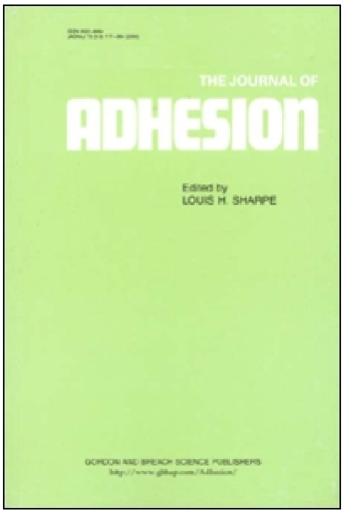

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Adhesion to Polyolefins with Flexible Adhesives

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Compounds based on polyolefins may find further use in the footwear industry as solings. However, a significant problem is the poor adhesion obtained with the urethane adhesives currently used. SATRA has recently attempted to develop practical bonding systems for commercial olefinic compounds. The use of flame treatments for polyethylene appeared to be a possible method of improving compatibility between the adhesive and substrate if an *iso*cyanate is present at the interface. Polypropylene does not respond to the flame treatment but reasonable bonds have been obtained after surface oxidation or by using a sensitiser in conjunction with UV irradiation. The use of dual compound moulding is described as a possible alternative means of obtaining adequate adhesion to difficult surfaces.

INTRODUCTION

The footwear industry uses a wide range of polymers to manufacture soling and upper materials. In the majority of cases the soling is attached to the upper using adhesives. The tendency in the UK is to use only one adhesive type to make this bond and during the past fifteen years the use of solvent urethane adhesives has increased to a position where they occupy 80% of the sole attaching market.

A basic disadvantage of a urethane adhesive is that apart from leather and PVC it is incompatible to varying degrees with the other materials used as solings and uppers. As in shoe manufacturing today it is possible to use more than 100 different combinations of materials for the sole/upper bond it is perhaps surprising that the urethane adhesive has become so popular. The main reason for its high usage is that surface treatments have been developed[1–3] which improve the compatibility between the urethane adhesive and

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the substrate surface. Unfortunately this involves the use of an intermediate step in the bonding operation which apart from necessitating extra capital expenditure also requires a higher usage of labour and is hence economically unattractive. Recently there has been some progress towards modification[4] of the urethane adhesive to provide better adhesion to some materials without surface treatment.

The position regarding availability of soling materials is more complicated. For many years leather occupied the prime role but as the demand for footwear exceeded the availability of hides it became necessary to seek alternatives. This led to the introduction of vulcanised rubbers and crepe and during the last twenty years there has been a continual influx of new compounded and in some cases uncompounded polymeric materials.

The footwear industry is a high volume consumer of these compounds but apart from specialised applications, requires a relatively low cost material. During the last decade there has been an increase in the number of polymers/compounds based on the polyolefins used in the footwear industry. Such compounds include ethylene vinyl acetate (EVA), ethylene propylene terpolymer rubber (EPDM) and ethylene propylene copolymers.

A shoe soling must possess adequate flex performance, good wear properties, anti-slip properties and good adhesion to upper materials. Not many of these newer compounds fulfil all these requirements and one of the main deficiencies at present is lack of adequate adhesion. Limited success has been obtained with bonding to EVA[5] and EPDM based compounds but severe problems exist with polyethylene and polypropylene whether as simple homopolymers or compounded. A great deal of work has already been done using electrical discharge treatments and chemical oxidation. However, in the main the emphasis has been on the use of inflexible adhesives such as the epoxy types. These, of course, are not relevant to sole attaching where the bond must be flexible as the shoe is flexed at each step.

It was, therefore, necessary to find a suitable surface preparation to improve the compatibility of flexible adhesives to a polyolefin surface. The other prerequisite was that the treatment should be inexpensive and easy to perform. These restrictions immediately exclude such methods as CASING[6] and corona discharge[7] and of the established techniques, only the chemical treatments and flaming methods remain.

BOND PREPARATION

In laboratory bond preparation the intention is to reproduce as closely as possible the bonding conditions used in the shoe factory. This can be done reasonably successfully but the major difference is that in a shoe the two surfaces to be bonded are contoured whereas laboratory bonds are made with two flat surfaces. The latter is done in order to be able to compare bonds between different materials, apart from economic considerations. The normal procedure adopted is as follows:

Soling material—surface preparation as required—apply adhesive—leave for required open time necessary for loss of solvent.

