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Waterproofness Results for the Surface Treatment of Heavy-Duty Leather for Adhesion Enhancement

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This article presents further work undertaken in respect to the use of specific primers for adhesion on leather surfaces. This research focused on the use of photo-reactive reagents and silane networks as primers and investigated their roles in seam strength and resistance against water ingress. A specific waterproof test was undertaken on treated samples in accordance with EN ISO 5403:2002. Samples treated with 4-(2,2'-iminodiethanol)-3-nitrophenylazide (azide 4) when primed only on one side of the test panel showed good resistance to water ingress. Samples treated with 3,5-dihydroxyphenyl-4-azidobenzoate (azide 7) or 3-(2-aminoethylamino)propyltriethoxysilane (AEAPES) on both sides of the test panels resulted in a seam that did not fail. However, double side treatment with these reagents generated a thicker glue line than single side treatment, which might present practical problems in terms of the flexibility of the resultant assembly during its life cycle.

Keywords: Leather; Surface primers; Waterproof testing

1. INTRODUCTION

Leather is a natural occurring material and has been used for various artefacts from the dawn of humanity. Its major constituent is collagen, which has well-known leather characteristics after re-tanning, colouring, fat-liquoring and finishing [1]. The tanning processes

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alters irremediably the peptide backbone chemistry and, subsequently, the leather's surface chemistry [1], which makes adhesion a problem in practice [2,3,4]. Various treatments are performed on surfaces to improve adhesion. The general treatments for adhesion technology go beyond the purpose of this article. In respect to leather surface we reported two methods of bonding based on increasing the degree of molecular contact between adhesive and the leather surface by enhancing adsorption [2,3,4]. Firstly, an Interpenetrating Polymer Network (IPN) was created by polymerization of monomers of the structure $X_3\text{-Si-R-Y}$ to form a cross-linked polysiloxane network which chemisorbed onto the leather surface *via* H-bonds or van der Waals interactions, whilst the Y group reacted with an isocyanate reagent to increase the overall hydrophobicity and adherence of the resultant IPN [4]. The monomer 3-(2-aminoethylamino) propyl-triethoxysilane (AEAPES) gave good results in peel testing (see Fig. 1), [4] the adhesion for these types of primer being achieved by mechanical interlocking involving the leather surface. Although the joints formed using an IPN-based network showed an increased total joint strength under dry and wet conditions, further improvements in adhesion under wet conditions were considered necessary to meet the stringent requirements for use of this technology in heavy-duty leather boots.

Secondly, we functionalised the leather surface by employing hydroxyl functionalised aryl azides such as: 4-(2,2'-iminodiethanol)-3-nitrophenylazide (azide 4) and 3,5-dihydroxyphenyl-4-azidobenzoate

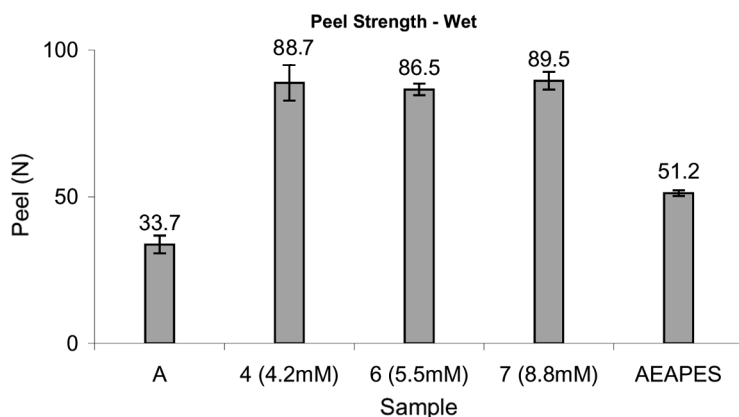


FIGURE 1 Peel strength for wet samples from [2,3,4]. A-abraded only, 4-azide 4 (4.2 mM), 6-azide 6 (5.5 mM), 7-azide 7 (8.8 mM).

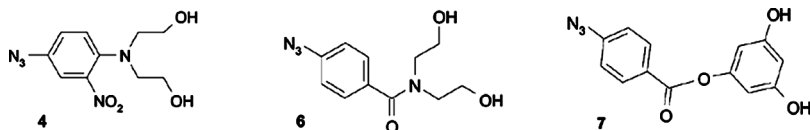


FIGURE 2 Azide primer structures [3].

