

**Project 3
Environmental Durability of Adhesive Bonds**

Report No 9

**Forensic Studies of Adhesive Joints.
Part 4 -Footwear**

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PART 4 - Footwear.

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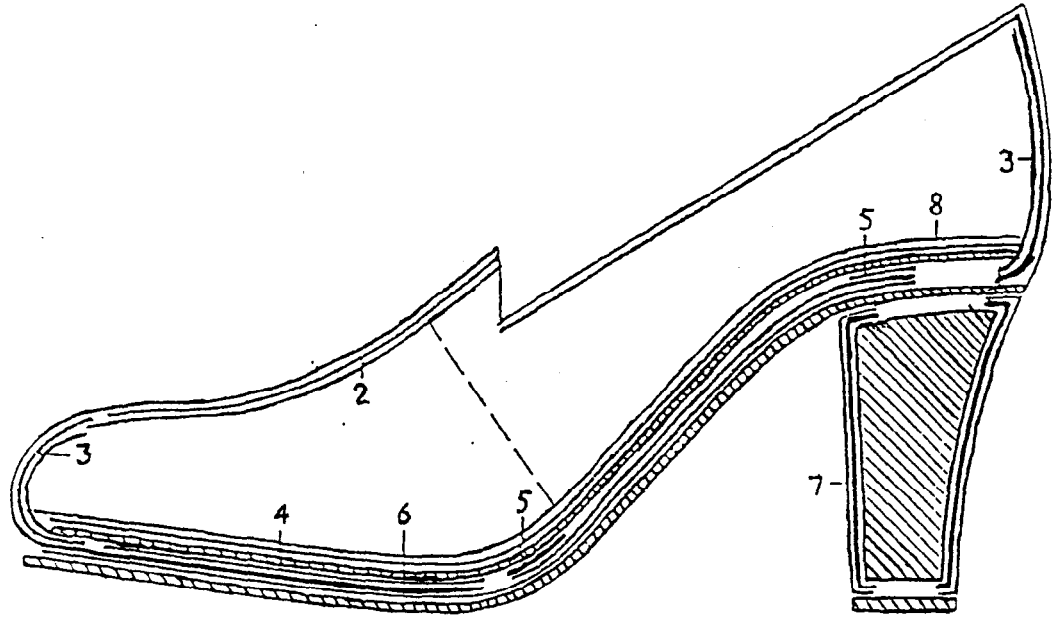
PART 4 - FOOTWEAR.

1. BACKGROUND

Although outwardly, other than to meet the demands of fashion, footwear design does not appear to have changed significantly over the last century, the techniques used in the manufacture of shoes have undergone revolutionary changes. These changes have resulted in a reduction in the production times for each item, as well as reducing the skill levels required for many of the operations.

The construction of modern footwear involves a widespread use of adhesives, the major exceptions being the sewing of uppers and in some cases, the attachment of heels with nails. Figure 1 shows, in general terms, the various roles in which adhesives have been used in footwear construction. Ancillary operations, such as the top line folding, linings and local stiffeners primarily make use of hot melt adhesives, typically polyamide or ethylene-vinyl acetate (EVA) co-polymers. These adhesives have generally superseded the earlier use of latex based adhesives, offering rapid application and bonding in automated production lines.

Of all the joints, probably the most demanding is that between the sole and the upper material. Not only is this joint the most heavily loaded but it is also exposed to a range of environmental agents, as well as being critical to satisfactory service life. Sole bonding was developed in the 1930's using natural rubber based adhesives. This usage expanded in the 1950's with the development of synthetic adhesives with improved tack, heat resistance and strength. Polyurethane adhesives were introduced in the mid 1960's with the ability to bond satisfactorily to PVC, due in part to their resistance to plasticiser agents. The use of adhesives in this location has now expanded such that around 90% of the UK footwear production incorporates adhesively bonded soles. It is this sole to upper joint that is considered in this forensic study.



Application	Adhesive Type	Typical peel strength (N/mm)
1. Topline folding	Hot melt - polyamide	
2. Linings	Latex - natural rubber Hot melt - polyamide, EVA	0.2 - 0.5
3. Toe puff Heel stiffener	Hot melt coating - EVA	0.5 - 1.0
4. Lasting	Hot melt - polyamide, polyester	0.5 - 1.0
5. Shank	Hot melt - EVA, polyamide	
6. Sole attachment	Solvent based polyurethane, polychloroprene	3 - 7
7. Heel Covering	Solvent based latex - polychloroprene	0.5 - 1.0
8. Insock	Latex - natural rubber, acrylate	0.2 - 0.5

Figure 1. Use of Adhesives in Footwear.
(Reproduced by kind permission of SATRA)

2. JOINT ASSEMBLY

2.1 Surface Treatment

As with all adhesive joints, correct surface preparation is of paramount importance to achieve the required level of performance from the adhesive bond. In this case, the area of the leather uppers to be bonded is prepared by a process of mechanical roughing. This removes the surface finishes, as well as removing the weakly attached surface grain layer of the leather and reveals the stronger underlying corium fibres.

