

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
17 July 2003 (17.07.2003)

PCT

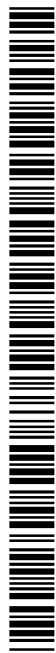
(10) International Publication Number  
**WO 03/057467 A2**

- (51) International Patent Classification<sup>7</sup>: **B32B 5/00**
- (21) International Application Number: PCT/GB03/00077
- (22) International Filing Date: 10 January 2003 (10.01.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0200462.0 10 January 2002 (10.01.2002) GB  
0218536.1 9 August 2002 (09.08.2002) GB
- (71) Applicant (for all designated States except US):  
**VOITH FABRICS HEIDENHEIM GMBH & CO. KG.** [DE/DE]; Kurze Strasse 11, 89522 Heidenheim (DE).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **PATEL, Sanjay** [US/US]; 116 Westminster, Summerville, SC 29485 (US). **DRAPER, Michael, David** [GB/GB]; 68 Mounsey Road, Bamber Bridge, Preston, Lancashire PR3 6LU (GB).
- (74) Agents: **GOODWIN, Mark** et al.; Wilson Gunn M<sup>c</sup>Caw, 41-51 Cross Street, Royal Exchange, Manchester M2 7BD (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 03/057467 A2**

(54) Title: SURFACE ENHANCEMENT OF INDUSTRIAL TEXTILES

(57) Abstract: An industrial textile comprises a polymeric substrate and a resin system grafted onto the substrate. The resin system comprises water-borne thermoplastic, optionally fluorinated, polyhydroxyether resin and/or one or more analogues thereof and at least one co-resin.

## SURFACE ENHANCEMENT OF INDUSTRIAL TEXTILES

The present invention relates to industrial textiles such as papermachine clothing and more particularly, but not exclusively, to press fabrics for use in the press section of a papermaking machine.

5 Paper is conventionally manufactured by conveying a paper furnish, usually consisting of an initial slurry of cellulosic fibres, from a forming section, through a pressing section and ultimately around a drying section of a papermaking machine.

Papermachine clothing is essentially employed to carry the paper web  
10 through these various stages of the papermaking machine. In the forming section the fibrous furnish is wet-laid onto a moving forming wire and water is allowed to drain from it. The paper web is then transferred to a press fabric that conveys it through the pressing section, where it is usually passed through a series of pairs of rotating cylindrical press rolls. Water is squeezed from the paper web and into the  
15 press fabric as the web and fabric pass through the nip together. In the final stage, the paper web is transferred to a dryer fabric and the majority of the remaining water is evaporated as the paper passes through the drying section.

Most papermachine clothing is nowadays made from textile materials usually comprising polymeric yarns and or fibres. In an attempt to extend the  
20 lifespan and improve the performance of these fabrics GB 1,512,558 teaches the application of a resin coating to the fabric yarns, the resin coating being applied as a solution in organic solvent. However, the use of such solvents leads to unacceptable environmental problems. US 4,439,481 relates to a press fabric to

which one of a number of suitable synthetic polymeric resins is applied. Suitable polymeric resins are said to include polyolefins such as polyethylene, ethylene copolymers, polypropylene, polyamides, fluorinated ethylene propylene, polyvinylchloride, polyvinylidene fluoride and acrylic polymers, B-stage  
5 thermosetting resins and liner epoxy resins. In the example, a fabric is immersed in a dip tank containing epoxy resin. The coating increases the stiffness of the press fabric and makes it more resistant to compression. This enhances the performance of the fabric in removing water from the paper web. However, the use of strong organic solvents is usually required in order to dissolve the epoxy  
10 resin prior to coating the fabric. This solvent must later be removed leading once again to environmental problems.

Such coatings described above have gone some way to improving the lifetime of papermachine press fabrics, but epoxy resins are brittle, lack toughness and exhibit poor abrasion resistance. Epoxies have low inter-molecular adhesion  
15 due to a lack of hydrogen bonding and because they also lack the appropriate chemical functionalities, there is also poor adhesion to the substrate. This means that the coatings tend to be non-permanent and therefore the felt surface is still prone to fibre shedding. The present invention has been made from a consideration of these problems

20 According to the present invention there is provided an industrial textile comprising a polymeric substrate and a resin system grafted onto the polymeric substrate, wherein said resin system comprises water-borne thermoplastic,

optionally fluorinated, polyhydroxyether resin and/or one or more analogues thereof and at least one co-resin.

The term "grafting" as used herein is used to refer to the attachment of a chemical unit to a main molecular chain.

5 The industrial textile has particular but not exclusive application in papermachine clothing.

The polymeric textile substrate may comprise a woven fabric and/or a non-woven fabric.

10 It has been found that these polyhydroxyether resins are tougher and less brittle than epoxy resins. This, together with other properties of the polyhydroxyether, that will be described hereinafter, led to a number of significant advantages over the use of prior art papermachine clothing with an epoxy resin coating or other conventional treatments thereon.

