol and trimethylol propane or mixtures thereof. A preferred triol component is glycerol. Another preferred triol component is trimethylol propane.

The molecular weight of the polyethylene glycol may be any which is convenient or may be a mixture of molecular weights (in which case it is the average molecular weight which is referred to hereinafter unless otherwise stated). Generally the molecular weight should be from 600 to 3500, for example about 1000. An average molecular weight of 700 - 1100, especially 800 - 900 is particularly desirable as excellent resins result, molecular weights in this range can be obtained by mixing high (eg 3000) and low (eg 600) molecular weight polyethylene glycols. Generally the molar ratio of polyethylene glycol to triol or tetrol will be from 2:1 to 1:2, more aptly 4:3 to 3:4 and very suitably about 1:1. Most aptly the polyethylene glycol comprises 20-30% by weight of the resin, preferably 22-28% by weight of the resin, for example 24-26% wt/wt of the resin.

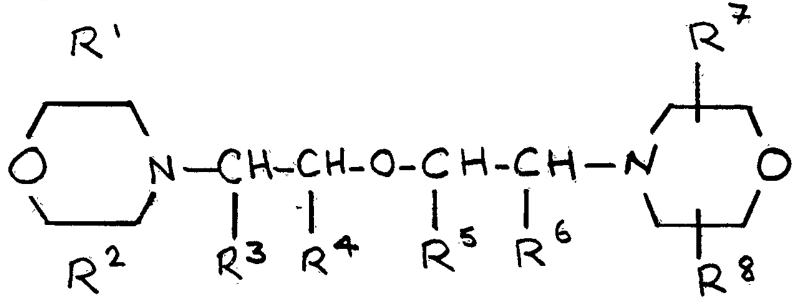
The isocyanate will be a polyisocyanate and most suitably will be a diisocyanate optionally in the presence of its higher homologues or condensation products. The resin of this invention will most aptly ontain 55-75% by weight of residues of aromatic isocyanate and preferably 60-72% by weight of residues of aromatic isocyanate, for example 70%. The favoured aromatic isocyanate for use in this invention is MDI optionally in admixture with its higher homologues. A suitable commercial grade of this is available as Isonate 143L or M143. Such MDI derived mixtures are preferred.

In the resin of this invention all or part of the aromatic isocyanate may have been incorporated into the form of a prepolymer in which it caps the polyethylene glycol or triol or tetrol.

The resins of this invention will usually have been formed by including water in the reaction mixture. This is normally found as dampness in the polyethethlene glycol and/or triol or tetrol, for example as 0.1 to 1.5% wt/wt of total polyols, more usually 0.2 to 1% wt/wt of total polyols.

Generally the resin will consist essentially of the residues of (a), (b) and (c) referred to hereinbefore (although minor amounts of other diols or triols may be used as long as they are used in small quantities which are not sufficient to adversely change the properties of the resin) together with a tertiary amine catalyst and other conventional additives such as stabilizers, antifoams and the like.

The tertiary amine catalyst is aptly a bis-tertiary amine such as a bisethylether derivative such as a compound of the formula:



wherein R^1 to R^8 are hydrogen atoms or methyl or ethyl groups. Aptly R^1 to R^8 are hydrogen atoms or methyl groups. Favourably R^1 to R^8 are hydrogen atoms. Favourably R^1, R^2, R^7 and R^8 are methyl groups and R^3 to R^6 are hydrogen atoms. Favourably R^1 to R^4 and R^6 to R^8 are hydrogen atoms and R^5 is a methyl group.

A preferred catalyst is di(2,6-dimethylmorpholino) diethylether.

The resin may comprise stabilizers such as sulphonic acid (for example methane or ethane sulphonic acid), succinic anhydride, benzoyl chloride or the like. The resin may also comprise other agents such as antifoams such as silicone oil, for example 0.5-5% and more usually 1-2% of silicone oil.

The amount of resin employed may be as desired but generally 40-50% of the total weight of resin plus substrate is resin.

The substrate may be any suitable substrate but knitted polymer or glass substrates are favoured of which glass substrates are preferred, for example a substrate such as in commercially available products such as Scotchcast or Dynacast. Other suitable substrates include woven and non-woven substrates, for example foams, apertured non-wovens and the like.