Plasticised PVC upper material—prepare surface by wiping with ethyl acetate—leave for 15 minutes—apply adhesive—leave for required open time.

Reactivate the adhesive on the sole by heating to between 80°C to 90°C using radiation from an electrically heated element. Place the upper material in contact with the soling and apply a pressure of 6 N/mm^2 for 15 seconds.

The bond was made from soling and upper materials 5 × 7 cm which before testing were cut into 3 × 5 cm test strips. All bonds were left for at least 48 hours at room temperature prior to testing.

BOND TESTING

The bonds were tested in peel as this is assumed to be the predominant mode of failure in the shoe. The bonds were mounted in the SATRA Cantilever Tensiometer (Figure 1) and the jaw separation rate used was 10 cm/min. This method of peel testing is conventionally referred to as the 180° peel. The two adherends to be separated are of different stiffness and the more flexible one is bent round to lie parallel with the stiffer adherend. However, the angle at the line of separation can rarely be regarded as even approaching 180° and it is only reasonable to assume that the angle is greater than 90°. In view of this it would perhaps be better to refer to this test as a peel back test and to accept that cleavage stresses are mainly responsible for the failure and that shear stresses are virtually absent.

INITIAL TREATMENTS

In all the work a very practical approach was adopted in that the adhesives and the substrates used were not specially prepared but were commercially available products.

The first test involved the immersion of both low density polyethylene and polypropylene in a solution of 2.5 % $K_2Cr_5O_7$ in 85 % w/w H_2SO_4 for five minutes at room temperature. After removal the surfaces were washed with