15 The term "water-borne thermoplastic polyhydroxyether resin" as used herein refers to a polyhydroxyether (eg a phenoxy) resin to which is grafted one or more ethylenically unsaturated monomers. It is desirable that at least one of the monomers contains carboxyl groups.

20 These polyhydroxyethers are ideally prepared as water-borne amine neutralised, carboxylated, polyhydroxyether resin coating compositions such as the type described in US 6,034,160 and US 5,574,079. Such a coating composition does not cause environmental problems as compared with the prior art epoxy resin coating compositions, which generally comprise organic solvents. The coating compositions of US 6,034,160 and US 5,574,079 have previously

been used in the coating of metals, but not textile materials. These documents describe a coating composition in the form of an aqueous dispersion of a water-miscible base and thermoplastic polyhydroxyether, the thermoplastic polyhydroxyether having a polydispersity of less than 4.0 and a number average  
5 molecular weight of between 7,000 and 12,000 and having grafted thereon one or more ethylenically unsaturated monomers. Polydispersity is the ratio of weight average molecular weight to number average molecular weight of a particular thermoplastic polyhydroxyether resin. The polyhydroxyethers preferably have a weight average molecular weight greater than about 20,000 and less than about  
10 45,000, i.e. much higher than epoxy resins which have a maximum molecular weight of about 8000. The ethylenically unsaturated monomers preferably have from about 3 to about 8 carbons and are ideally selected from the group consisting of methyl methacrylate, ethyl acrylate, n-propyl methacrylate, butyl acrylate, acrylonitrile, methacrylonitrile, styrene, alpha-methyl styrene and p-vinyl toluene.  
15 The ethylenically unsaturated monomers could also be made to have lower surface energy. The surface energy of at least a part of the industrial fabric is ideally less than 20 dynes/cm. One way of achieving this is to use fluorinated analogues.

At least one of the ethylenically unsaturated monomers preferably contains sufficient carboxyl groups to provide from about 1 to 100 carboxyl groups per 10  
20 monomeric units of thermoplastic polyhydroxyether. This monomer is preferably selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid.

Papermachine fabrics tend to be manufactured from synthetic materials, such as polyamide, which is commonly used for press fabrics. This, and any other suitable substrates, onto which the resin is capable of being grafted, can be used.

Press fabrics generally comprise a fibrous batt needled to a woven or non-  
5 woven base fabric. The grafting operation of the invention effectively encapsulates the individual batt fibres of the press fabric with an inter-penetrating network, thus providing improved mechanical properties (toughness and durability) and increasing the stiffness of the fabric. In particular, the use of the modified polyhydroxyether of the invention provides improved resistance to  
10 abrasion, chemical degradation, heat and high pressure shower damage. The grafting process results in improved fibre bonding within the fibrous batt so as to reduce fibre shedding. Overall surface wear and localised wear are significantly reduced. The grafting process also increases the stiffness in the Z direction of the fabric, which provides enhanced efficiency of paper dewatering at the nip of the  
15 press machine. In the case of seamed press fabrics, in addition to these benefits, it has been found that the batt flap can be held more securely during the life of the felt and that the increased stiffness aids seaming, by maintaining loop alignment during the seaming operation.

The papermachine clothing of the invention additionally offers resistance  
20 to chlorine, which emanates from the bleaching agents added to whiten pulp, and other chemically oxidative materials, as well as to so-called "wad-burn". Wad burning is the name given to the phenomenon that occurs when a piece or "wad" of the formed paper web breaks away and becomes lodged at the entrance to the

nip of the wet press section. The lodged wad creates a high frictional force against the press fabric. The heat of friction generated by this occurrence can result in the melting and fusion of the thermoplastic press fabric fibres, thereby creating an impermeable non-porous area of fabric that thereafter prevents the passage of water. The traditional remedy is the use of expensive aramid as batt components due to their extremely high temperature resistance, but it has been found that they tend to flatten or prematurely break-away causing localised porosity reductions. The phenoxy treatment avoids the need to use these. The grafting formulations of the invention have a high temperature resistance and consequently protect the batt fibre surface from such wad burn damage.

The grafting of the polyhydroxyether resin coating onto press fabric fibres and their consequent encapsulation results in minimal reduction in air permeability. Furthermore, the process of the invention has no negative impact on press fabric dewatering.

To achieve the optimum performance properties for a press fabric application, a co-resin is used. The polyhydroxyether formulation can be modified if so desired, with, for example, any of the following components including:- one or more property modifying polymers; one or more specific surface enhancing agents and/or any one or more crosslinkers.

1. The property modifying polymer preferably includes any of the following either alone or in combination:- polyacrylates, epoxy-esters, alkyds, polyvinyl alcohols, polyvinyl acetates, polyesters, polysiloxanes, polyepoxides and most preferably polyurethane or modified polyurethane.