(azide 7) [2,3]. These compounds decompose upon UV irradiation to generate very reactive nitrene species which bind to the leather surface. Azide molecules were designed to possess at least one hydroxyl functionality to enhance the binding with a one-component polyurethane type adhesive commercially available [2,3]. As a result, the leather surface is enriched with hydroxyl groups and this helps adhesion *via* physical bonds (H-bonds) and covalent bond formation with the adhesive (see Fig. 1).

One of the conclusions of our earlier work [2,3] was that aryl azide structures 4&6 (Fig. 2) provided solid adhesive bonds under dry (increased by 99%) and wet testing conditions (increased by 163% and 157%, respectively, compared with the standard procedure, Fig. 1). The adhesion for these types of primers was achieved by employing H-bonding and van der Waals forces between the newly introduced OH functionalities and the adhesive in solution. Although the work undertaken was specific for a heavily treated leather surface (Salz Leathers US, now closed) with undisclosed waterproof wax, the principles of surface activation described could be extended to other surfaces.

This article investigates the improvements achieved in the seam sealing properties towards water penetration of these adhesives using the molecular by designed adhesion primers azide 4, azide 7, and AEAPES. In practice, the effects of water towards the durability of adhesive joints have been addressed by various authors [5,6], the use of a known standard in this case providing a bench mark for future reference [7,8]. The testing was undertaken using a test machine as described in EN ISO 5403, Sect. 4.1.1–4.1.3.

2. TESTING OF SEAMS FOR WATER PENETRATION

Seam adhesives should ideally provide protection but also prevent water ingress by providing an effective seal. In this respect, the structural strength of the adhesion assembly was determined by estimating the peel strength using the T-peel test after 24 h water soaking [2,3,4].

The T-peel tests used were undertaken using ASTM D1876–72 as a reference and consisted of peeling apart two lap bonded pieces of leather (25.4 mm wide, 10 test samples) fastened in the roll-over jaws of a tensiometer (Hounsfield-now Tinius Olseu, Salford, Surrey, UK with H.T.M. series software) at a constant speed and measuring the average force (N) required to separate the parts over a fixed distance (127 mm).

The structural strength can be defined as an intrinsic material property, the physical strength given by a material's substance. Any assembly constructed by joining two or more parts with the aid of an adhesive would have a maximum resistance to stress as determined by the each constituent.

In Fig. 1 we present for comparison purposes the results of our earlier work in respect to the degree of structural strength achieved for water soaked assemblies. Based on the peel strength studies of our work, specific water tests were undertaken by the Defence and Clothing Textile Agency (now closed) in accordance with EN ISO 5403 on Salz leather samples treated for adhesion with surface primers.

3. MATERIALS

The adhesive used was Solibond PU39 (Crispin Adhesives, Ltd., Leicester, UK), an opaque one-component polyurethane polymer solution which hardens upon solvent evaporation. [Manufacturer's specification: d 0.86–0.88 g cm⁻³, drying time at 20°C: 10 to 30 min. Solvents: acetone, ethyl acetate (EtOAc)].

Azide 4

A mixture of 4-fluoro-3-nitrophenylazide (1.18 g; 0.0065 M), diethanolamine (2,2'-iminodiethanol) (0.68 g; 0.0065 M) and EtOAc (20 cm³) was heated overnight on an oil bath with stirring, at 50°C. The reaction mixture was washed with water (3 × 20 cm³), dried (MgSO₄), and evaporated *in vacuo* to give the product as a red solid, re-crystallized from EtOAc to give 3 (38%). [¹H NMR (CDCl₃) 7.41 (d, J = 8.8, ArH), 7.35 (d, J = 2.6, ArH), 7.17 (dd, J = 2.6, 8.8, ArH), 3.7 (t, J = 5.1, 2x-CH₂-OH), 3.3 (t, J = 5.1, 2x-(CH₂)-N), 2.3 (bs, 2x-OH); HRESIMS (high resolution electrospray ionisation mass spectrometry) calculated for C₁₀H₁₄N₅O₄ (M+H) 268.1045, found 268.1042; IR (ν) 2110 cm⁻¹ (N₃)].