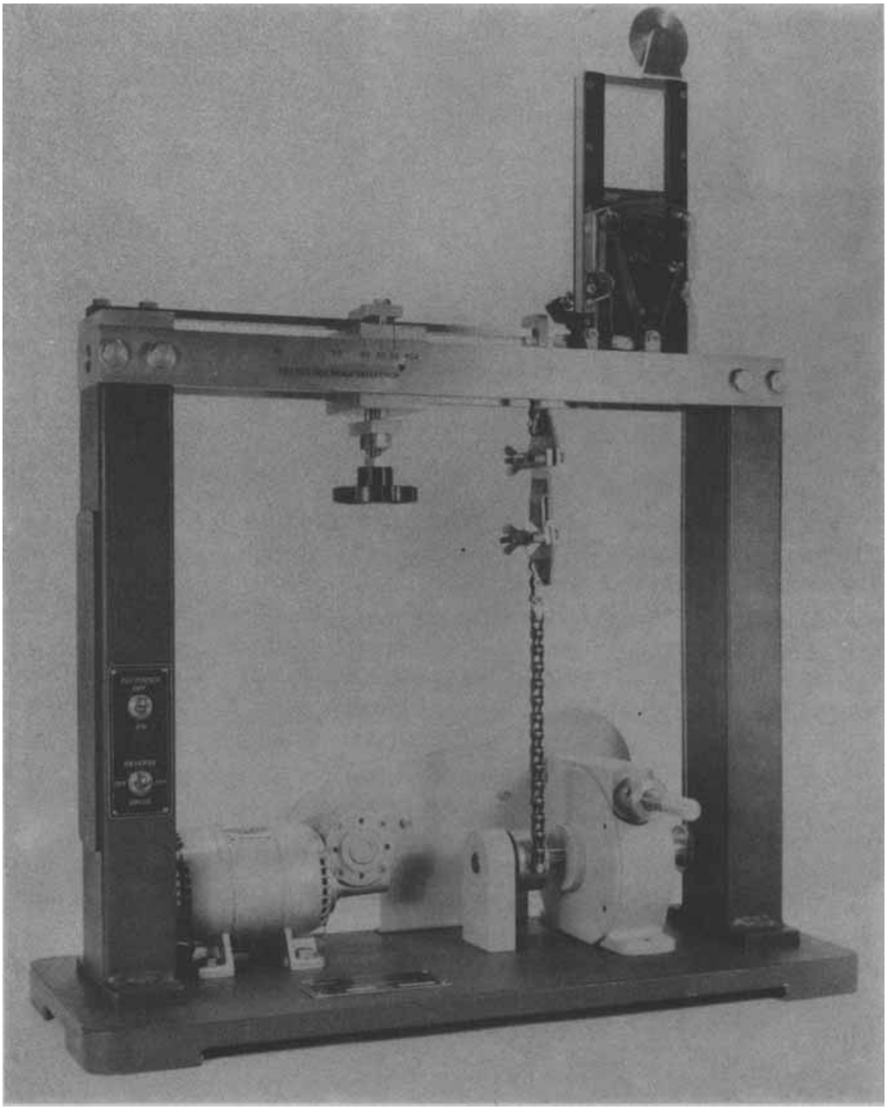

FIGURE 1 SATRA cantilvever tensiometer.

water and allowed to dry for 20 hours before bonding with a urethane adhesive. The maximum bond strength obtained with polyethylene was 1.1 N/mm and with polypropylene 0.2 N/mm.

In a further test the same two polyolefins were immersed for 5 seconds in the vapour of boiling trichloroethylene. Again after leaving for 20 hours bonds were made but the maximum bond strength obtained was only 0.4 N/mm.

Both the above treatments had been found effective by Garnish and Haskins[8] when using an epoxy adhesive, but were not satisfactory with a urethane adhesive. In fact the bond strength was much lower than the 5 N/mm which is the requirement for this type of assembly when the failure is by adhesion.

In the footwear industry the use of chlorination as a surface preparation is quite common.[1–3] Unfortunately a polyolefin is not amenable to simple direct chlorination. However, it was speculated that by flaming the surface it may be possible to introduce some unsaturation which would then permit the addition of chlorine to the surface. An attempt was made to ascertain the value of such a treatment on low density polyethylene. The surface was slowly passed through a medium roaring bunsen flame and allowed to cool before being treated with a solution of an organic chlorine donor. The bonds were made with both a single part urethane adhesive and a two part adhesive. This is the same as the single part with the addition of about 4 % of a polyisocyanate immediately prior to use.

Examination of the flame treated surface using infra red ATR techniques did not reveal any unsaturation. The results in Table I tended to substantiate this as the control test without chlorination surprisingly produced the higher bond strength. Additionally it was apparent that the two part urethane was producing a significantly higher bond strength than the single part adhesive. It therefore seemed that the *iso*cyanate was contributing to the bonding system.

FLAME TREATMENT OF SURFACES

As the flame treatment produced a reasonable bonding surface on low density polyethylene this approach was pursued and other polymers were considered in an attempt to develop a practical bonding system. In the first place it was

TABLE I

Initial trial of the flame treatment on polyethylene

Surface preparation	Adhesive	Bond strength (N/mm)
Flame—chlorinated	Two part urethane	1.8
Flame	Two part urethane	3.1
Flame	Single part urethane	0.6

necessary to introduce some degree of standardisation into the method of flaming.

This was done using the simple assembly shown in Figure 2 where the sample was pulled over the oxidising part of a medium roaring bunsen flame at a rate of 0.7 cm/sec. Using this technique various polyolefins were treated and the results are given in Table II.

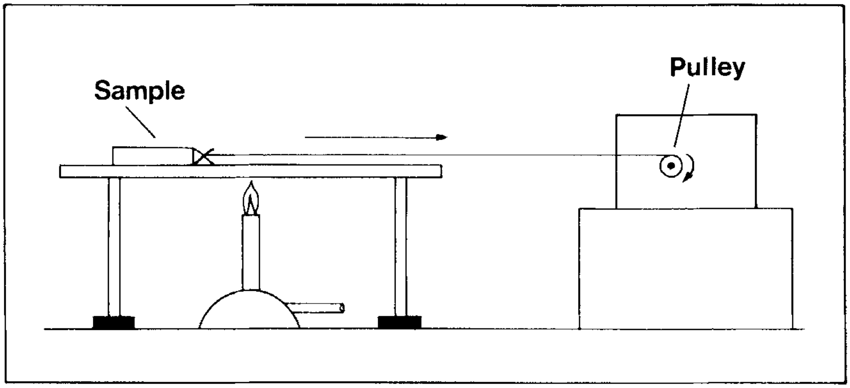

FIGURE 2 Apparatus for flame treatment.