2. The specific surface enhancing agent preferably includes any of the following either alone or in combination:- amines, cyclic ureas, inorganic fillers, fluoro polymers, silicones and siloxanes and most preferably hydrophilic silicones and/or polydimethyl siloxanes.
- 5 3. The crosslinker preferably includes any of the following either alone or in combination:- epoxies, oxazolines, carbo-diimides, polyethylene imines, polyaziridines, aliphatic polyisocyanate, blocked isocyanates and preferably melamine-formaldehyde.

The polymeric formulation is preferably provided as a waterborne  
10 dispersion, comprising from 1% to 40% solids by weight. The polymeric formulation is applied either to selective stratum or throughout the body of the press fabric, being grafted to the individual fibres of the batt, with the aid of high temperatures, where required. Heat curing results in crosslinking and encapsulation of the individual fibres. Suitable application methods include  
15 spraying, application as a foam and by a lick-up or kiss roll process.

The formulation can also, in the case of a seamed press fabric, be solely applied to the seam area to reinforce the seam, and consequently more securely hold the batt flap in position. Application to the seam area alone will significantly stiffen the seam, which will in turn aid alignment of the seam loops during fitting,  
20 thereby easing the installation process.

This band across the seam could potentially also help to serve the purpose of a "trade line" or "bar-mark", which can be useful if a particular machine is prone to unwanted resonance. The bar-mark provides a reference line to enable

the fabric to be correctly skewed by the machine crew to minimise the resonance effect. A coloured pigment, additive or dye can, if so desired, be added to improve the visibility of this line. A small roller applicator may be used to apply this band across the seam. This band is advantageous also because it does not  
5 decrease the porosity of the region where it has been applied, but yet improves the abrasion resistance. The band need not necessarily be across the seam.

In one embodiment of the invention just one or both edges of the fabric could be treated, or the edges could be treated with a formulation with increased solids content. A formulation with increased solids content would give a higher  
10 contact area with the sheet and a lower porosity, the denser surface helping the sheet to adhere to the felt. Edge seals/reinforcements are of importance for guidance, to resist abrasion and to increase the stiffness of the belt.

Press fabric samples with solids "add-on" to original fabric weight of the modified polyhydroxyether formulation of the invention have been prepared with  
15 up to 44% solids. In theory, any solids add-on is achievable. A solids add-on of from 2% to 8% and preferably substantially 6% has been found to give the best compromise of properties, eg. sufficient resistance to wear and abrasion damage, sufficient stiffness, plenteous fibre-fibre bonding with a minimal reduction in permeability – typically less than 10%.

20 The polymeric formulation of the invention has been designed so that once applied to a press fabric, controlled drying and heat setting procedures both cure the resin and graft it onto the polyamide press fabric fibres. The choice of crosslinker is made to suit the curing conditions available. Specific crosslinkers

can be chosen in order to achieve optimum cure time and temperature to be compatible with the process conditions available. Typical drying and heat setting, conditions may, for example, include passing the coated press fabric through air boxes set at 120°C, followed by subjection to a hot cylinder set at 165°C for a  
5 dwell time of 3 minutes. This will cure and graft the treatment onto the press fabric fibres. Proper selection of co-resins and crosslinking agents allows generation of inter-penetrating polymeric networks around these batt fibres.

These are typical conditions. In theory, the treatment can be dried to any temperature over sufficient time. Curing and grafting onto the fibres will start to  
10 take place above typically 150°C, although the addition of catalysts, such as p-toluene sulphonic acid can be used to reduce this curing temperature and/or time required.

In order that the present invention may be more readily understood a specific embodiment thereof will now be described by way of example only with  
15 reference to the accompanying drawings, in which:-

Fig. 1 is an SEM of a press fabric in accordance with the invention showing the modified polyhydroxyether material grafted onto the individual fibres of the batt;

Fig. 2 is a scan of a press fabric in accordance with the invention obtained  
20 using Fourier Transform Infrared Spectroscopy (FT-IR);

Fig. 3 shows, for comparison purposes, an SEM of a standard press fabric;

Fig. 4 is a bar chart showing the % weight retained of fabrics of the invention and prior art fabrics on a Nipcoflex<sup>®</sup> press;

Fig. 5 is a bar chart showing the lifespan of fabrics of the invention and prior art fabrics in the pick-up position; and

Fig. 6 is a bar chart showing the lifespan of fabrics of the invention and prior art fabrics on the second press of a pilot machine.

5

### EXAMPLE

A press fabric comprises a batt of fibres needled to a woven or non-woven base cloth. A modified polyhydroxyether [hereinafter "MPHE"] formulation is applied throughout the body of the fabric. The MPHE formulation comprises an anionically stabilised aqueous colloidal dispersion of a carboxylated polyhydroxyether resin. The formulation further comprises a water-based polyurethane dispersion, a hydrophilic silicone based copolymer and a trimethoxy high imino functionality melamine-formaldehyde based crosslinker. This was chosen because of its affinity for crosslinking both primary and secondary hydroxyl, carbonyl and amino (NH-) groups at relatively low temperatures without the need for a catalyst.

