(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

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

PCT

(10) International Publication Number
WO 03/057977 A2

(51) International Patent Classification[7]: D06M 14/00

(21) International Application Number: PCT/GB03/00076

(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'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 03/057977 A2

(54) **Title:** PAPERMAKING BELTS AND INDUSTRIAL TEXTILES WITH ENHANCED SURFACE PROPERTIES

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

PAPERMAKING BELTS AND INDUSTRIAL TEXTILES WITH ENHANCED SURFACE PROPERTIES

The present invention relates to industrial fabrics and has particular relevance to fabrics on which non-woven materials may be formed by hydroentanglement and other formation techniques for the "Nonwovens" market sector and to papermakers' fabrics, such as forming fabrics, dryer fabrics and TAD fabrics, i.e. fabrics for use in the production of paper products using through-air drying (TAD) installations. TAD fabrics are conventionally used in the manufacture of paper towels, facial tissue, bathroom tissue, table napkins and the like.

US 6,017,417, US 6,331,230 and WO 01/44568 describe the manufacture of tissue and the like using through-air drying. Typically in such processes a slurry of cellulosic fibres is fed onto a forming fabric or between two forming fabrics, where the paper web is formed and partially dewatered before the web is transferred, often via a transfer fabric, to a TAD fabric for further water removal via one or multiple TAD units. The web is then fed via the TAD fabric to a presser roll where a nip is formed between the TAD fabric and a Yankee cylinder. Here the paper web transfers to the Yankee cylinder where further drying and creping takes place. In one variation of this process, the Yankee cylinder has been removed, thus eliminating the pressing nip. In this case, the web is transferred from the TAD fabric to a further fabric.

It is conventional to spray a chemical release agent, e.g. silicone oil onto the TAD fabrics in order to provide good sheet release, whether it be to aid the transfer of the sheet on to another fabric or on to the Yankee cylinder, after exiting the presser roll nip. There are a number of potential problems associated with using a chemical release agent in the TAD process, two of these being that they are messy to utilise and very expensive.

TAD fabrics are flat-woven fabrics, which are spliced, adhesive being applied to the terminal ends in the joint area to provide supplementary strength and to keep these terminal ends in-plane. It has been found that when no adhesive is present, the chemical release agent tends to facilitate the process of allowing the terminal ends to relax under operating temperatures, which causes them to come out of plane of the fabric. Once out of plane, damage to, or rupture of, the sheet will inevitably occur and the seam will slowly fatigue until premature failure occurs. The use of adhesive in the joint area helps to keep the terminal ends in place but adversely affects the porosity of the fabric at the joint, which can in turn have an unfavourable affect on product quality and machine performance. Ideally, a seam should have the means for terminal end restraint without utilising adhesive.

Furthermore, chemical release agent has been found to accumulate on the fabric causing waste fibre build-up and so blocking of the surface. This again affects the rate of drying and thus paper quality.

Probably the most critical problem with the use of the chemical release agent is the fact that it remains in the recycled white water system. Most modern paper machines tend to have closed water systems, and so the water that is removed from the cellulosic stock during the papermaking process and the reclaimed fabric shower water is collected, recycled and then reused as shower water and also to dilute the new cellulosic stock. In the interim period, the water is stored in holding tanks and here the minute beads of chemical release agent coalesce into larger globules. It is extremely difficult to separate the chemical release agent from the water and the globules end up coating these tanks, which finally make their way back into the system. When the globules find their way into the cellulosic stock, there are potentially a number of problems which all result in a reduction of paper quality and machine operating efficiency.

The paper stock is a complex, charged system, with additives, such as cationic retention aids, added in order to ensure that all of the individual components of the stock bond together. When oil gets into this system it interferes with these charges and suppresses the effectiveness of the additives. This in turn will lead to higher operating costs since additional amounts of additives will be needed to achieve the desired sheet properties.