The preparation of the soles depends largely on the material being used. The primary aims of the preparation are to remove surface contaminants, such as plasticiser and silicones, to enhance the wettability of the surface, and to modify the surface chemistry to improve the compatibility with the adhesive. For polymeric soles chemical preparation treatments are generally used. The two most common processes used are solvent wiping of PVC soles to remove surface plasticiser and a halogenation process which saturates the butadiene in rubbers, thus making the material more compatible with the adhesive.

2.2 Adhesive

The adhesives typically used for shoe sole bonding are one part polyurethanes, containing approximately 20% solids in a solvent base, often methyl ethyl ketone (MEK). Often the adhesives include resins and chlorinated rubber to improve tack and heat resistance. Reactive additives are not generally used, although isocyanate is sometimes added as a curing agent to improve adhesion and heat resistance. This type of adhesive has the desired properties of reasonable gap filling properties, combined with good spot strength (green strength).

A bead of adhesive, approximately 10 mm wide, is applied to the perimeter of both components and allowed to dry. Prior to assembly the adhesive is heat activated on at least one surface (usually the sole), by passing it under infra red heaters to raise the adhesive temperature to 80°C. The two components are then brought together and pressed for approximately 15 seconds to form the joint. Laboratory tests indicate that typically the sole/ upper joint strength is around 5 N/mm, based on a standard format peel test for footwear developed by SATRA.

3. SERVICE HISTORY

For regularly used items of footwear, the life expectancy is on average one year from purchase. During this time, the adhesive joint is subjected to a range of chemical and environmental conditions, depending on the nature of the shoe. The joint is often subjected to moisture, both from the environment, and perspiration from the wearer.

Results from a number of wear trials, carried out on footwear over this length of time, indicate that the majority of failures that occur are due to errors in the original bonding process, for example insufficient or over enthusiastic surface preparation, rather than environmentally provoked failure of the adhesive. This is borne out by laboratory tests performed on polyurethane joints typical of the sole to upper joint, which have indicated that saturation of the joint at temperatures below the glass transition temperature for the adhesive has little effect on the medium term strength of the joint.

The shoes used for this forensic study had all been returned to the retailers by customers due to defects in the shoe sole joint. Of the shoes available, those where failure was attributable to adhesive starvation, or clear incorrect preparation were eliminated from the subsequent investigations. All of the shoes identified as suitable were gentlemen's dress shoes, with the exceptions of shoes 2 which were a men's casual shoe, and shoes 5, which were a boy's school shoe. Detailed individual service histories are not known, but examination of the condition of the in-sole and sole provides some indication of the extent of usage. Additional service history data can be assumed from the nature of the shoe - ie fairly rough usage in the case of the boy's shoe. In all cases the shoes had been returned within one year from purchase.

4. MECHANICAL TESTING

Mechanical testing was carried out on a number of the available shoes. Sections of the upper / sole joint were cut **from** the shoes as shown in the photographs (Figure 2). These were then tested using a modified peel test **configuration**, similar to that used by **SATRA**¹. The results are shown in Table 1.

Shoe Number	Shoe/side	Failure Mode	Peel strength (N/mm)	Comment
Shoe 1	LHS/RHS	Cohesive	8.53	Toe of LH shoe debonded
	LHS/LHS	Inter&al*	1.6	
	RHS/RHS	Cohesive	5.5	
	RHS/LHS	Interfacial*	3.5	
Shoe 3	RHS/LHS	Interfacial	1.99	Failure of RH side of LH shoe.
	RHS/RHS	Interfacial	2.96	
	LHS/LHS	Inter&al	0.72	
	LHS/RHS	Interfacial	Failed	
Shoe 4	RHS/LHS	Leather	3.31	Generally good. Local toe disbond on LH shoe.
	RHS/RHS	Cohesive / Leather	4.47	
	LHS/RHS	Leather	3.08	
	LHS/LHS	Cohesive / Leather	4.86	
Shoe 5	LHS/LHS	Interfacial	6.66	Toe of RH shoe disbonded (Child's shoe)
	LHS/RHS	Interfacial	9.75	
	RHS/RHS	Interfkial	4.46	
	RHS/LHS	Interfacial	4.67	

★ Failure occurred in the *interface between* the two layers of adhesive.

Table 1. Results of mechanical testing

Typical results obtained during wear trials carried out by SATRA ² indicate that a well made sole to upper joint bond strength would be around 3.5 to 4 N/mm. Peel strengths of 1 to 2 N/mm were generally indicative of either poor heat activation of the adhesive prior to bonding or insufficient or uneven pressure during pressing. A strength of between 2 and 3 N/mm was generally indicative of either poor leather being used; the weak surface layer not being properly removed; poor sole preparation prior to bonding; or insufficient application of adhesive.

The peel strength results obtained for shoe 1 suggest that either the heat activation of the adhesive or the clamping pressure were uneven. On both shoes, the **left** hand side is notably weaker than the right hand side, corresponding with a change in the appearance of the failure surfaces. Visual inspection of the nominally interfacial failure surfaces showed adhesive remaining on both the leather upper and the sole, however, the characteristic whitened fibrils indicating failure within the adhesive layer were not present. This confirms that the two beads of adhesive did not coalesce during the original manufacturing process, either due to uneven heating or clamping pressure.

Results of the tests on shoe number 2 were void and so are not included in the table of results.

