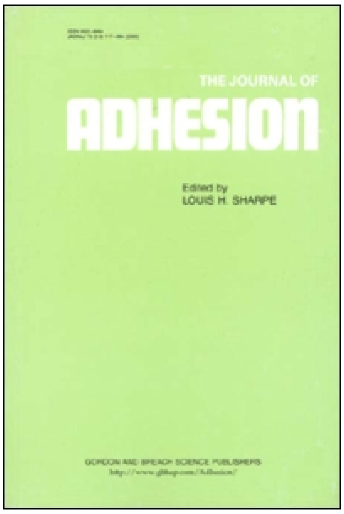

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Behaviour of Urethane Adhesives on Rubber Surfaces

D. Pettit[a]; A. R. Carter[a]
[a] Shoe and Allied Trades Research Association, Kettering, Northants, England

To cite this Article Pettit, D. and Carter, A. R.(1973) 'Behaviour of Urethane Adhesives on Rubber Surfaces', The Journal of Adhesion, 5: 4, 333 — 349
To link to this Article: DOI: 10.1080/00218467308072234
URL: http://dx.doi.org/10.1080/00218467308072234

J. Adhesion, 1973, Vol. 5, pp. 333–349

Printed in Northern Ireland

Behaviour of Urethane Adhesives on Rubber Surfaces[†]

D. PETTIT and A. R. CARTER

Shoe and Allied Trades Research Association,
SATRA House, Rockingham Road, Kettering, Northants, England

(*Received February 2, 1973*)

The paper presents the results of chemical investigations into some of the bonding problems of the footwear industry and pays particular attention to the importance of the substrate surfaces.

The importance of the presence of metal soaps on rubber surfaces and their detrimental effect on adhesion is pointed out together with the concomitant beneficial effects of solvent soap dispersing treatments on subsequent adhesion.

The special needs of the footwear industry for a single adhesive system capable of adhering strongly to a wide range of substrates led to the requirement of improving the bond of urethane adhesives to rubber surfaces. The role of free isocyanates in promoting this bond is outlined.

The practical advantages of halogenating rubber surfaces in conferring excellent adhesion properties on moulded rubber surfaces when used with solvent urethane adhesives are pointed out. The observed phenomena associated with halogenation are discussed qualitatively in relation to proposed theories of adhesion.

1 INTRODUCTION

In 1967, a colleague, E. F. Hall, discussed[1] the adhesive techniques used in the footwear industry and the test methods employed. At the present time, about 40 percent of the soles used in UK footwear manufacture are units made of rubber and attached with adhesive and during the past 5 years considerable advances have been made in the methods used to bond them.

The work of SATRA's Adhesion and Chemical Research Department naturally has a very strong practical bias, for the surfaces we have to deal

---

[†] This paper was presented at the Tenth Annual Conference on Adhesion and Adhesives held at The City University, London, England, April 1972.