Another problem is that globules in the stock act as a debonder and reduce the sheet strength. Machine refining must be increased to compensate for the loss in sheet strength, which will make the sheet harder to dewater and/or dry and, in some cases, result in a loss in machine speed and/or output.

During manufacture the sheet side of conventional TAD fabrics is sanded so as to increase the surface contact area of the fabric from between 6-12% to between 20-30%. This is required in order to ensure good transfer of the paper web for example from the TAD fabric to the Yankee cylinder and good final sheet strength. The sanding process usually encourages the onset of micro-fibrillation of the yarn components on the paper-facing side, a problem that is accentuated through the use of high pressure showers. These fibrils eventually cause a reduction in the fabric's permeability, which in turn will lead to a poor drying profile and subsequently lead to lower machine output.

TAD fabrics are conventionally made from polyester yarns, designed to improve their dry heat, hydrolysis and abrasion resistant properties. The operating environment on a TAD machine accelerates polymer degradation due to these phenomena, which ultimately cause fabric failure to occur. Fabric cleanliness is also an issue with conventional dryer and TAD fabrics in that dirt or so-called "stickies" tend to adhere to the fabric surface, which can cause holes in the sheet. Conventional TAD fabrics may also suffer from a lack of rigidity leading to cross-machine direction undulations in the fabric particularly post the TAD cylinder/s. Occasionally the undulations can be so severe as to cause irreversible localised folding of the fabric, necessitating its removal from the machine.

The present invention has been made from a consideration of these problems.

According to one aspect of the present invention there is provided an industrial textile comprising a polymeric substrate and a resin system grafted onto the polymeric substrate, via a primer, 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.

The primer facilitates good adhesion between the resin system and the polymeric substrate.

The industrial textile of the invention may comprise a woven and/or nonwoven fabric.

In one embodiment of the present invention there is provided a TAD fabric comprising, a polymeric substrate and a resin system grafted onto the polymeric substrate, via a primer, wherein said resin system comprises water-borne thermoplastic, fluorinated, polyhydroxyether resin and/or one or more analogues thereof and at least one co-resin.

A fluorinated polyhydroxyether resin is preferred in TAD applications so as to provide excellent sheet release.

Examples of analogues of polyhydroxyether resins include polyurethane modified polyhydroxyether resin, epoxy end-capped polyhydroxyether resin and polycaprolactone modified polyhydroxyether resin.

The polymeric substrate of this and the further aspects of the invention ideally comprises PET (polyester), PPS (polyphenylene sulphide), PCTA (poly 1,4 cyclohexalene dimethylene terephthalate), PEN (polyethylene naphthalate) or PEEK (polyetheretherketone). The substrate can also be of hybrid construction where, for example, one of the warp yarns or weft yarns would be made of PET and the other of the warp yarns or weft yarns would be made of PVDF (polyvinylidene fluoride)..

The water-borne surface enhancement composition of the invention does not cause environmental problems as compared with the prior art epoxy resin coating compositions.

The permanent chemical modification of the conventional polyester, modified polyester, PPS, PEEK or any suitable polymeric substrate for the manufacture of TAD fabrics, in accordance with the invention provides a number of benefits including the enhancement of hydrophobic properties giving permanent superior paper web sheet release thus eliminating, or at least minimising the need to continuously apply a temporary chemical release agent to the TAD fabric. A further benefit of the inherent film bonding strength of the resin composition is the possibility of eradicating the need for the adhesive currently applied to the terminal ends in the seam area.

The TAD fabrics of the invention also exhibit reduced fibrillation in that the treatment of the fabric, post the surface grinding stage, envelopes, captures and locks back into the surface any protruding fibrils so as to reduce the risk of these being the source of cellulosic fibre build-up, as well as of large scale fibrillation. In addition, the treatment smooths out the micro rough area, created during grinding, by filling in the valleys between the fibrils.