For shoe 3 all four test results are lower than might be expected from a good joint. There is, however, a notable **difference** in the strengths of the two shoes. Inspection of the failure surfaces showed no evidence of adhesive remaining on the sole surface. This consistent **interfacial** failure of the joint indicates that preparation of the shoe sole prior to bonding was not sufficiently rigorous.

The results **from** shoes 4 are generally quite good, with strengths around those typical of a good joint. The lower test results were associated with a change in locus of failure from cohesive in the adhesive layer, to failure within the leather.

Test results **from** the boy's school shoe, shoes 5, were consistently high, with results **from** the failed right hand shoe being marginally lower than for the other. In all four tests the locus of failure appeared to be in the interface between the shoe sole and the adhesive.

In all cases the eventual failure, resulting in the return of the shoe, occurred in that region of the bond line identified as the weakest in the peel tests. The observed loci of failure were broadly in line with the earlier SATRA results.

It cannot be determined from the mechanical tests alone whether there has been any reduction in strength due to environmental effects or if the failures have been entirely due to poor preparation during manufacture. Experimental evidence ³ has shown that in accelerated ageing tests where the adhesive was hydrolysed at 120°C, there is considerable degradation in the peel strength of the joints (Figure 3). However, these tests were carried out at well over the de-crystallisation temperature (ca. 45°C) of the adhesive so a **different** reaction mechanism may be affecting the results. The same report also describes tests carried out at lower temperatures (Figure 4) where the degradation is much less severe. This work suggests that failure due to moisture ingress is unlikely to occur within the shoes' lifetime in normal wear conditions.

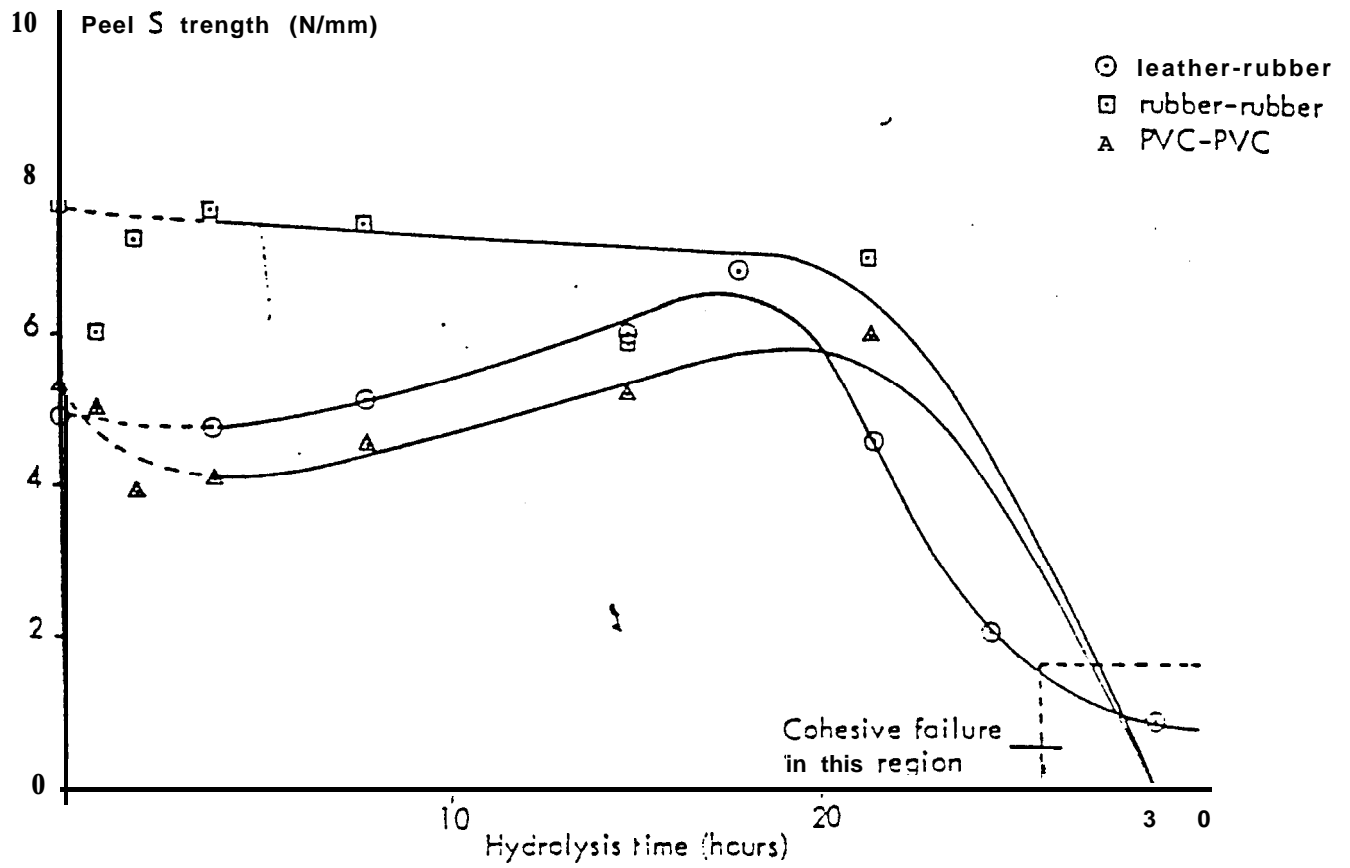


Figure 3. Peel Strength of Joints (Hydrolysed at 120°C).