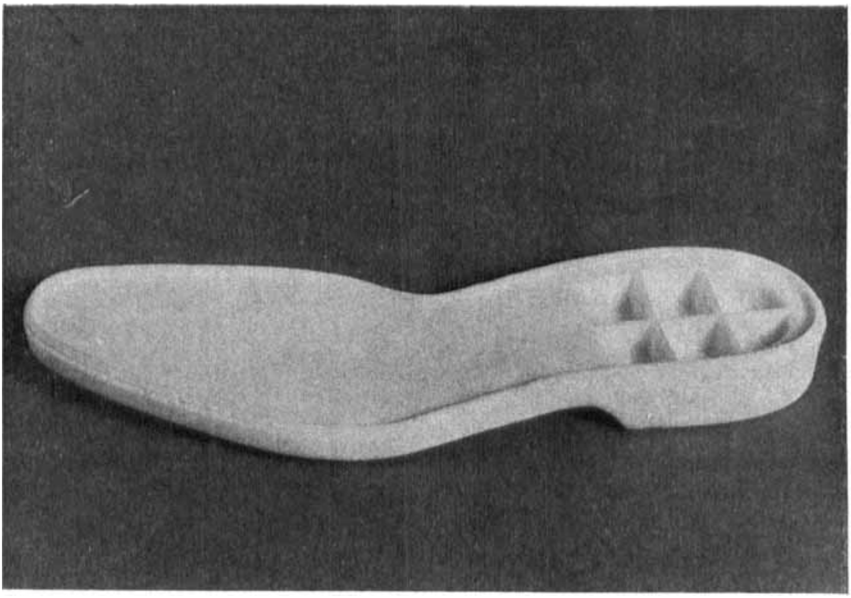

FIGURE 1 Typical moulded rubber unit shoe sole.

with are not ideal and a typical commercial moulded unit sole is illustrated in Figure 1. Such units are usually based on a styrene-butadiene copolymer (SBR) with between 15 and 30 additional components in the compound formulation comprising fillers, antioxidants, processing oils and vulcanizing chemicals. As can be appreciated when dealing with such a mixture it is extremely difficult to determine the nature of the surface to which one is bonding.

Vulcanised SBR rubber is the main rubber currently used in our industry but natural rubber, thermoplastic rubber and ethylene-propylene terpolymer rubber (EPDM) all of which have some degree of unsaturation, are all considered in this paper as also are the saturated hydrocarbons polyethylene and polypropylene.

Typical bonding conditions employed in the shoe industry and the main type of upper materials to which they have to bond are shown in Table I.

It is essential that the initial "grab" of the adhesive film is good enough to spot or accurately place the sole and that no slippage or separation occurs on removal from the press. This means that the green strength of the adhesive must be high. During service the adhesive is continually subjected to flexing forces and is required to be resistant to temperatures of at least 60°C. Polychloroprene and urethane adhesives can fulfil these requirements.

The main upper material used is still the traditional leather which, because

TABLE I

Bonding conditions and substrates

Materials used	Bonding conditions
Rubber sole PVC sole Leather sole Urethane sole Leather upper PVC upper urethane upper	2 way stick Open time Sole 1 hour—2 weeks Open time Upper ½ hour—2 hours Reactivation—Heat reactivate sole to 85°C Bonding—15 seconds at 5.6 kg/cm^2

of its origin, is a variable material. Urethane adhesives behave better in some respects than polychloroprene adhesives on greasy leather because excessive grease and fatty acids present can more readily adversely affect polychloroprene adhesives.

With a shoe upper of polyvinylchloride (PVC) it is more satisfactory to use urethane adhesives as these are not softened by migrating plasticizer and their specific adhesion to the PVC is superior to that obtained with a neoprene adhesive.

Polychloroprene or urethane adhesives can be used with the polyurethane upper materials but we have seen evidence to suggest that polychloroprenes may not behave normally on a urethane poromeric material. This evidence concerning adhering poromeric to poromeric when the polychloroprene adhesive films on the two substrates failed to coalesce on being brought together.

Urethane adhesives may, therefore, be preferred to polychloroprene for these types of upper materials but the latter adhesives have long been used and are still being used to bond to leather very successfully. However, there is currently a trend towards the increasing use of urethanes. For this reason, our work has been concentrated on the adhesion of rubbers with urethane adhesives since this is a vital area in mixed productions involving some PVC and therefore needing a urethane adhesive.

II POLYCHLOROPRENE BONDING OF SBR RUBBER

Vulcanized SBR rubber can usually be bonded perfectly satisfactorily with a polychloroprene adhesive if the rubber surface is freshly prepared by scouring or splitting. Unfortunately, the bond to a rubber surface not freshly prepared is often inferior. This is illustrated by the bond strengths shown in Table II.