The added chemically grafted layer also reduces the rate of thermal degradation by forming a permanent, heat resistant barrier. Also, due to the oleophobic nature of the surface enhancement, because of the addition of fluorine, the fabric tends to stay cleaner. In addition, improved x/y fabric rigidity, through binding of the cross-over points, results in less tendency towards undesirable cross-machine corrugation.

It is also believed that the hydrophobic surface modifications have the effect of reducing the capillary action, particularly at the md and cmd yarn cross-over points, that retain the water in the fabric post showering. This means that devices, such as the vacuum box and/or air knife, used to remove residual water, are able to work far more efficiently. The result is that the lower the amount of residual fabric water post cleaning, the lower the drying load on the TAD's, and so the more efficient is the drying and the lower the overall energy consumption.

The water-borne thermoplastic polyhydroxyether grafted layer with co-resins and modifiers also has a more universal application in the manufacture of other papermaker's fabrics, such as forming fabrics, press felts, tissue fabrics and dryer fabrics.

Papermachine clothing is essentially employed to carry the paper web 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 nips formed by rotating cylindrical press rolls. Water is squeezed from the paper web and into the press fabric as the web and fabric pass through the nip together. In the final stage, the paper web is transferred either to a yankee dryer, in the case of tissue paper manufacture, or to a dryer fabric, the majority of the remaining water being evaporated as the paper passes around a number of steam heated dryer cylinders.

Many known forming fabrics, press fabrics and dryer fabrics, like TAD fabrics, suffer from adherence by stickies, poor wear-resistance, poor fabric-stability and/or stiffness. There are a number of patents which have attempted to address, in particular, the problem of contamination.

US 5,019,428 describes the application of modified polyurethanes containing perfluoroaliphatic groups to fibre-materials to provide oil- and water-repellent finishing.

US 5,395,868 and 5,207,873 disclose a coating solution for papermaking fabrics that includes as its primary components polytetrafluoroethylene, urethane copolymer and polyacrylamide. US 6,284,380 discloses papermaker's fabrics having a polyurethane based coating including a copolymer of perfluoroalkyl acrylates. These coatings are claimed to render these papermaker's fabrics contamination resistant. It is noted however that in none of the above prior art is there an indication that there is a priming process involved, even though it is well known that the adhesion of coatings to polyester and some other polymers is difficult, due to the lack of bonding sites on the polymer's surface. ("Surface Modifications of PET by Alkali Treatment", Textile Progress, Vol. 20, No. 2, 1989 by S.H. Veronian and Textile Research Journal 1978, Vol. 48, No. 4, by A.D. Weigmann). In addition, being non-waterborne additives, the prior art coatings are likely to be less environmentally friendly than water-borne chemicals, because of the possibility of the generation of undesirable volatile organic compounds. One further drawback of the prior art coatings containing polytetrafluoroethylene is that it may be necessary to deploy high curing temperatures, which may be disadvantageously close to the polymeric substrate's heat setting and melting temperatures.

In another embodiment of the present invention there is provided a papermaker's fabric comprising a polymeric substrate and a resin system grafted onto the polymeric substrate, via a primer, 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.

For the avoidance of doubt, the papermaker's fabric as hereinbefore described has, as one of its many potential applications, application as a non-TAD tissue-making fabric.

The papermaker's fabric of the invention has a preferred application as a forming fabric. Here the added chemically modified surface of the invention results in virtually no overall loss in cfm, but gives a reduction in the adherence of stickies, which saves the customer wash-up time, as well as reducing the need for continuous high pressure cleaning showers and chemical treatments. It also results in an increase in the fabric stability, due to bonding at the cross-over points and a reduction in the apparent carrying of water because of the filled cross-over points.

The papermaker's fabric of the invention has further application as a dryer fabric. Here the preferred polymeric substrate would include any of PET, PPS, PCTA, PEN or PEEK.

The chemically modified substrate of the invention results in the reduction in the adhesion of stickies, the stiffening of the fabric and the protection of the dryer fabric yarns by insulating them from the heat and also preventing the ingress of water in to the yarn cross-over locations, with virtually no loss of cfm.