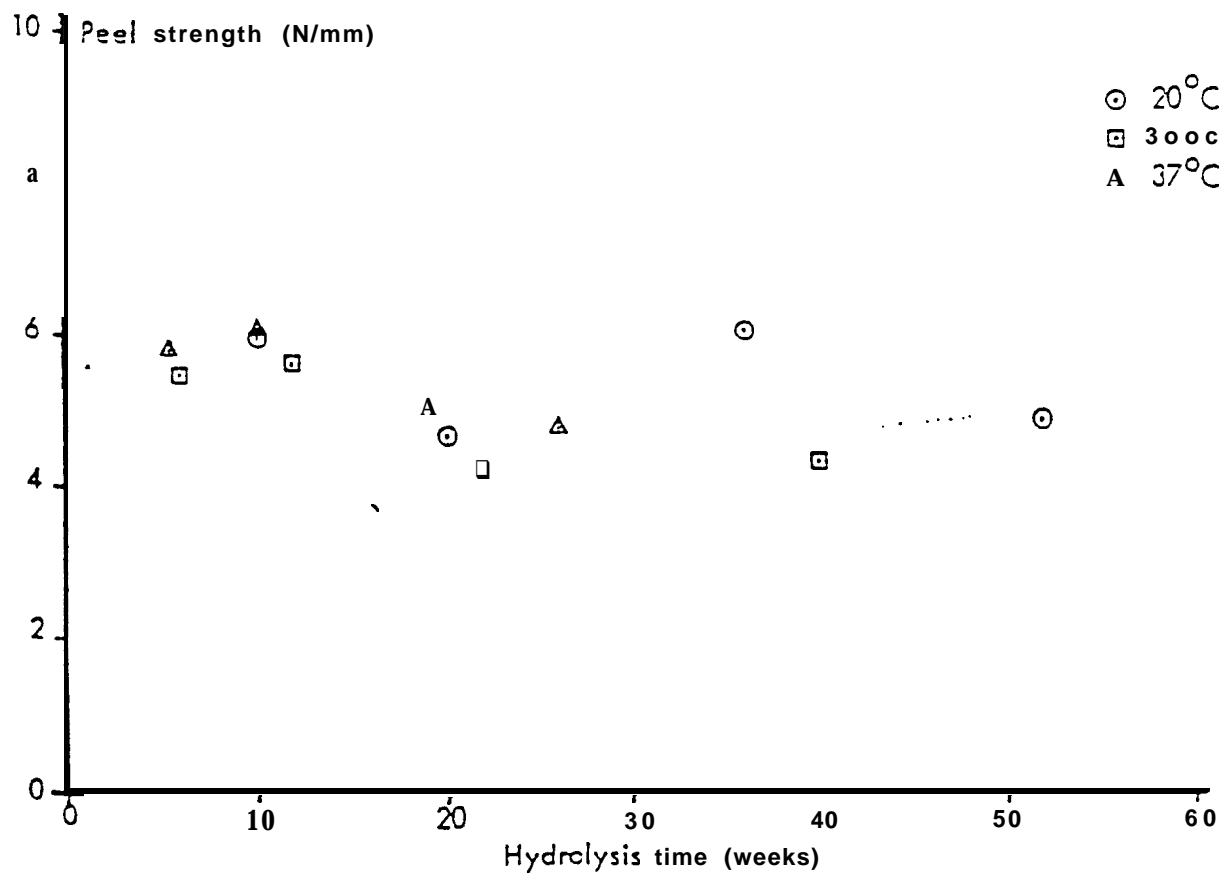


Figure 4. Peel Strength of Leather/Rubber Joints (Hydrolysed at 20, 30 and 37 °C).

5. ELECTRON MICROSCOPY (LVSEM)

The use of an electron microscope is able to help in the identification of the true locus of failure of the joint. As the materials of the shoe are poor electrical conductors, a low beam energy is required to prevent the charging of the samples whilst being viewed. To further assist, the samples were sputter coated with a thin layer of gold prior to inspection.

Shoe 5 was selected for further investigation as, being the boy's shoe it was the most likely to have experienced most wetting and external usage. The condition of the in-sole and sole also indicated that these shoes had been extensively worn prior to their return. The specimens investigated with the microscope were removed from the area of the initial failure of the shoe, at the toe of the right hand shoe.

In the subsequent discussion the two surfaces of the joint investigated are referred to as sole and upper sides. In view of the apparent interfacial failure at the sole surface, the surface referred to as the "upper" surface appeared, by eye, to be the residual adhesive surface.

Figure 5 shows a view of the sole surface, at a magnification of x70. At this level of magnification a large number of localised damage sites were visible, as shown in the photomicrograph. From the image it is apparent that some of the PVC surface has fractured when the joint failed.

Figure 6 shows the surface of the adhesive, at the same magnification. This clearly shows the root site of one of the pulled fibrils of adhesive. This can be compared with the surface topology resulting from a region at the extreme edge of the joint, where the adhesive was not in contact with other material, shown in Figure 7. In this image the relatively smooth surface of the adhesive can be seen, covering the fibrous roughened surface of the prepared leather.