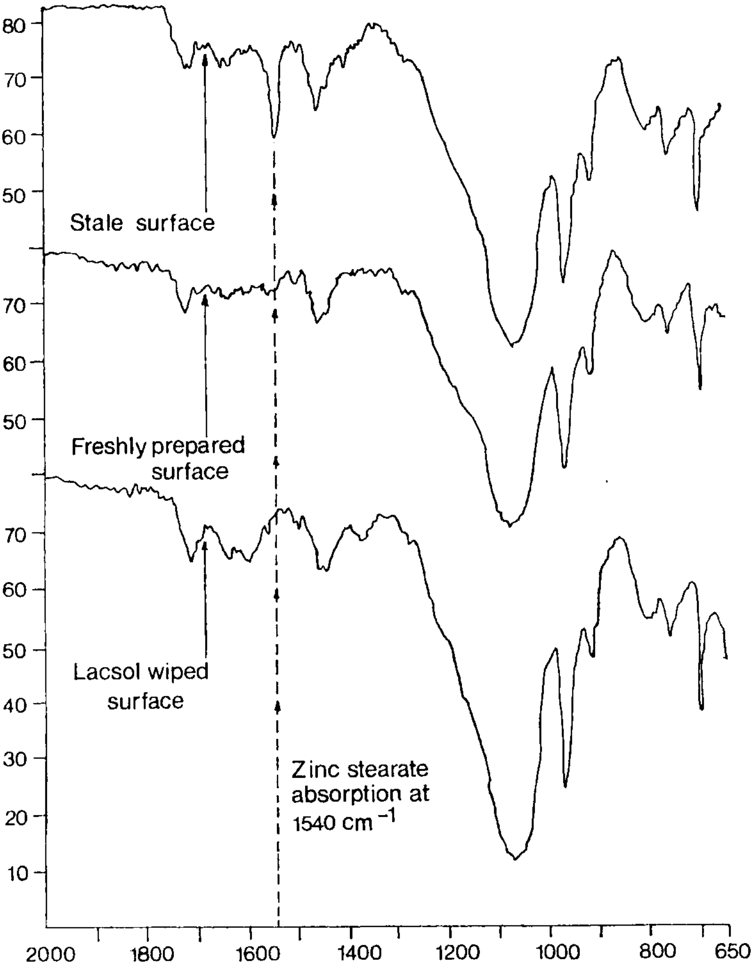

FIGURE 2 Infra red attenuated total reflectance (ATR) spectra showing the occurrence of zinc stearate on the surface of a typical mineral filled vulcanized styrene-butadiene rubber soling material.

TABLE II

Bonds to freshly prepared and stale rubber surfaces with polychloroprene adhesives

	Freshly prepared surface		Stale surface	
Polychloroprene adhesive	Bond strength kgf/cm	Type of bond failure	Bond strength kgf/cm	Type of bond failure
A	9.8	100AR	1.8	100AR
B	5.7	100AR	1.3	90AR 10IC
C	6.3	100AR	1.4	100AR

AR = Adhesion to rubber failure IC = Incomplete coalescene failure

[a]The figure preceding the letters denoting the type of failure indicates the percentage of bonds showing this failure.

Some years ago, we examined this problem and found that a frequent reason for this deterioration in the adhesion was a soap migrating to the rubber surface. The evidence for this is given in Figure 2 consisting of attenuated total reflectance (ATR) infra red absorption spectra of a freshly prepared rubber surface and a stale rubber surface. The presence of the soap, formed during vulcanization, on the stale surface is shown by the appearance of the 1540 cm^{-1} peak. Staling and appearance of a soap bloom can take place very quickly in a moist atmosphere. A chemical treatment "Lacsol" was developed to remove this soap from the rubber surface and good bonds resulted from its use.

III POLYURETHANE BONDING OF SBR RUBBER

The urethane adhesives used in the footwear industry are commonly polyester polyurethanes and these were introduced to the industry about 8 years ago.

The urethane elastomers are most frequently based on glycol/dibasic acid polyesters which are converted to high molecular weight urethanes by chain extension with MDI. The elastomers usually have a high tendency to crystallize.

These thermoplastic urethanes are used in three main types of urethane adhesives in the footwear industry:

i) Single part—which contain no free isocyanate.

ii) Two part—this is a single part urethane to which free isocyanate is added immediately prior to use.

iii) Pre-reacted—this is a mixed urethane and isocyanate where the isocyanate is not sufficiently quick reacting to cause gelling or a very short shelf life.