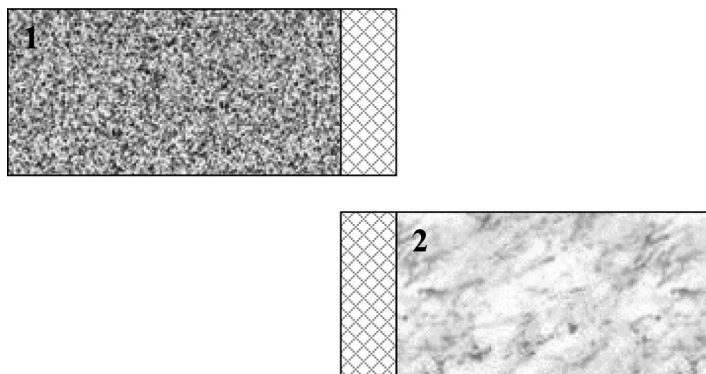


FIGURE 3 Test samples (were bonded only over hatched areas), 1 – flesh side, 2 – grain side.

Azide 7

To a refluxing solution of 4-azidobenzoic acid (1.63 g; 0.01 mol) in CH_3CN (10 cm^{-3}) was added 1,1'-carbonyldiimidazole (1.9 g; 0.012 mol). The solution was refluxed until it went clear and then left stirring for a further 30 min. Phloroglucinol (1.26 g; 0.01 mol) was added and the mono-substituted ester precipitated after 10 min as a white solid. EtOAc was added to dissolve the precipitate and the solution washed with water, dried (MgSO_4), and evaporated (*in vacuo*) to give 7 (Fig. 2, 0.21 g; 80%) as a colourless solid. [mp 170–175°C; IR (ν) 2090 cm^{-1} ; $^1\text{H NMR}$ (CD_3COCD_3) 8.5 (s, OH), 8.0, 7.2, 6.2 (m, Ar); EIMS calc for $\text{C}_{13}\text{H}_{13}\text{N}_4\text{O}_4$ 289.09368, found 289.0933].

4. TEST DESCRIPTION

The method was initially based on SLP 23 of the Society of Leather Trades' Chemists, on method IUP/11 of the International Union of Leather Chemists' Societies and BS 3144:1968 technique being intended for determining the water-proofness of any leather. In our specific case the test was applied to two pieces of Salz leather bonded together. Practically, the leather specimen is wetted on one surface and is flexed and compressed in the same manner as the sole of a shoe during walking. Measurements are made in respect to the duration of flexing which is just sufficient to cause water penetration from one face to the other, the percentage gain in weight due to water absorption during specified time intervals, and the mass of water

transmitted through the specimen from the face in contact with the water to the other face during a specified time interval (six hours)*.

5. SPECIMENS

The specimens are leather rectangles (100×40 mm) cut to size from larger panels. The surface treatment and testing for adhesion was reproduced according to our initial studies on the subject [2–4]. The specimens were superficially abraded with abrasive paper (Buehler P60, Buehler Ltd., Coventry, UK, both grain and inner flesh side) on specific areas at the edge of each specimen over an area of *ca.* 10×6 mm (the hatched area in Fig. 3, not to scale). The adhesive (Solibond PU39, Crispin Adhesives Ltd, Leicester, UK) was spread with a spatula only over the roughened areas. The panels treated with the adhesive were left in the open at RT for solvent flash-off. The total flash-off time was 14 min (determined experimentally elsewhere [2,3]) which was divided into two parts: a 9 min allowance for solvent evaporation in the open atmosphere, followed by a 5 min photo irradiation at a distance of 30 cm using a convection cooled 75 W Xenon arc lamp (Ushio America Inc., Cypress, CA, USA) vertically mounted on an A-1010 lamp unit.

The lamp was fitted with a pyrex window and f/4.5 reflector (Photon Technology International-PTI, Ford, W. Sussex, UK) and was powered by a direct current power supply (LPS-220) with igniter (PTI). The spectral characteristics of the xenon lamp were continuous in the visible range, extending far into the ultraviolet and near infra red (NIR). After flash-off and irradiation the panels were pressed together (*ca.* 0.4 kg cm^{-2}), the adhesive coated side to the superficially roughened side (over the hatched areas in Fig. 3), for a minimum of 5 min and allowed to set overnight at RT².

Quantities of compounds 4 and 7 were dissolved in EtOAc (8 cm^3) uniformly mixed with adhesive (80 cm^3) and the resultant mixture applied to leather panels for T-peel testing. The washings and roughening procedures applied to the leather panel before adhesion increases its surface area, make it porous, and introduce the necessary hooks and grooves to effect adhesion *via* mechanical interlocking

*The following ISO standards are indispensable for the application of this method: ISO 2418—Leather, chemical, physical and mechanical and fastness tests—sampling location; ISO 2419—Leather, physical and mechanical tests—sample preparation and conditioning; ISO 3696:1987—Water for analytical laboratory use—specifications and test methods. The test apparatus and all the necessary auxiliary equipment is described in EN ISO 5403, sect. 4.1 to 4.9. The sampling and sample preparation was followed using the same standard, sect. 5.