Figure 5. Micrograph of Shoe Sole.

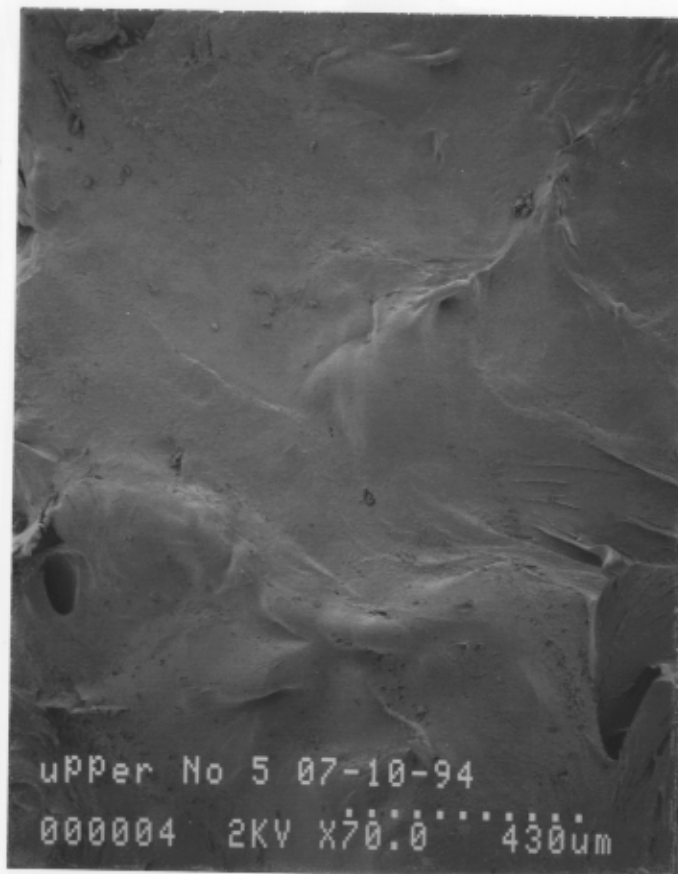


Figure 6. Micrograph of Fracture Surface (Adhesive Side).

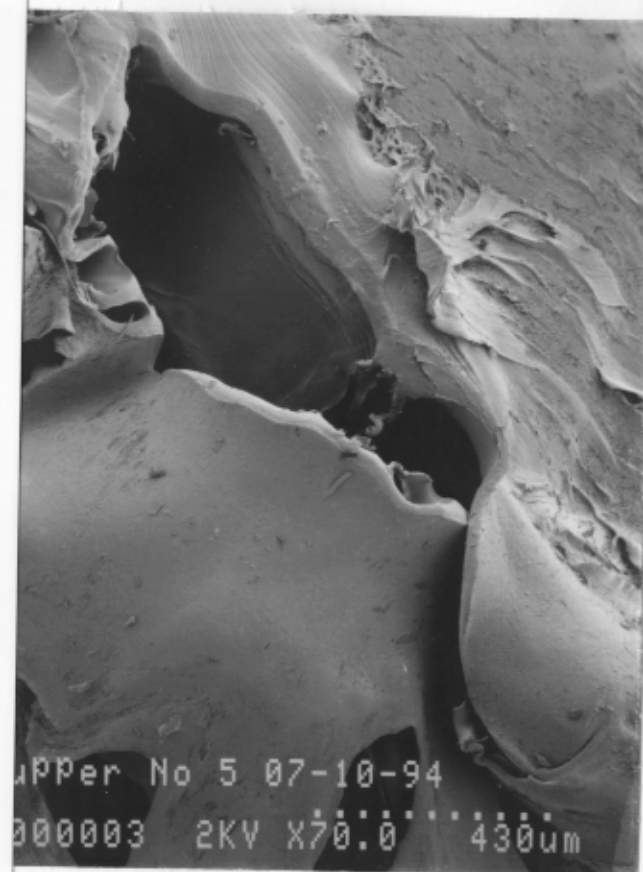


Figure 7. Micrograph of Adhesive Surface.

6. X-RAY PHOTOELECTRON SPECTROSCOPY

Information about the chemical composition of the failure surfaces was obtained using XPS ⁴. As with the SEM work, the samples were obtained from shoe 5. These samples were taken from a region just next to the debonded area, which had been recently pulled apart, to ensure, as far as possible, that the adhesive was free from contamination. In total four samples were analysed. Samples from either side of the fixture were analysed, as well as “standard” samples obtained from areas remote from the adhesive joint, to provide initial chemical composition data for the leather upper and sole material, as shown in Figure 8. The sole standard was taken from a horizontal slice through the sole, whilst the leather upper standard was obtained from above the joint.

In common with the other tested samples from this pair of shoes, the failure locus appeared to be at the interface between the sole and the adhesive. The adhesive had come away with, and remained attached to the leather, leaving what appeared to be a clean area of sole.

Wide spectra were obtained from each sample (Figure 9) to provide the initial broad chemical composition, the results of which are shown in table 2. The large amount of oxygen and carbon in each of these samples are very similar and are typical of organic materials such as leather and oil based polymers such as the adhesive and the PVC sole.