The chemically modified substrate of the invention has particular application when the polymeric substrate comprises PET, PPS, PCTA, PEN or PEEK. Other possible polymeric substrates could be one or more thermoplastic elastomers such as PU.

In a further embodiment of the present invention there is provided an industrial fabric comprising a polymeric substrate and a resin system grafted onto the polymeric substrate, via a primer, 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 present invention also has application in the manufacture of non-woven materials for the nonwovens sector. Nonwovens can either be dry or wet formed. To add strength, the sheet is then hydroentangled or a bonding agent is applied to the web and then cured.

In a further embodiment of the present invention there is provided a hydroentanglement screen on which nonwoven materials may be formed by hydroentanglement, said screen comprising, a polymeric substrate and a resin system grafted onto the polymeric substrate, via a primer, 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 chemically modified substrate of the invention displays increased wear resistance, superior sheet release, a reduction in water carriage back into the hydroentanglement zone and a reduction in the incipient carrying of water because of the filled cross-over points.

In a further embodiment of the present invention there is provided a conveying fabric on which latex impregnation of conventionally air-laid materials occurs, said conveying fabric comprising, a polymeric substrate and a resin system grafted onto the polymeric substrate via a primer, 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 use of a latex binder is an extremely messy process and results conventionally in the need for unscheduled machine shut-downs in order to clean the contaminated substrate. The chemical surface modification of the invention will reduce or eliminate the need for these shut downs and extend the life of the fabric beyond current levels. Contamination of the conveying fabric can also arise from the presence of dry binders such as low melt fibres; the chemically modified surface once again renders easy removal of such contamination.

The various fabric screens used for the manufacture of nonwoven products described herein may be woven or nonwoven. In one embodiment the screens could comprise a non-woven, spiral link fabric, as described in US 4,345,730.

In a further embodiment of the present invention there is provided a screen on which a spun bonding process occurs, said screen comprising, a polymeric substrate and a resin system grafted onto the polymeric substrate via an intermediate primer, 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.

In a further embodiment of the present invention there is provided a screen on which a melt blowing process occurs, said screen comprising, a polymeric substrate and a resin system grafted onto the polymeric substrate via an intermediate primer, 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.

Papermachine fabrics tend to be manufactured from synthetic materials, such as polyester, which is commonly used for TAD fabrics, forming fabrics and dryer fabrics. This, and any other suitable substrates onto which the resins are capable of being grafted, can be used. As alluded to earlier, it has been known that permanent adhesion of materials to polyester is notably difficult to achieve because of a lack of surface reactive sites on the polymer's outer surfaces, and the inability of any modifying medium to penetrate the substrate to any useful degree. It is a feature of the invention to pre-activate the surface of the substrate by means of a priming step. This may involve the use of a physical priming method, such as Plasma or Corona treatment. However, a chemical primer step is preferred. Such primers will be described in more detail hereinafter. Once primed, a second resin mixture is grafted to the polyester through this primer. The second resin mixture layer can be designed to impart specific properties to the fabric. In the present invention, the main component of the second layer is a "water-borne thermoplastic polyhydroxyether resin" and/or analogues thereof, ideally together with one or more other co-resins.

In a further embodiment of the invention there is provided an industrial fabric comprising a polymeric substrate, wherein a primer is secured to the polymeric substrate and wherein a resin system comprising water-borne thermoplastic, optionally fluorinated, polyhydroxyether resin and/or one or more analogues thereof and at least one co-resin is grafted onto said substrate via a primer, and wherein the polymeric substrate comprises any of PET, PEN, PPS, PCTA or PEEK.

Ideally the water-borne thermoplastic polyhydroxyether resin is fluorinated.

The resin mixture comprising the aforesaid polyhydroxyether and/or one or more analogues thereof and one or more co-resins, ideally comprising polyurethane and/or a polyurethane derivative. The resin mixture may also further comprise one or more siloxanes, preferably an amine functional siloxane.