The bond strength obtained with the two samples of low density polyethylene and the ethylene vinyl acetate were adequate, although the polypropylene did not respond. It was apparent that the use of two coats of adhesive on the treated surface gave a higher bond strength than a single coat. The reason for this increase in bond strength may be due to the cleavage stress being spread over a slightly greater area and in subsequent tests two coats of adhesive were always used. With the bonds in Table II the time

TABLE II

Flamed surfaces of polyolefins bonded with a two part urethane

Flamed surface	Number of coats of two part urethane adhesive	Bond strength (N/mm)
Low density polyethylene	1	5.9
	2	8.0
Low density polyethylene	1	4.2
	2	6.5
Polypropylene	1	0.2
	2	0
Ethylene vinyl acetate (14 % VA)	1	9.2
	2	10.2

between the flame treatment and the application of the adhesive was ¼ hour. However, it was possible to extend this to about 10 hours which suggests that the treatment has some degree of practical permanency.

In the previous tests it was shown to be necessary to use a urethane adhesive containing free *iso*cyanate. Such two part urethane adhesives are sometimes inconvenient as they may have a short pot life. It was, therefore, decided to use a single part adhesive in conjunction with an isocyanate wipe of the flame treated surface. This work was done with both low density and high density polyethylene. After flaming, the surfaces were left for ¼ hour and then a solution of 4,4′ di-*iso*cyanato diphenyl methane was brushed on. After leaving for a further ¼ hour the single part urethane adhesive was applied and the bond was made in the normal way.

TABLE III

Crude MDI as a primer for flame treated polyolefins—various dilutions

Primer on sole before application of single part urethane adhesive	Type of polyethylene	Bond strength (N/mm)
0.1% crude MDI in MEK	LDPE	>11.8 Max
	HDPE	5.7
4% crude MDI in MEK	LDPE	12.2 Max
	HDPE	8.0
10% crude MDI in MEK	LDPE	12.7 Max
	HDPE	7.9

MEK = methyl ethyl ketone.

These results in Table III demonstrate that the use of a single part adhesive is feasible providing an isocyanate is present at the substrate-adhesive interface. It is also possible to use quite a low concentration of *iso*cyanate which of course is of practical importance.

ADHESION MECHANISM

Attempts were made to investigate the mechanism by which flaming improved the adhesion. As mentioned previously, infra-red ATR examination of treated surfaces did not show any unsaturation. In fact this technique was not sensitive enough to show any definite changes after flame treatment.

Scanning electron microscope studies, however, revealed marked changes in the surface after flaming.

Figure 3 shows the surface of low density polyethylene before and after flame treatment. The flamed surface has a distinct ridge effect and this is

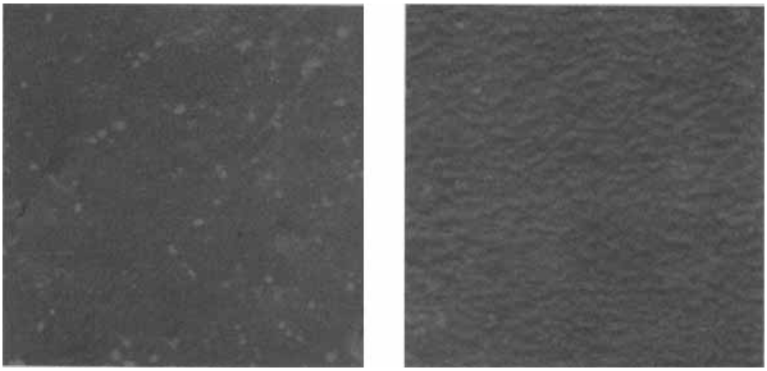

FIGURE 3 Scanning electron micrographs of low density polyethylene surface before and after flame treatment (× 500).

also apparent with high density polyethylene and ethylene vinyl acetate after flaming. Polypropylene however was completely different and showed some quite large holes in the surface after the flame treatment.

Critical surface tensions (CST) were determined[9] on surfaces before and after flaming by measuring the contact angles made on them by water, glycerol, formamide and aniline. These liquids were used in the absence of a suitable homologous series by plotting[10] cos θ against $(\gamma_L)^{-1/2}$ where θ is the contact angle made by the liquid of surface tension against the surface.

By using this technique the results in Table IV were obtained. The CST of the untreated surfaces is generally higher than expected although it must be stressed that in all cases these were moulded surfaces of commercial plastics and not specially prepared. However, apart from the polypropylene, the effect of flame treatment was to raise the CST.