Element	Upper Standard	Upper Adhesive	Sole Adhesive	Sole Standard
C	75.40	73.25	74.72	77.45
O	17.55	15.83	15.45	12.56
Cl	1.39	6.63	5.87	8.98
Ba	0.00	0.20	0.16	0.33
Si	3.86	3.41	3.21	0.67
Ca	0.68	0.68	0.60	0.00
N	1.13	0.00	0.00	0.00

Table 2. Sample composition (Atomic %).

From the sole standard, the characteristic elements of the sole are chlorine and barium. These elements can thus subsequently be used to identify sole derived material on the fracture surfaces. The detailed Cl, p spectra (Figure 10) of the material confirm that the sole is manufactured from moulded PVC.

The presence or otherwise of the leather can be identified by the silicon, nitrogen and calcium atoms. Of these three elements, it is the nitrogen which is specific to the leather, the other two elements being constituents of the leather surface finish.

Both chlorine and barium atoms are also detectable on both faces of the fractured joint. This indicates that some of the sole surface was lifted off with the adhesive when the joint underwent the peel test and suggests that there was good adhesion with the sole.

To support this theory, the detailed spectra of the chlorine peak, Figure 10, for the two fracture surface samples have the same characteristic step as the PVC sole standard. For the leather standard, however, the step is not as pronounced. This implies that the chemical composition at the fracture face is very similar to that of the bulk sole material, and both samples contain PVC.

The absence of nitrogen in the chemical composition of the fracture surface indicates that there is no surface leather at the fracture site. This is thus consistent with the belief that the failure occurred at the interface between the sole and the adhesive, and that the leather upper was not involved in the failure.

These results indicate that there was an initial weakness in the surface of the moulded sole. It was not possible to identify whether this weakness was introduced during the initial moulding of the sole or as a consequence of incorrect bonding procedures being carried out. Similarly, it was not possible to assess whether the actions of the service environment had served to exacerbate the weakness, leading to premature failure of the sole joint.

The presence of silicon and calcium in the fracture surface might indicate that some of the leather polishing materials may have contaminated the joint. It is known that there is a large amount of silicon contamination in the factory' resulting from the polishing process. The levels of silicon are however, not significantly greater than in the well bonded section of the shoe, where peel test results were relatively high. This suggests that this slight contamination does not cause a noticeable weakening of the joint.