The ratios of the various components made into aqueous solutions to provide the formulation were as follows:-

	<u>Parts by Solids</u>
Carboxylated polyhydroxyether	4.1
Water based Polyurethane dispersion	1.2
Polysiloxane copolymer	1.0

The cross-linker is added in an amount 1 part solid crosslinker to 3 parts of the combination of solid polyhydroxyether and solid polyurethane.

A solution of typically 14.4% solids was used as the formulation, although this can be significantly higher or lower, for example between 1 to 40% solids,  
5 depending on the chosen method of application.

Referring to Fig. 1 Scanning Electron Microscopy (SEM) clearly shows the MPHE formulation encapsulating the press fabric fibres. A FT-IR spectrograph of such a material is shown in Fig. 2. Fig. 3 shows an SEM picture of a standard press fabric for comparison.

10 Press fabric samples treated with MPHE formulation and subjected to water extraction tests using standard Soxtherm 2000 (trade mark) extraction equipment, completely retained the treatment, thus proving that permanent grafting to the press fabric fibre had been achieved.

Clear visual differences were observed when press fabric samples treated  
15 with the MPHE formulation of the invention were subjected to (1) a Taber Abrasion test (wet abrasion test against a Tungsten carbide abrasion sheet), (2) Martindale (Dry) abrasion tests, where samples were abraded for 15,000 cycles against a carborundum sandscreen head under a pressure of  $90 \text{ g/cm}^2$ , the abrading head being replaced every 1000 cycles and (3) High Pressure Fibre Adhesion  
20 Tests (FAT) which involves running a sample around an enclosed rotating circular drum, whilst at the same time showering it with high pressure water. Lost fibre can be collected for measurement. An abrasive bar can also be introduced to replicate mechanical abrasion. In addition, on using the FAT test, the samples

with modified polyhydroxyether resin formulation grafted onto them consistently showed 50% less batt loss compared to untreated control samples, after the same exposure conditions.

In all cases, samples with modified polyhydroxyether grafted onto them far out performed similar control samples and samples treated with other standard press fabric chemical treatments.

A high speed, in-house developed friction test developed to give an indication of the resistance to wad burning was utilised. This test showed that press fabric samples with the MPHE formulation of the invention grafted onto them required more than double the length of time taken by control samples to commence melting, after exposure to the same test conditions. This provides a clear indication that the MPHE formulation will impart resistance to wad burning.

Cleaning agents and aggressive chemicals used in the paper furnish can attack and destroy press fabrics. A laboratory test developed to investigate accelerated chemical oxidative degradation showed that press fabric samples grafted with the MPHE formulation significantly resisted chemical oxidative degradation compared to samples without the MPHE treatment. The standard press fabric control samples lost over 10% more fibre and were considerably more visibly degraded than the samples encapsulated with the MPHE formulation of the present invention.

Press fabric samples treated with the MPHE formulation of the invention have now been tested on an in-house pilot paper machine. Fig. 4 clearly shows that a press fabric treated with the MPHE formulation retains significantly more

weight, i.e. suffers considerably less fibre loss, than previous standard press fabrics that have run similar lives on the same position of this pilot machine.

Fig. 5 and Fig. 6 show the lifespan of several fabrics on two different paper machines. All the samples in Fig. 5 refer to press fabrics that have run on the pick up position of a pilot machine. All the samples in Fig. 6 concern press fabrics that have run on the second press of a pilot machine. Both clearly illustrate that applying the MPHE formulation to a press fabric significantly increases the lifetime of that press fabric.

It is to be understood that the above described example is by way of illustration only and that many modifications and variations are possible.

Claims

1. An industrial textile comprising a polymeric substrate and a resin system grafted onto the polymeric substrate, wherein said resin system comprises water-borne thermoplastic, optionally fluorinated, polyhydroxyether resin  
5 and/or one or more analogues thereof and at least one co-resin.
2. An industrial textile according to claim 1, wherein the polymeric substrate comprises a woven fabric and/or a non-woven fabric.
3. An industrial textile according to claim 1 or claim 2, wherein the polymeric substrate is a press fabric.
- 10 4. An industrial textile according to any preceding claim, wherein at least part of the resin system consists of a water-borne amine-neutralised, carboxylated, polyhydroxyether resin.
5. An industrial textile according to any preceding claim, wherein the polyhydroxyether resin has a weight average molecular weight greater  
15 than substantially 20,000 and less than substantially 45,000.
6. An industrial textile according to any preceding claim, wherein one or more ethylenically unsaturated monomers is grafted to the polyhydroxyether resin.
7. An industrial textile according to claim 6, wherein at least one of the  
20 ethylenically unsaturated monomers contains one or more carboxyl groups.