In an attempt to study the reaction between the *iso*cyanate and the flamed surface twenty 5 x 7 cm test samples of polyethylene were flame treated and then immersed in a 0.01 % solution of *iso*cyanate. The reduction in the

TABLE IV

Critical surface tensions on untreated and flamed surfaces

Samples	Original unflamed surface CST mN.m^{-1}	Flamed surface left for 10 mins to 90 mins CST mN.m^{-1}
LDPE	31	40
LDPE	36	40
HDPE	40	44
EVA (14 % VA)	34	42
PP	46	36

strength of the *iso*cyanate solution was measured and a corresponding control test was done using the same number of unflamed surfaces. The same result was obtained for the control and test solutions which was unfortunate as it was not therefore possible to estimate the number of active sites on the treated surface.

In view of the limited information obtained from this investigation it was only possible to speculate on an adhesion mechanism.

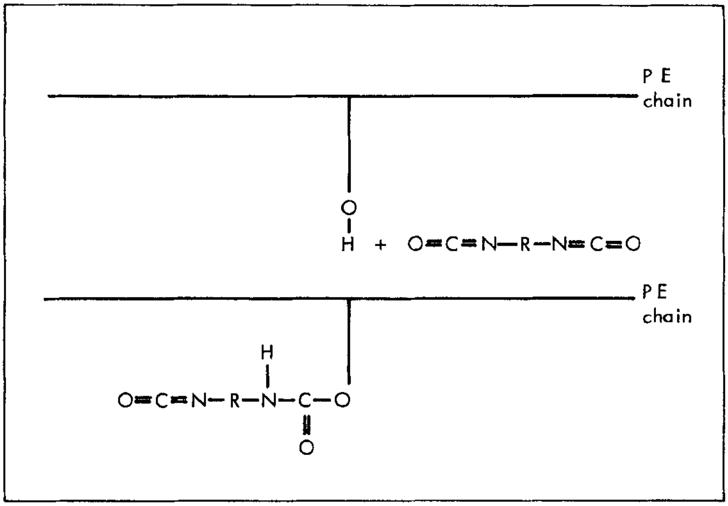

FIGURE 4 Possible reaction between a flame treated polyethylene surface and a di-isocyanate.

Although not apparent from the chemical study it was clear from the adhesion results that *iso*cyanate is required at the interface. *Iso*cyanate treatment alone will not improve the adhesion and therefore it is likely that during flaming active sites are formed at the surface which can then react with an applied di-*iso*cyanate as shown in Figure 4. If these active sites were hydroxyl groups a urethane link would be formed and the pendant *iso*cyanate group would be available for further reaction with the applied adhesive.

In addition the scanning electron micrographs showed a change in the topography which may increase the surface area and the contact angle studies indicated an increase in the ability to wet the surface after flame treatment.

ADHESION TO POLYPROPYLENE

The flame treatment was found to be an effective method of surface preparation for polyethylene, ethylene vinyl acetate, some grades of ethylene-propylene terpolymer rubbers and even nylon. Unfortunately when used in conjunction with a urethane adhesive, it was ineffective on polypropylene and it is possible that the flame treatment is causing some chain scission with polypropylene which results in a weak boundary layer.

In view of this Smith[11] examined alternative surface treatments for polypropylene with the objective of obtaining a practical bonding system for use in the footwear industry.

TABLE V

Effect of time on the bond strength of $KMnO_4$ oxidised polypropylene

Time between oxidation and bonding	Bond strength (N/mm)
4 hours	3.7
30 hours	4.6
2 days	3.8
5 days	3.2
8 days	4.0

The bond strengths shown in Table V were obtained by immersing the polypropylene for 12 minutes at 60°C in a 10% $KMnO_4$ solution in 10% H_2SO_4. After removal the surface was washed with water and left to dry for various times before wiping with a dilute di-*iso*cyanate solution and bonding with a urethane adhesive. Examination of the treated surface by infra-red ATR techniques showed the presence of some carbonyl groups and contact angle measurements indicated an increase in the critical surface tension.