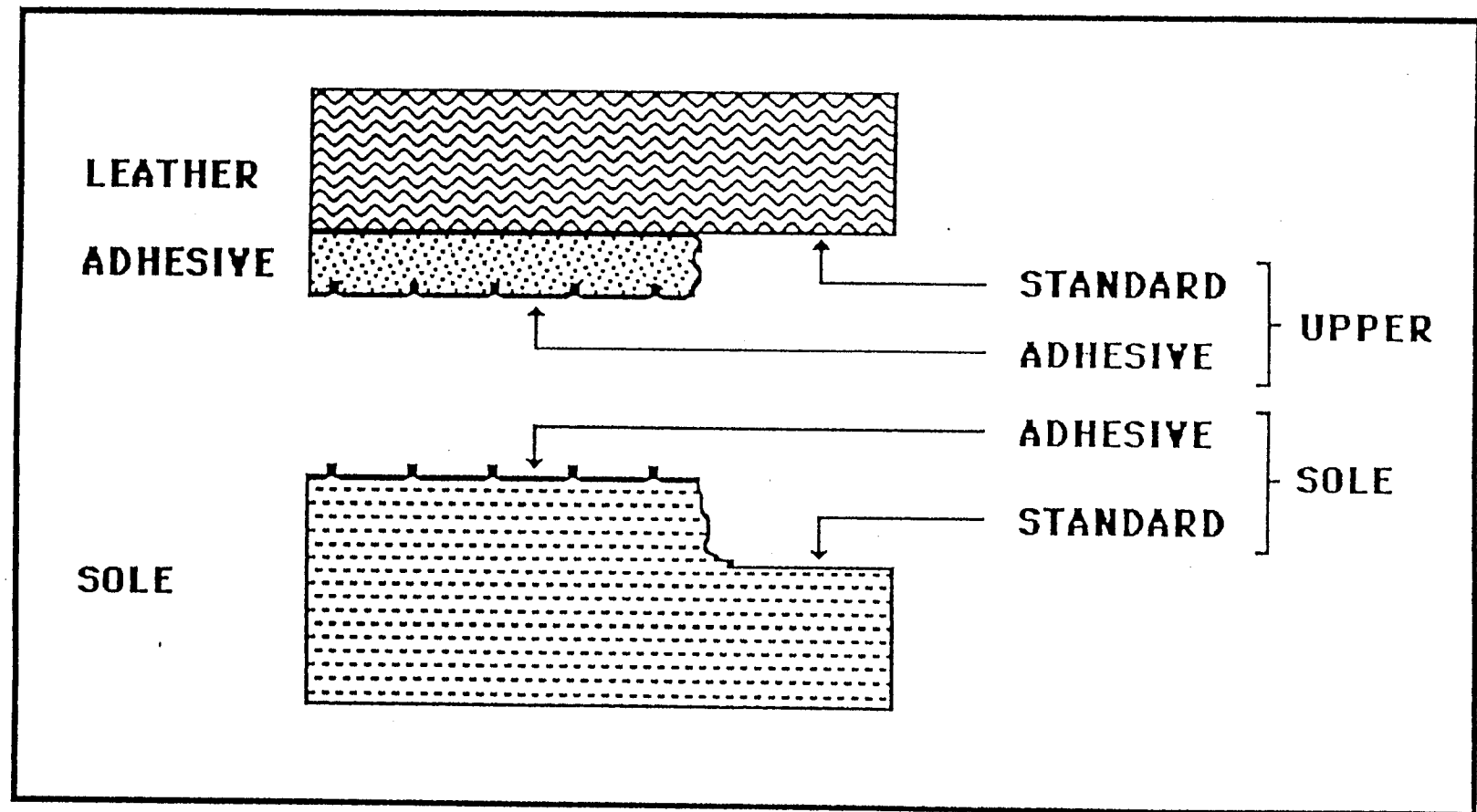


Figure 8. Position of Samples for XPS Analysis.

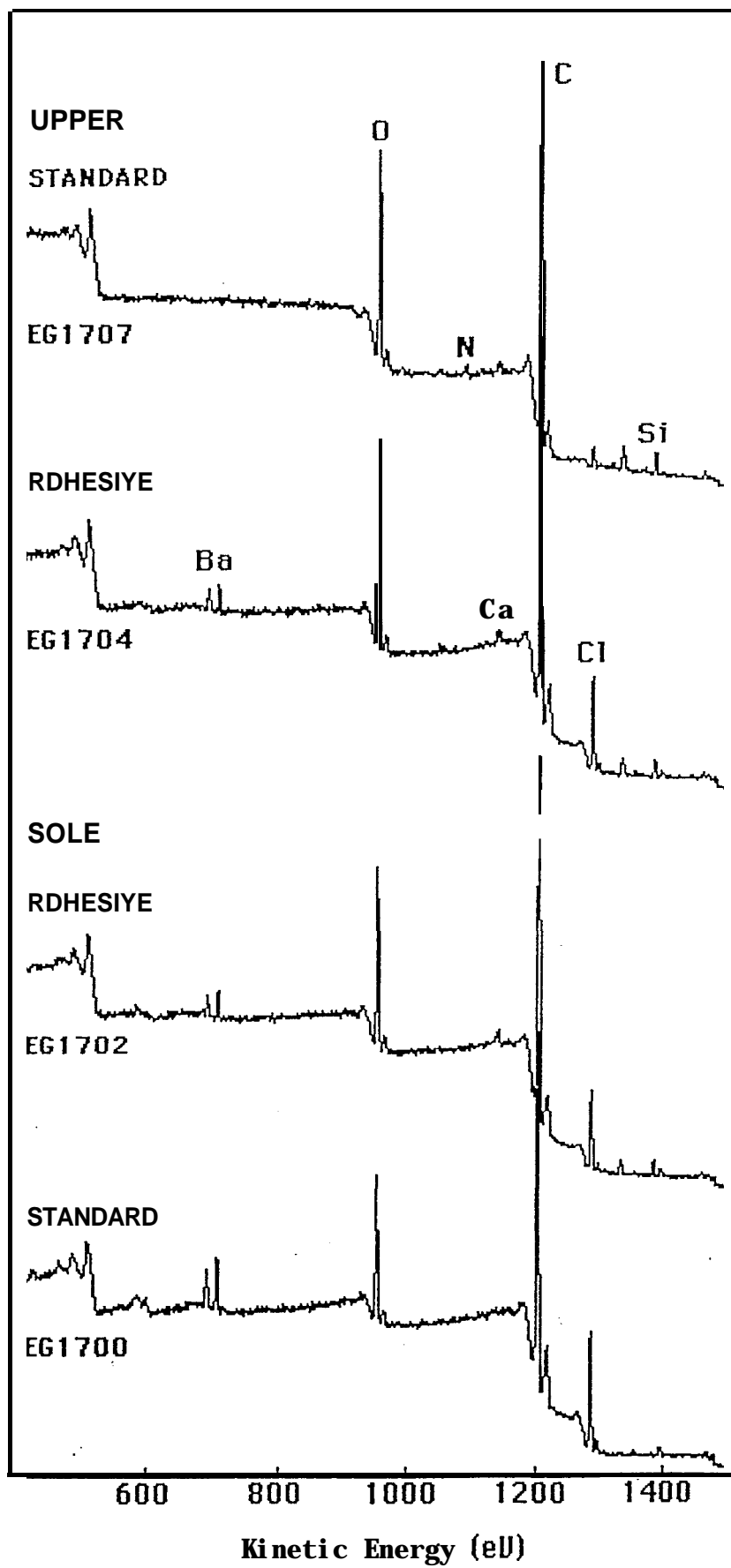


Figure 9. Wide XPS Spectra.