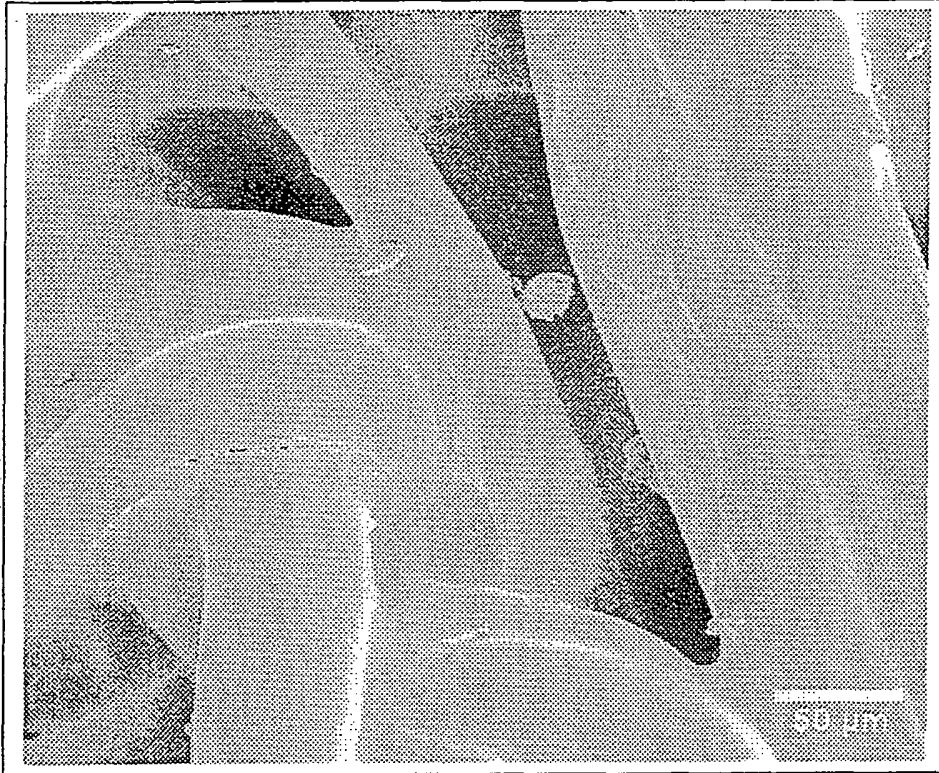
8. An industrial textile according to claim 6 or claim 7, wherein at least one of the monomers contains sufficient carboxyl groups to provide from about 1 to 100 carboxyl groups per 10 monomeric units of polyhydroxyether.
9. An industrial textile according to any of claims 6 to 8, wherein the ethylenically unsaturated monomers have from substantially 3 to substantially 8 carbons.
10. An industrial textile according to any of claims 6 to 9, wherein the ethylenically unsaturated monomers comprise any of the following, either alone or in combination:- methyl methacrylate, ethyl acrylate, n-propyl methacrylate, butyl acrylate, acrylonitrile, methacrylonitrile, styrene, alpha-methylstyrene and p-vinyl toluene.
11. An industrial textile according to any preceding claim, wherein the surface energy of at least a part of the surface of the industrial fabric is less than substantially 20 dynes/cm.
12. An industrial textile according to any of claims 6 to 11, wherein the ethylenically unsaturated monomers are fluorinated.
13. An industrial textile according to any of claims 6 to 12, wherein the ethylenically unsaturated monomers are selected from any of the following either alone or in combination:- acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid.
14. An industrial textile according to any preceding claim, wherein the at least one co-resin includes any of the following components:- one or more

property modifying polymers; one or more specific surface enhancing agents and/or any one or more cross-linkers.