TABLE VI

Reproducibility of Bragole treatment on a polypropylene sample

Test strip number	Bond strength (N/mm)
1	6.0
2	6.0
3	4.7
4	5.0
5	6.7
6	5.7
7	6.3
8	4.7
9	4.3
10	3.7
Average	5.3

A second method studied was that by Bragole[12] in which the polypropylene surface was subjected to ultra violet radiation in the presence of a sensitiser. Using a 1 minute immersion in a 15% solution of benzophenone in dichloromethane followed by a 10 second exposure to a UV source of the medium pressure mercury arc type a receptive surface was obtained. The results in Table VI show the bond strengths obtained with a urethane adhesive after wiping the treated surface with a dilute di-*iso*cyanate solution. The bond strengths are quite high and generally would be adequate for the shoe industry.

It is speculated that this treatment produces free radicals which can result in cross-linking and hydroxyl formation on the surface of the polypropylene. In fact Smith[11] was able to confirm the presence of hydroxyl groups on the treated surface and also showed an increase in the critical surface tension.

Both the treatments used on polypropylene have enhanced practical value in that the time between treatment and adhesive application may be extended to at least one week. This provides the opportunity for the manufacturer to treat the sole units rather than allowing the footwear manufacturer to become involved with rather complex preparations.

DUAL COMPOUND MOULDED SOLES

During the past five years there has been a significant increase in solings which have two distinct layers combined to give a wearing surface and a different bonding surface.

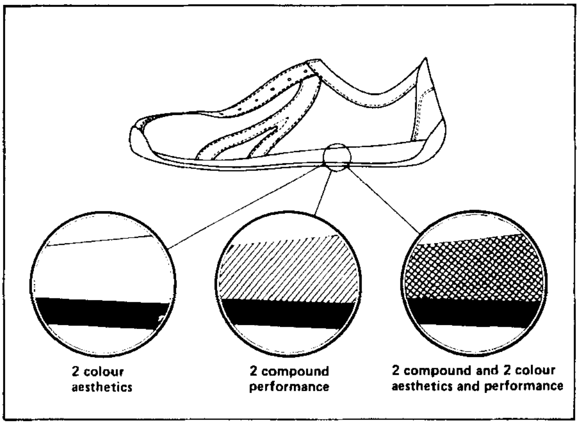

FIGURE 5 Dual compound moulding concept.

The concept is shown in Figure 5 where the two layers may differ only in the type of pigment to give improved aesthetics. Alternatively two different compounds may be used to provide better performance, but usually the performance and the aesthetic functions are combined. The non-wearing layer may be considered as a link between the wearing surface and the upper part of the shoe when direct adhesion between them is difficult. This has been investigated in a recent study[13] where 25 different thermoplastic compounds were injection moulded onto 30 inserts. The compatibility was assessed using the peel test and the results relevant to polyolefins are shown in Table VII.

TABLE VII

Bonds obtained by insert moulding

Compound injected	Insert material	Bond strength (N/mm)
LDPE	EVA	1.3–11.5
	EPDM	1.3– 4.3
HDPE	EVA	6.1– 6.7
	EPDM	0.9– 6.9
Polypropylene	EPDM	4.3– 5.0
	SBR	3.3
	Cross linked EVA	2.9

The bond strength required between the two layers of the sole is about 2 N/mm and hence each of these combinations are practically possible. It is therefore feasible to injection mould a polypropylene wearing surface onto a thin sheet of vulcanised SBR to produce a two layer unit. The SBR could then be halogenated[1] and easily bonded to the upper part of the shoe with a urethane adhesive. Such a system would of course avoid the necessity of becoming involved in surface preparations for the polypropylene.

CONCLUSIONS

This work has been directed towards the very practical objective of attaching a polyolefin based sole unit to the upper part of the shoe with a flexible adhesive.

Polyethylene homopolymers and some copolymers can be bonded adequately with a urethane adhesive after a simple surface flame treatment providing an *iso*cyanate is present at the adhesive-substrate interface. Polypropylene does not respond to the flame treatment. However, surface oxidation or the use of UV radiation in conjunction with a sensitiser provided a surface suitable for bonding with the *iso*cyanate-urethane system.

The established technique of dual compound moulding has been used as a means of obtaining satisfactory adhesion to difficult bonding surfaces.

As the work had a practical bias a more in-depth study of the adhesion mechanisms involved is required. Also the actual methods used in the treatments described would need developing further for commercial use in the footwear industry.

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