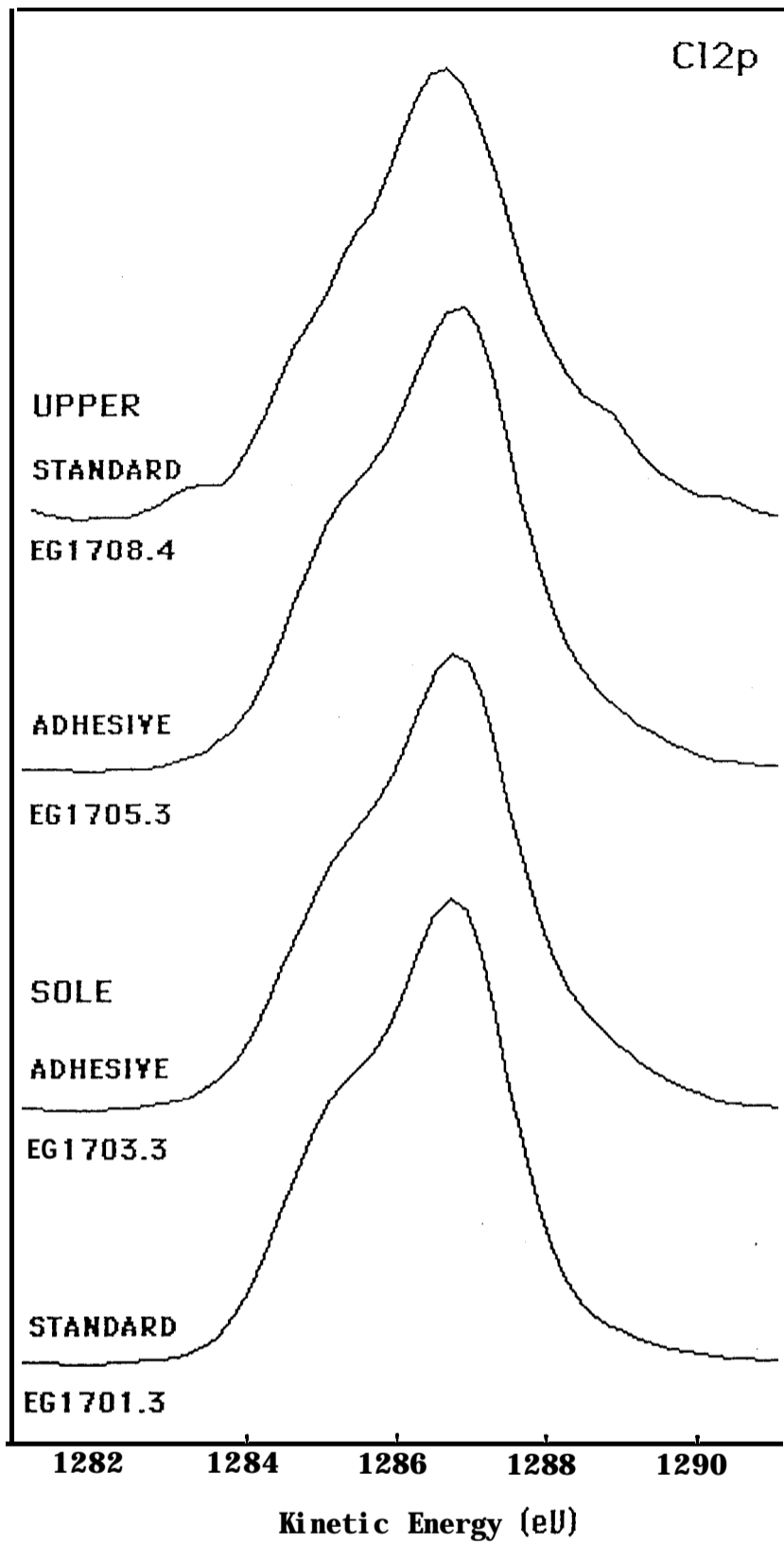


Figure 10. Detailed Cl_{2p} Spectra.

7. CONCLUSIONS

The use of adhesives to bond soles to leather uppers is, these days, common practice. These joints are subjected to relatively high loads, extremes of temperature, and moisture (perspiration and rain). The joint is also critical to the finished article of footwear providing satisfactory service life. Despite this, the joint generally performs well in service, with relatively few failures.

In general those failures which do occur can be traced back to deficiencies in the manufacturing process. Five pairs of shoes were selected for investigation, based on an initial assessment of the probable causes of failure. Of these five, it was subsequently found that two of the failures were due primarily to manufacturing process faults, and one set of results was void. These results indicate that correct bonding procedures are of paramount importance to achieving long term durability.

A pair of boys school shoes was selected for detailed investigation, on the grounds that these were the most likely to have seen the most demanding environmental exposure. Inspection following peel testing showed what appeared to be interfacial failure. Results of SEM and XPS analyses, however, showed that some of the surface PVC of the sole had been removed with the adhesive, indicating a good level of bonding.

The results of the various experimental techniques have not been able to identify environmental degradation as a significant cause of joint strength degradation. This is backed up by laboratory experimentation, where it was shown that, in the medium term, polyurethane adhesive joint strength is relatively un-affected by exposure to moisture at natural ambient temperatures. The samples taken, however, are not fully representative as they all come from shoes returned within one year. Many shoes last longer than this and it is not known what the eventual cause of failure of these shoes are.

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