These resins are ideally cross-linked so as to form an interpenetrating polymeric network.

In a further embodiment of the invention there is provided a method of making tissue paper including the use of a TAD fabric, in which during said method no chemical release agent is applied to said TAD fabric, and wherein water-borne thermoplastic, optionally fluorinated, polyhydroxyether resin and/or one or more analogues thereof and at least one co-resin are grafted onto a least a part of said polymeric substrate, via an intermediate primer.

The term "water-borne thermoplastic polyhydroxyether resin" as used herein refers to a polyhydroxyether (e.g. 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.

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 as well as US

4,374,875, US 4,559,247 and US 4,355,122 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 amorphous thermoplastic polyhydroxyether, the thermoplastic polyhydroxyether having a polydispersity of less than 4.0 and a number average 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 45,000, i.e. much higher than epoxy resins which have a maximum molecular weight of about 8,000, which by comparison means that phenoxy has far greater toughness and a higher Tg. In addition, the major advantage of polyhydroxyether resins above epoxy resins is that they have primary and secondary hydroxyl groups for reactivity and cross-linking. The ethylenically unsaturated monomers preferably have from about 3 to 8 carbons and are ideally selected from the group consisting of methyl methacrylate, ethyl acrylate, n-propyl methacrylate, butyl acrylate, acrylonitrile, methyacrylonitrile, styrene, alpha-methyl styrene and p-vinyl toluene.

At least one of the ethylenically unsaturated monomers preferably contains sufficient carboxyl groups to provide from about 1 to 100 carboxyl groups per 10 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. The polyhydroxyether resins are ideally fluorinated.

A preferred resin is PKHW-34F, which has a long fluorinated carbon chain, which is supplied by Phenoxy Associates. It is common knowledge that for fluorocarbon repellents on a fabric approximately 10 fully fluorinated carbon atoms are needed in a normal alkane chain to achieve maximum repellency (Fluorinated Surfactants and Repellents, Second Edition, Erik Kissa, page 531).

The fluorinated resin, along with co-resins and cross-linking agents act to lower the surface energy of the fabric to less than about 20 dynes/cm, thereby improving paper sheet releasability due to the increased hydrophobicity. This hydrophobicity has been achieved through the synergistic action of the fluorine and silicone groups in the resin mixture. The oil and dirt repellency is solely attributable to the fluorine atoms present.

Additionally, an alternative fluorinated polymer, ideally having hydroxyl groups, may be added to the formulation. An example of such a material is LUMIFLON 4400 SERIES made by Asahi Glass and sold in USA by AGA Chemicals. LUMIFLON is a non-ionic water emulsion of a ter-polymer made of vinyl ether-type macro monomer having a hydrophilic long chain and secondary hydroxyl groups, fluoroethylene and vinyl ethers. A further similar material is marketed under the trade mark ZEFFLE by Daikin America, Inc.

To achieve the optimum performance properties the polyhydroxyether formulation preferably includes any of the following co-resins and crosslinkers including:-

1. one or more amine-functional siloxanes ideally in the form of an emulsion. The siloxane provides water repellency. Examples of such a material are NULASTIC 24E and NUSIL 19E as supplied by Nulastic Incorporated.

Further examples include Tegophobe (1400, 1500 and 1600 series) and Tego Proteck 5000 and 5100 series, as marketed by Degussa, and Dow Corning silicones, e.g. 2-9034, which are added for water repellency purposes.

2. polyether based aliphatic polyurethanes containing carboxyl and/or hydroxyl groups for providing flexibility and water resistance. An example of such a material is Solucote 1023 and 1013, as supplied by Solulol Corporation. Other examples include Syncure polyurethanes from Noveon and polyurethanes from Stockhausen, Reichold, C.K. Witco, Hauthaway e.t.c.