Each of these types can be modified by the inclusion of further compounds.

The early single part urethanes would not bond to rubber at all well. By adding free isocyanate to the adhesive an improvement in bond strength was obtained. However, two part adhesives have not been readily accepted by the shoe industry in the U.K. and in an attempt to overcome the incompatibility between the rubber and the urethane adhesive, the present authors advocated an isocyanate wipe of the rubber surface.

TABLE III

Bonds to polymers with a urethane adhesive

	No treatment		Isocyanate wipe	
Rubber (freshly prepared surface)	Bond Strength kgf/cm	Type of bond failure	Bond Strength kgf/cm	Type of bond failure
Resin rubber (1)	1.6	100AR	4.5	10AR 40SR 50R
Resin rubber (2)	1.6	100AR	6.1	100SR
Polyethylene	0	100ASM	0	100ASM
Polypropylene	0	100ASM	0	100ASM

AR = Adhesion to rubber failure
R = Rubber failure
SR = Surface rubber failure
ASM = Failure of adhesion to soling material

Table III shows the typical increases in bond strength obtained with the isocyanate wipe on resin rubber surfaces (heavily filled) whereas pure saturated hydrocarbon surfaces do not benefit from this treatment.

It has been reasonably proposed[2] that the isocyanate reacts with reactive hydrogen atoms on the rubber or filler surface and so acts as a bridge between the rubber and the urethane adhesive. The results obtained with

TABLE IV

Effect of extending time between isocyanate treatment and adhesive application

Time between isocyanate wiping and urethane adhesive application	Bond strength kgf/cm	Amount of AR failure
Immediate	9.1	50%
1 day	4.5	65%
1 week	1.8	90%

AR = Adhesion to rubber failure

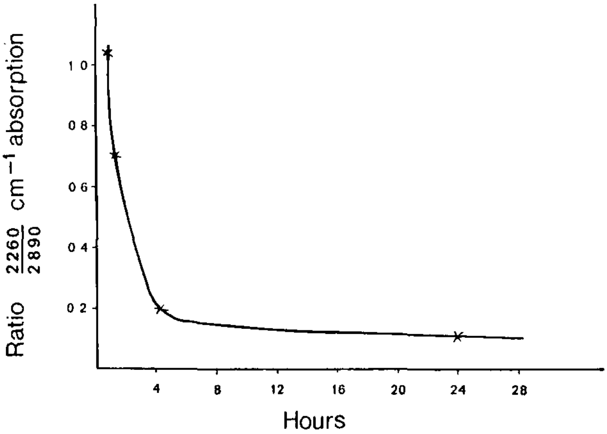

FIGURE 3 Reduction in free isocyanate on rubber surface with time after isocyanate wiping. Determined by ATR spectra of the treated surface and the relative loss of the isocyanate absorption band intensity.

polythene and polypropylene which show no improvement after the wipe treatment tend to support this supposition.

However, the results in Table IV show that the beneficial effect of the isocyanate wipe diminishes as the time between wiping and adhesive application is extended. This suggests that it may be necessary to have free isocyanate present for good results. That is, the isocyanate group may need to react chemically with both the rubber and the urethane adhesive. In support of this reasoning it should be noted that it is necessary to employ a polyfunctional isocyanate molecule in the wipe formulation.

The graph in Figure 3 demonstrates that within a few hours of wiping, the amount of free isocyanate on the surface is greatly reduced presumably by reaction with atmospheric moisture in addition to the surface. This explains why the adhesion decreases as the time between isocyanate wiping and adhesive application is extended.

IV BONDING THERMOPLASTIC BLOCK COPOLYMERS

During 1968, the problem of bonding to the new thermoplastic rubber (TR) arose. These rubbers are block copolymers and do not require vulcanization to give them dimensional stability. Bonding was found to be very difficult with the conventional polychloroprene and urethane adhesives available even after the surface pre-treatments described previously. Special adhesives, although perhaps effective, were found to have working disadvantages for shoe production.