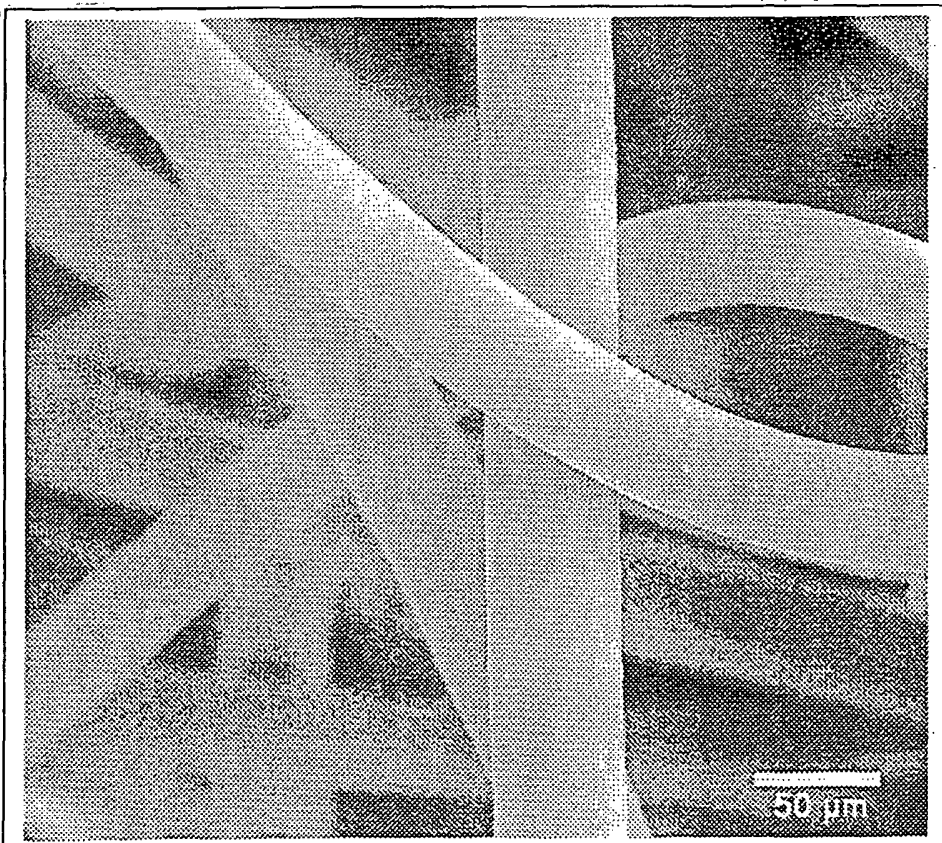
15. An industrial textile according to claim 14, wherein the property modifying polymer includes any of the following either alone or in  
5 combination:- polyacrylates, epoxy-esters, alkyds, polyvinyl alcohols, polyvinyl acetates, polyesters, polysiloxanes, polyepoxides and most preferably polyurethane or modified polyurethane.
16. An industrial textile according to claim 14, wherein the specific surface enhancing agent includes any of the following either alone or in  
10 combination:- amines, cyclic ureas, inorganic fillers, fluoro polymers, silicones and siloxanes and most preferably hydrophilic silicones and/or polydimethyl siloxanes.
17. An industrial textile according to claim 14, wherein the cross-linker includes any of the following either alone or in combination:- epoxides,  
15 oxazolines, carbo-diimides, polyethylene imines, polyaziridines, aliphatic polyisocyanate, blocked isocyanates and preferably melamine-formaldehyde.
18. An industrial textile according to any preceding claim, wherein the resin system is a water-borne dispersion applied to the substrate as 1% to 40%  
20 by weight.
19. An industrial textile according to any preceding claim, wherein the resin system is applied throughout the body of the substrate.

20. An industrial textile according to any of claims 1 to 18, wherein the resin system is applied only to part of the substrate.
21. An industrial textile according to claim 20, wherein said part of the substrate comprises at least one of a seam or one or both edges thereof.
- 5 22. An industrial textile according to any preceding claim, wherein the resin system is applied to the substrate by spraying, application as a foam or by a lick-up or kiss roll process.
23. An industrial textile according to any preceding claim, wherein the substrate has a resin solids add-on of from 2% to 8%.
- 10 24. An industrial textile according to any preceding claim, wherein the resin system is cured by drying and heat setting procedures.
25. An industrial textile according to claim 24, wherein the polymeric formulation is cured at a temperature greater than 150°C.
26. An industrial textile according to claims 24 or claim 25, wherein one or  
15 more catalysts are added to the resin system to reduce the cure temperature.
27. An industrial textile according to claim 26, wherein the catalyst comprises p-toluene sulphonic acid.