3. one or more cross-linkers such as a blocked isocyanate and/or an epoxidised siloxane monomer, an oxazoline, a carbo-diimide, a polyethylene imine, a polyaziridine, melamine formaldehyde resin, or an aliphatic polyisocyanate. An example of a blocked isocyanate is Grilbond IL-6 from EMS Grilon, and an example of an epoxidized siloxane monomer is Coatosil 1770 from Osi.

4. one or more wetting agent such as Coatosil 1211 from Osi, fluoro-surfactants such as Fluwet OTN from Clariant GmbH, ethylene-propylene oxide or ethylene-propylene oxide/siloxane or ethylene propylene oxide surfactants, such as Silwet from C.K. Witco or Surfynol from Air Products.

Ideally the cured, grafted layer should be in the form of an Interpenetrating Polymeric Network (IPN). A mixture of cross-linkers may be selected to provide this, as well as to suit the finishing process. The cross-linkers, due to their functionality react with themselves i.e. further polymerising at a given temperature and simultaneously cross link with e.g. the hydroxyl and carboxyl functional groups present in the other resins such as PKHW-34F and polyurethanes, giving a much higher cross-link density and an IPN.

Before the aforementioned grafted layer is applied it is preferable at least in the case of polyester, to pre-activate the substrate with a priming step.

The primer consists of an activating species, a substrate specific penetrant and a wetting agent. It ideally contains a caprolactam blocked isocyanate in water. An example of a caprolactam blocked isocyanate is IL-6 from EMS Grilon. This can be used alone or in combination with a water-based epoxide, such as Grilbond G1701, as practised in the tyre reinforcement industry (c.f. TyreTech, Asia 196, Günter Kurz). Other blocking agents can be Ketoxime or Phenol. These can be used singularly or in combination. Alternatives to primers containing blocked isocyanates are for example, waterborne polyesters, such as AQ 29 D from Eastman Chemicals and the NS Series from Takamatsu Oil and Fat Co., Ltd., and alkoxy silane primers from United Chemical Technologies Inc.

Additionally the primer preferably comprises the following additional components:-

1. an alkyl phthalimide serves as a water soluble penetrant for polyesters. It acts on the polyester to open up surface pores allowing the blocked

isocyanate and any dyestuff to penetrate and secure to the polyester and so activate the surface of the polyester to bond to the subsequently applied coating layer. An example of this is Cindye DAC 999 from Stockhausen.

2. one or more pre-dispersed dyes, used as a witness to penetration into the substrate yarns. An example of this is LUMACRON S3 BS Red 150% or Lumacron Navy 300% from Dohmen UK Ltd.

3. one or more wetting agents as discussed hereinbefore.

4. one or more levelling and dispersion agents.

5. one or more binding agents.

6. one or more anti-foaming agents.

7. one or more emulsifiers.

8. one or more anti-settling agents.

The primer is preferably applied by a kiss roll, dried at about 125°C followed by a dye fixation and surface activation step at 190°C (160 – 240°C).

The second resin mixture is again preferably applied by a kiss roll followed by water removal at about 125°C and a final grafting and curing (cross linking) step at 190°C (160 – 240°C). 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 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. Application by means of foaming or spraying techniques, or like industrial processes, is feasible.

It can be seen that the primer step creates a substrate with reactive sites and the second step produces the cured, grafted IPN structure. Both steps are finished at 190°C, which is about 10-15 °C below the heat-setting temperature of a polyester fabric. The grafting and cross-linking steps renders the fabric stiff. The low surface energy modification forms an integral part of the substrate, such as PET, and is able to withstand high pressure showers up to 600 psi or 40 bar.

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 reference to the following example:-

EXAMPLE 1

A woven polyester TAD fabric was primed via a kiss roll with the primer composition set out below typically at a concentration of 4.5% solids.

3.33ml premixed Lumacron red dye solution (conc. 330g/l)

20g/l Cindye DAC 999 – alkyl phthalimide

40g/l Grilbond IL-6 – blocked isocyanate

5g/l CoatoSil 1211 – wetting agent

Water

The primer was dried at about 125°C followed by a dye fixation and substrate activation step at 190°C.