The resin may be prepared by placing the aromatic isocyanate in an reactor optionally together with any stabilizer such as benzoyl chloride, succinic anhydride or the like and antifoam, warming to about 55°C under dry nitrogen, adding thereto the polyethylene glycol and stirring for 1 hour at about 55°C, adding any additional stabilizers such as methane sulphonic or ethane sulphonic acids over five minutes and then adding the catalyst and stirring for a further 30 minutes. The resulting resin can be spread onto a substrate at the required weight.

The resins comprising components a, b and c as set forth hereinbefore with respect to the splinting materials also form part of this invention.

The following Examples illustrate this invention.

Example 1

The following formulation produces a low tack strong cast when spread on conventional knitted glass substrate at 44% mass weight =

Isonate 143L	2427.5g
PEG 1000	850.8g containing 0.1% water
Trimethylol Propane	118.8g containing 1.45% water
Succinic Anhydride	34.0g
Methane Sulphonic Acid	1.0g
Antifoam	34.0g
KL 26	34.0g

Isonate 143L is partly polymerised MDI available from Dow (sometimes called M143). PEG 1000 is a polyethylene glycol of molecular weight 1000. The Antifoam is MSA silicone. KL 26 is bis(2,6-dimethylmorpholino) diethylether.

The Isonate 143L and antifoam are charged into a glass reactor and heated to 55°C. The ground succinic anhydride is added with agitation (agitation throughout hereafter). The PEG 1000 is added in 3 aliquots at 10 minute intervals and reacted for 30 minutes. The trimethylol propane is added in 3 aliquots at 10 minute intervals and reacted for 60 minutes. Methane sulphonic acid is added dropwise over 5 minutes and mixed for 10 minutes. The KL26 is added over 10 minutes and mixed for 10 minutes. The resin is then allowed to cool and discharged into a dried vessel which is then sealed.

This resin is spread at 25°C onto a suitable substrate under dry conditions (eg 2-5% RH). The resulting bandages were found to have coefficient of friction of 0.5 after immersion in water.

Example 2

A resin was prepared using the following :

Trimethylol Propane (+1.35% water)	170.34g
Polyoxyethylene Glycol (+0.1% water)	1224.54g
Isonate M143	3460.43g
Succinic Anhydride	48.55g
Methane Sulphonic Acid	1.46g
Antifoam	48.55g
Di(dimethylmorpholino)diethylether	46.13g

The resin was coated onto a knitted glass substrate at 48% wt/wt. The PEG had a molecular weight of 1000. The antifoam was as in Example 1.

Example 3

A resin was prepared analogous to that of Example 2 replacing the succinic anhydride with 24.27g of benzoyl chloride. The resin was coated onto a knitted glass substrate at 44% wt/wt.

Example 4

A resin was prepared analogous to that of Example 2 replacing the trimethylol propane with an equivalent amount of glycerol. The resin was coated onto a knitted glass substrate at 45% wt/wt.

Example 5

Resins were prepared and coated as in Example 1 with the following formulation:

Isonate M143	10579.9g	2977.7g
PEG 1000	3639.1g	-
Glycerol	361.1g	63.8g
Succinic Anhydride	154.8g	43.7g
Methane Sulphonic Acid	4.4g	1.3g
KL 26	123.9g	7.2g
Silicone Oils	745.8g	43.7g
PEG 2000	-	1332.5g

Examples 6-10

Polyethylene glycols of 'nominal' molecular weights were prepared by blending the amounts of PEG 600 and PEG 3000 shown in the following Table 1.

Table 1

PEG 600(gm)	PEG 3000 (g	Nominal M.Wt	Example No
8902	1098	700	6
7488	2512	800	7
6482	3518	900	8
5034	4966	1100	9
2525	7475	1600	10

The components shown in Table 2 were formed into resins by the following procedure:

The succinic anhydride, isocyanate, and antifoaming agent were charged to the reactor and heated over a water bath maintained at 50°C. When the temperature of the reactants had reached 45°C the PEG was added in two aliquots, the temperature rise being allowed to stabilize before addition of the second aliquot. The mixture was stirred for a further 20 minutes after which the glycerol was added and the mixture stirred for yet a further hour.