1/4



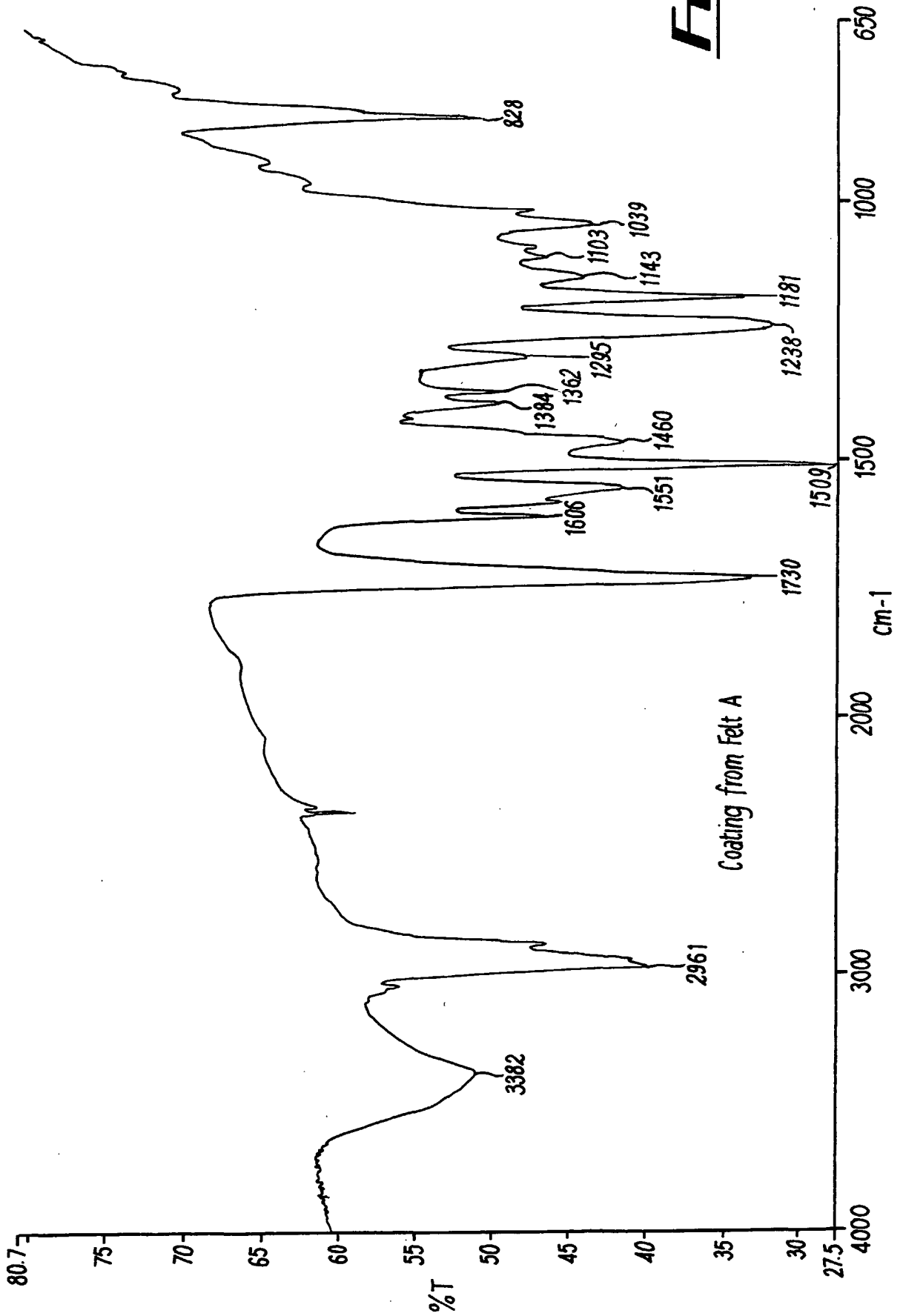
**Fig. 1**

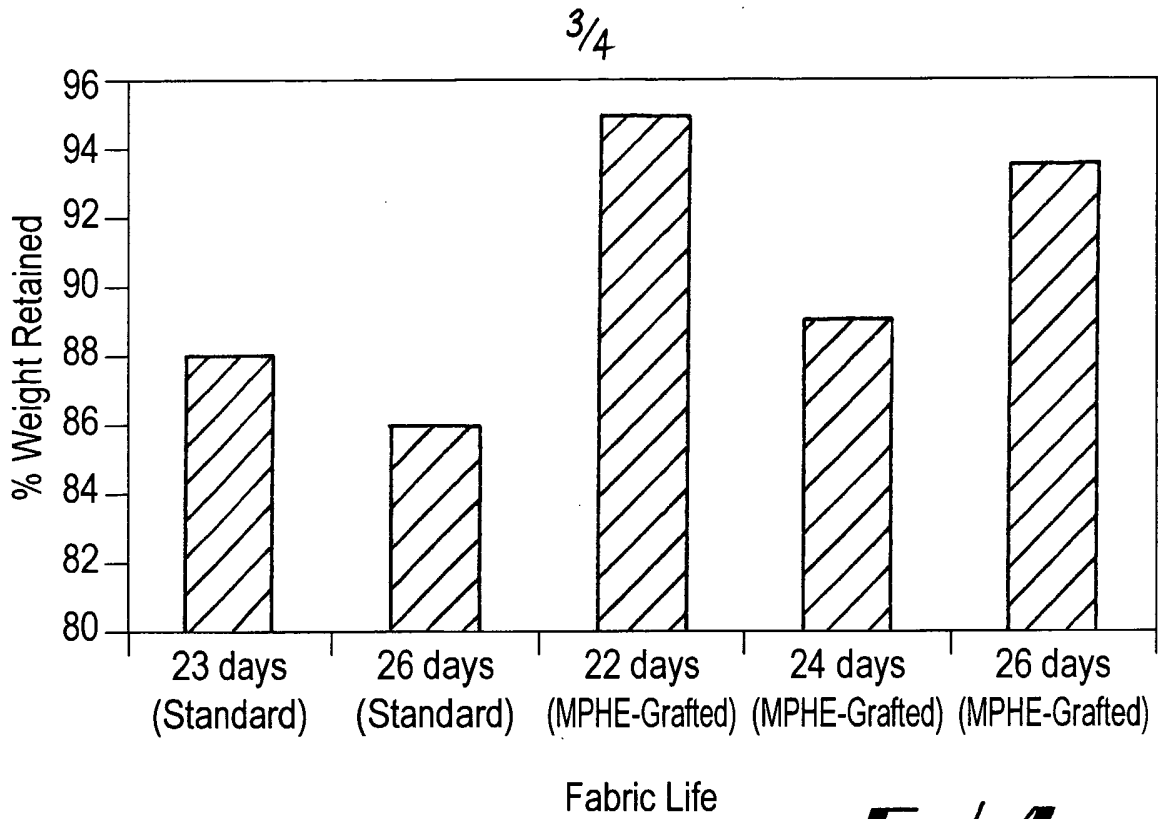


**Fig. 3**

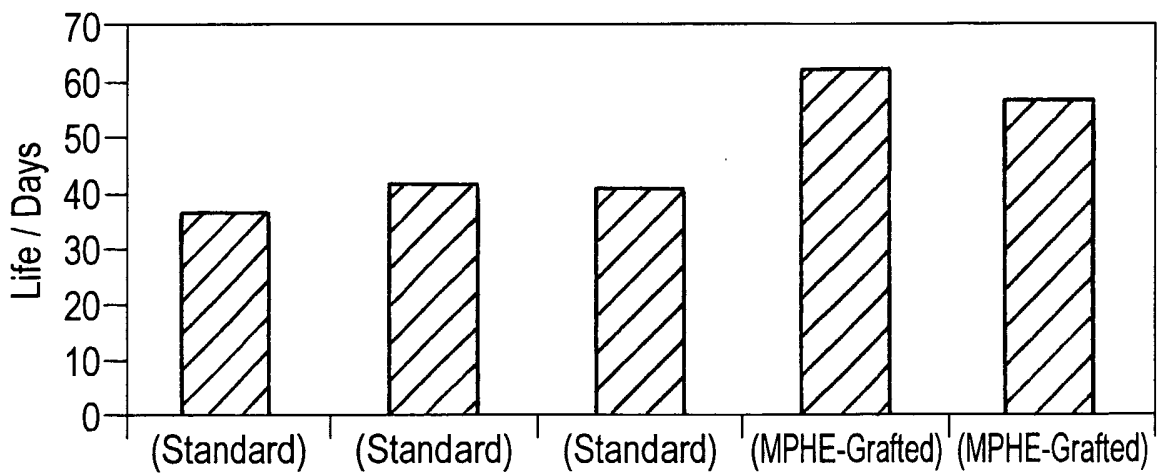