A second resin mixture was then applied using a kiss roll. The components of the second mixture are listed below. The concentration of the second mixture was typically 4.2% solids.

54.4g/l Phenoxy PKHW 34F -a hydroxyl functional fluorinated polyhydroxyether

33g/l Solucote 1023 – a carboxyl functional polyurethane

20g/l Nulastic 24E – amine functional siloxane emulsion

The aforementioned components together form the dispersed resin material. The two cross-linking agents listed below serve to create the cured and grafted IPN.

1.5g/l CoatoSil 1211 – wetting agent

2g/l CoatoSil 1770 – cross linker – epoxidized siloxane monomer

12g/l Grilbond IL-6 – caprolactam blocked isocyanate -crosslinker

Water

The chemically modified substrate is then dried at about 125°C prior to a final grafting and curing (cross-linking) step at approximately 190°C.

The resulting TAD fabric had a water repellency rating of 6 (a Du Pont version of AATCC water repellency test; highest achievable is 6) and an oil repellency of 4 (AATCC test; highest achievable rating is 6). These are both drop test methods in which drops of liquids of different surface tensions are placed on the coated fabric and its spreading observed (Test Methods, Erik Kissa, page 550, quote 174).

In addition, our results showed there to be virtually no overall loss in cfm (a measure of fabric permeability, cubic feet/square foot/per minute at 12.7mm water gauge). As an example, the air permeability of the TAD fabric was measured at 3 different stages of manufacture in cfm:

Control Sample:	705
Sanded Sample:	687
Treated Sample:	680

EXAMPLE 2

The procedure of Example 1 was repeated using the primer and resin formulation as shown below.

Again, a woven polyester TAD fabric, was primed via a kiss roll using a primer at a concentration of 4.5% solids.

Primer composition

20g/l Lumicron Blue Dye

20g/l Cindye DAC 999 – alkyl phthalimide

30g/l Grilbond IL-6 – binding agent

2g/l Coatosil 1211 – wetting agent

1.5g/l Coatosil 1770 – binding agent

3g/l Synthapal DEG – levelling and dispersing agent

Water

This was dried at 125°C followed by a dye fixation and substrate activation step at 190°C.

Second resin mixture

50g/l PKHW 34F10 – a hydroxyl functional fluorinated polyhydroxyether

60g/l PU 10-96-1 – reactive polyurethane

7.5g/l Coatosil 1770 – cross-linker

4g/l Grilbond IL-6 – cross-linker

1.0g/l Fluowet OTN – fluorinated wetting agent

Water

This treatment provided a TAD fabric with a water repellancy rating of 6 and an oil repellancy of 6, both as determined using the AATCC tests as referred to in Example 1.

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

Claims

1. An industrial textile comprising a polymeric substrate and a resin system grafted onto the polymeric substrate, via a primer, 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.

2. An industrial textile according to claim 1, wherein the substrate is a woven and/or non-woven fabric.

3. An industrial textile according to claim 1 or claim 2, wherein the polymeric substrate is a TAD fabric and wherein said resin system comprises water-borne thermoplastic, fluorinated, polyhydroxyether resin and/or more analogues thereof and at least one co-resin.

4. An industrial textile according to any preceding claim, wherein the resin system comprises at least one of the following analogues of polyhydroxyether resins:- polyurethane modified polyhydroxyether resin, epoxy end-capped polyhydroxyether resin and polycaprolactone modified polyhydroxyether resin.

5. An industrial textile according to any preceding claim, wherein the polymeric substrate comprises any of the following either alone or in combination:- PET (polyester), PPS (polyphenylene sulphide), PCTA (poly 1,4 cyclohexane dimethylene terephthalate), PEN (polyethylene naphthalate), PVDF (polyvinylidene fluoride) or PEEK (polyetheretherketone).