TABLE 1 Water Penetration Time for Control Samples

Sample	Initial mass (g)	Final mass (g)	% Water absorption	Penetration (min)	Comments
Stitched only	8.66	13.83	60	31	Penetration through seam
PU 39 only	10.00	10.87	7	210–240	Penetration through seam

mechanisms in the first instance. Any azide dissolved in an organic solvent (acetone or EtOAc) if applied to this surface would quickly penetrate the superficial layer and enter the corium.

Weighing of the specimens was performed in a conditioned laboratory (20°C and a 65% relative humidity according to ISO 2419) immediately prior to testing, immediately after the first sign of water penetration, and at the end of the testing period, using a calibrated four decimal place electronic balance. Thickness was not measured as it is not required by the standard.

Samples with adhesive sealant only (Solibond PU39) and with no surface treatment were investigated and used as a reference (Table 1). For comparison, the stitched seams were tested using the same procedure and the results are presented in Table 1. The waterproof test was undertaken subsequently for samples treated with azide 4, on one side of the test panels and azide 7 and AEAPES when both sides of the test panels were treated. The results are presented in Tables 2–4. The purpose of the exercise was to research practical solutions to deter water ingress through the seams under extreme conditions. Therefore, at this point, water absorption was of little

TABLE 2 Water Penetration Time for Azide 4, Single Sided

Sample	Initial mass (g)	Final mass (g)	% Water absorption	Penetration (min)	Comments
1	8.37	9.05	8	No penetration	Sample did not fail in 6 hr
2	7.48	8.39	12	No penetration 1–1.5	Seam did not fail Pin-holes through leather
3	7.76	8.64	11	No penetration 2–2.5	Seam did not fail Pin-holes through leather

TABLE 3 Water Penetration Time for Azide 7, Double Sided

Sample	Initial mass (g)	Final mass (g)	% Water absorption	Penetration (min)	Comments
1	7.08	7.50	6	No penetration	Seam did not fail
2	8.45	9.28	10	No penetration	Seam did not fail
3	6.40	6.72	5	No penetration	Seam did not fail

interest, but it has to be mentioned that from a manufacturing point of view this might generate problems in respect to the service life of the final product (shoe or boot).

6. DISCUSSION

The results demonstrate that seams without stitching but using the base adhesive alone allow water penetration in *ca.* 240 min through the seam structure (Table 1). The penetration could be due to discontinuities in the adhesive layer which lead to development of interstitial channels that allow water ingress across the seam. In the case when only stitches were used, the penetration occurred through the stitches' holes.

The best results were obtained with azide-type primers, as in all cases it was not the seam but the leather substrate that failed. This effect is observed when only one surface of the assembly was coated with the primer and adhesive, respectively. AEAPES was believed to create IPN-type networks across the surface [4] and in this case was applied on both surfaces to be bonded. The treatment also shows a considerable improvement in comparison with the use of the adhesive alone. In this case, AEAPES was used on both panels, creating a thick glue line across the seam which might generate problems during functioning of the final product.

TABLE 4 Water Penetration Time for AEAPES, Double Sided

Sample	Initial mass (g)	Final mass (g)	% Water absorption	Penetration (min)	Comments
1	7.21	8.44	17	No penetration	Seam did not fail
2	8.20	9.29	13	No penetration	Seam did not fail
3	8.58	9.84	15	No penetration	Seam did not fail

7. CONCLUSIONS

Overall, the use of surface primers clearly presents a considerable improvement towards the effectiveness of the waterproof seal. Our previous work suggested the active adhesion takes place when azide-type primers are used, due to covalent bonds generated at the leather surface. In Tables 2 and 3 one notices no water penetration for both azide primers, when only one side of the test panel was adhesive treated with azide 4 and two sides were treated with azide 7, respectively. But, under the same testing conditions, the seam had a better behaviour when both surfaces of test samples were coated with the adhesive solution (*i.e.* with azide 7, bearing in mind the adhesion mechanisms involved are essentially the same, for both compounds [2,3]). The observation to be made is towards the glue line thickness; the use of double layers (as in coating of both panels) might present practical problems in terms of the resultant flexibility of the assembly and production costs (the use of more primer).

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