The methane sulphonic acid was added slowly and the mixture stirred for 10 minutes whereupon the catalyst was added. The whole reactant mass was stirred for 30 minutes, allowed to cool to ambient temperature and discharged from the reactor.

Table 2

Example (gms)	6	7	8	9	10
Glycerol	62.31	71.30	74.33	78.94	93.27
PEG ·	1164	1168	11761	1197	1202
Isonate M143(1)	3154	3141	3130	3105	3085
Succinic Anhydride	43.8	43.8	43.8	43.8	43.8
Methane Sulphonic Acid	1.31	1.31	1.31	1.31	1.31
Anitfoam MSA	43.8	43.8	43.8	43.8	43.8
Catalyst(2)	30.66	30.66	30.66	30.66	30.66

(1) diphenylmethane-4,4^1-diisocyanate containing polycarbonimide adducts.

(2) bis (2,6-dimethyl morpholino-N-ethyl)ether.

Bandages were prepared by coating the resin onto a conventional fibre glass substrate and squeezing out the excess resin.

The resin coated substrates were then dipped into water and wound onto a mandrel, five layers thick to produce a number of casts. Each cast was removed from the mandrel and its strength determined, after the elapse of a predetermined period of time, by a flexural regidity test. The strength tests results are shown in Table 3 which also gives comparative results for a conventional splinting resin on the same substrate as that employed for the resins of the invention.

Table3

	strength at:	
Example	15 mins	30 mins
6	2.59	2.87
7	2.62	3.13
8	2.46	2.90
9	1.91	1.63
10	1.91	2.17
Comparative	1.75	2.20

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. An orthopaedic splinting material which comprises a substrate which carries an isocyanate functional resin containing residues of (a) polyethylene glycol, (b) a triol or tetrol of molecular weight less than 200 and (c) an aromatic polyisocyanate in which resin the weight ratio of (a) + (b) to (c) is less than 1:1.

2. An orthopaedic splinting material as claimed in claim 1 wherein the polyethylene glycol has a molecular weight of 600 to 3500.

3. An orthopaedic splinting material as claimed in claim 2 wherein the polyethylene glycol has a molecular weight of 700 to 1100 from a mixture of high and low molecular weight polyethylene glycols.

4. An orthopaedic splinting material as claimed in any of claims 1 to 3 wherein (b) is glycerol.

5. An orthopaedic splinting material as claimed in any of claims 1 to 3 wherein (b) is trimethylolpropane.

6. An orthopaedic splinting material as claimed in

any of claims 1 to 5 which also comprises a tertiary amine catalyst.

7. An orthopaedic splinting material as claimed in any of claims 1 to 6 wherein the polyethylene glycol residues comprise 22-28% of the resin by weight.

8. An orthopaedic splinting material as claimed in any of claims 1 to 7 wherein the aromatic isocyanate residues comprise 60-72% of the resin by weight.

9. An orthopaedic splinting material as claimed in any of claims 1 to 8 wherein the substrate is a knitted glass substrate.

10. A resin when used in an orthopaedic splinting material which comprises components (a), (b) and (c) as set forth in any of claims 1 to 9.

11. An orthopaedic splinting material substantially as herein described with reference to the Examples.

DATED this 19th day of December, 1991.

SMITH & NEPHEW PLC
By its Patent Attorneys
DAVIES COLLISON CAVE

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 89/00249

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC4: A 61 L 15/07, C 08 G 18/48, 18/76

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC4	A 61 L; C 08 G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4377645 (GUTHRIE ET AL) 22 March 1983, example 1 --	1-10
A	US, A, 4427003 (FENNIMORE ET AL) 24 January 1984, see whole document --	1-10
A	US, A, 0 172379 (BAYER AG) 26 February 1986, see whole document --	1-10
A	EP, A1, 0086621 (JOHNSON & JOHNSON PRODUCTS INC) 24 August 1983, see whole document --	1-10
A	US, A, 4547561 (CRISTIAN WEGNER) 15 October 1985, see whole document --	1-10

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 16th June 1989	Date of Mailing of this International Search Report 14.07.89
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer P.C.G. VAN DER PUTTEN

International Application No. PCT/GB 89/00249

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4285073 (MICHAEL SZYCHER) 25 August 1981, see whole document --	1-10

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 89/00249

SA 27722

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 03/03/89
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