6. An industrial textile according any preceding claim, wherein the industrial textile comprises warp yarns and weft yarns, one of said warp yarns or weft yarns being made from PET and the other of said warp yarns or weft yarns made from PVDF (polyvinylidene fluoride).

7. An industrial textile according to any of claims 1 to 5, wherein the industrial fabric is a spiral link fabric.

8. An industrial textile according to any preceding claim, wherein the polyhydroxyether resin is fluorinated.

9. An industrial textile according to any preceding claim, wherein the resin system comprises polyurethane and/or a polyurethane derivative.

10. An industrial textile according to any preceding claim, wherein the resin system comprises one or more siloxanes.

11. An industrial textile according to claim 10, wherein said one siloxane is an amine functional siloxane.

12. An industrial textile according to any preceding claim, wherein the resin system is cross-linked.

13. An industrial textile according to any preceding claim, wherein one or more ethylenically unsaturated fluorinated monomers is grafted to the polyhydroxyether resin.

14. An industrial textile according to any preceding claim, wherein the polyhydroxyethers are prepared as a water-borne amine-neutralised, carboxylated, polyhydroxyether resin.

15. An industrial textile according to any preceding claim, wherein the polyhydroxyethers of the resin have a weight average molecular weight greater than substantially 20,000 and less than substantially 45,000.

16. 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.

17. An industrial textile according to any preceding claim, wherein the resin system comprises polyether-based aliphatic polyurethanes containing carboxyl and/or hydroxyl groups.

18. An industrial textile according to any preceding claim, wherein the resin system comprises one or more cross-linkers.

19. An industrial textile according to claim 18, wherein the cross-linker comprises any of the following either alone or in combination:- a blocked isocyanate and/or epoxidised siloxane monomer, an oxazoline, a carbo-diimide, a polyethylene imine, a polyaziridine, melamine formaldehyde resin or an aliphatic polyisocyanate.

20. An industrial textile according any preceding claim, wherein the resin system comprises one or more wetting agent(s).

21. An industrial textile according to claim 20, wherein the wetting agent is selected from fluorosurfactants, ethylene-propylene oxide, ethylene-propylene oxide/siloxane or ethylene propylene oxide surfactants.

22. An industrial textile according to any preceding claim, wherein the resin system once cured is in the form of an Interpenetrating Polymeric Network (IPN).

23. An industrial textile according to any preceding claim, wherein the primer comprises an activating species, a substrate specific penetrant and a wetting agent.

24. An industrial textile according to any preceding claim, wherein the primer contains a caprolactam blocked isocyanate in water, which can be used alone or in combination with a water-based epoxide.

25. An industrial textile according to any preceding claim, wherein the primer contains a water-borne polyester.

26. An industrial textile according to any preceding claim, wherein the primer comprises any of the following either alone or in combination:- an alkyl phthalimide, one or more pre-dispersed dyes, one or more wetting agents, one or more levelling and dispersion agents, one or more binding agents, one or more anti-foaming agents, one or more emulsifiers and one or more anti-settling agents.

27. An industrial textile according to any preceding claim, wherein the primer is applied by spraying, application as a foam or by a lick-up or kiss roll process.

28. An industrial textile according to any preceding claim, wherein during the modification of the industrial textile, the primer is dried at about 125°C.

29. An industrial textile according to any preceding claim, where during the modification of the industrial textile the primer is surface activated at between 160°C-240°C.

30. An industrial textile according to claim 29, wherein the primer is surface activated at 19O°C.

31. 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.

32. An industrial textile according to any preceding claim, wherein during the modification of the industrial fabric water is removed from the resin system at 125 C.

33. An industrial textile according to any preceding claim, wherein during the modification of the industrial textile the resin mixture is grafted and cured at a temperature in the range from 160 to 240 C.

34. An industrial textile according to claim 33, wherein the resin mixture is grafted and cured at substantially 190 C.