2/4

**Fig 2**



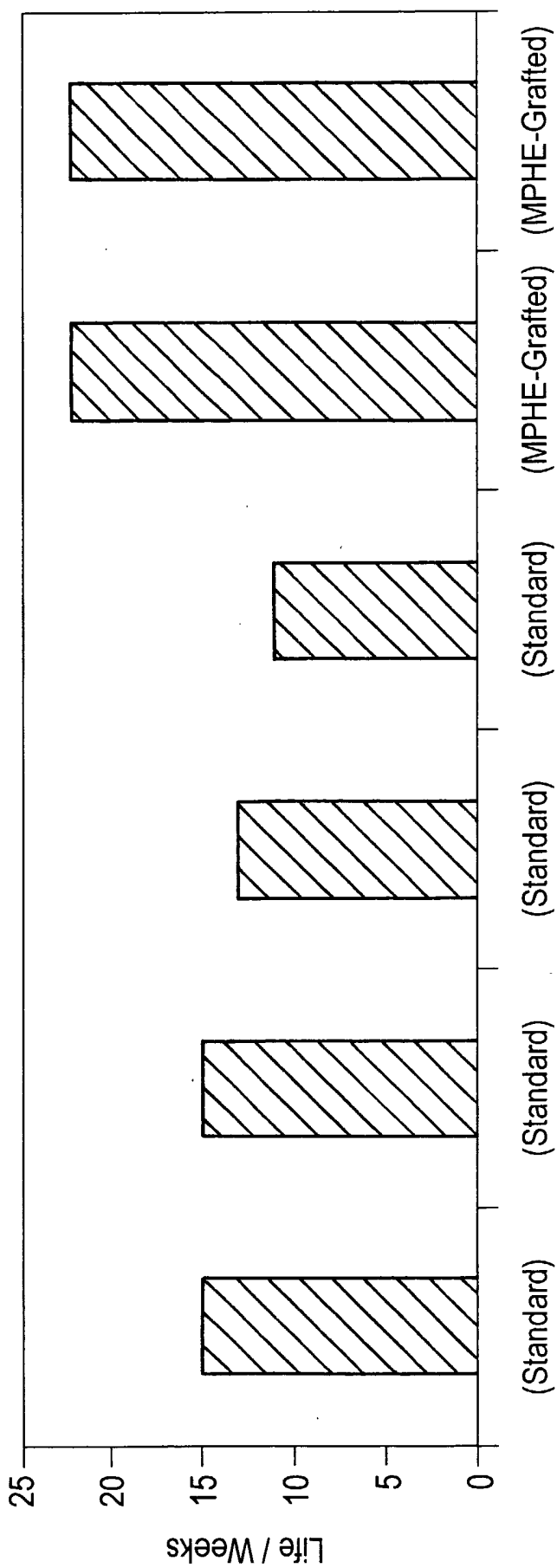


**FIG 4**



Press Fabrics run on Pick Up position

**FIG 5**



**Fig 6**

4/4