In conjunction with the manufacturers of Cariflex Thermoplastic Rubber (Shell International Chemicals Limited) we examined halogenation techniques and found these to be successful when a urethane adhesive was subsequently used for bonding. This technique was extended to vulcanized SBR and natural rubbers and the results are shown in Table V.

TABLE V

Bonds to dip chlorinated rubbers with a urethane adhesive

Rubber (original surface)	No treatment		Chlorinated	
	Bond strength kgf/cm	Main type of bond failure	Bond strength kgf/cm	Main type of bond failure
SBR	1.8	AR	7.5	R
Natural	0.4	AR	3.5	R
Thermoplastic	0.7	AR	8.2	R

AR = Adhesion to rubber failure R = Rubber failure

A very significant feature of this work was that if the rubber surface is chlorinated, then the necessity to prepare the rubber surface mechanically is usually eliminated. Thus, a chemical treatment has replaced the traditional mechanical abrasive method and the adhesion results obtained are superior. Although halogenation as a means of promoting adhesion was not new its practical applications were certainly not realised.

Table VI indicates that, surprisingly, all halogenated surfaces do not respond very well to polychloroprene adhesives.

TABLE VI

Bonds to dip chlorinated rubbers with a polychloroprene adhesive

Substrate (original surface)	No treatment		Chlorinated	
	Bond strength kgf/cm	Type of bond failure	Bond strength kgf/cm	Type of bond failure
SBR	1.8	100AR	2.3	100AR
Natural rubber	0.7	50AR 50SR	5.2	50SR 50R
Thermoplastic Rubber (TR)	1.4	100AR	1.2	100AR

AR = Adhesion to rubber failure SR = Surface rubber failure
R = Rubber failure

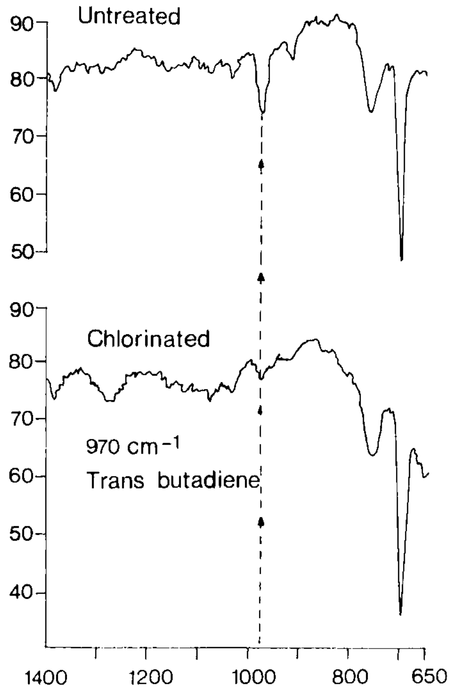

FIGURE 4 ATR spectra showing the reduced absorption at 970 cm^{-1} (*trans* butadiene structure) following chlorination of thermoplastic rubber.

Figure 4 shows ATR infra red absorption spectra of surfaces of a TR rubber before and after halogenation. It is apparent that the chlorination is causing a reduction in the 970 cm^{-1} peak due to 1-4 *trans* unsaturation in the butadiene molecule. The changes in the *cis* peak are masked by the styrene absorption.

One of the likely chemical reactions occurring during halogenation is a simple addition of halogen to the double bond in the butadiene molecule. However, this treatment is carried out by immersing rubbers for 1 minute in an aqueous solution of sodium hypochlorite and hydrochloric acid to give a chlorine concentration of 0.1 percent wt/vol and it is likely that substitution, crosslinking and cyclization may also be occurring. In fact, we have clear evidence which shows that insolubilization of the surface layer of a TR rubber to a depth of about 5 μm occurs. Halogenated TR was insoluble at the 0.2 percent level in dichloro methane, carbon tetrachloride, ethyl methyl ketone, ethyl acetate, dimethyl formamide, tetrahydrofuran.

In addition to chemical changes on the rubber surface, the stereoscan photographs of TR rubber in Figure 5 demonstrate that this treatment is

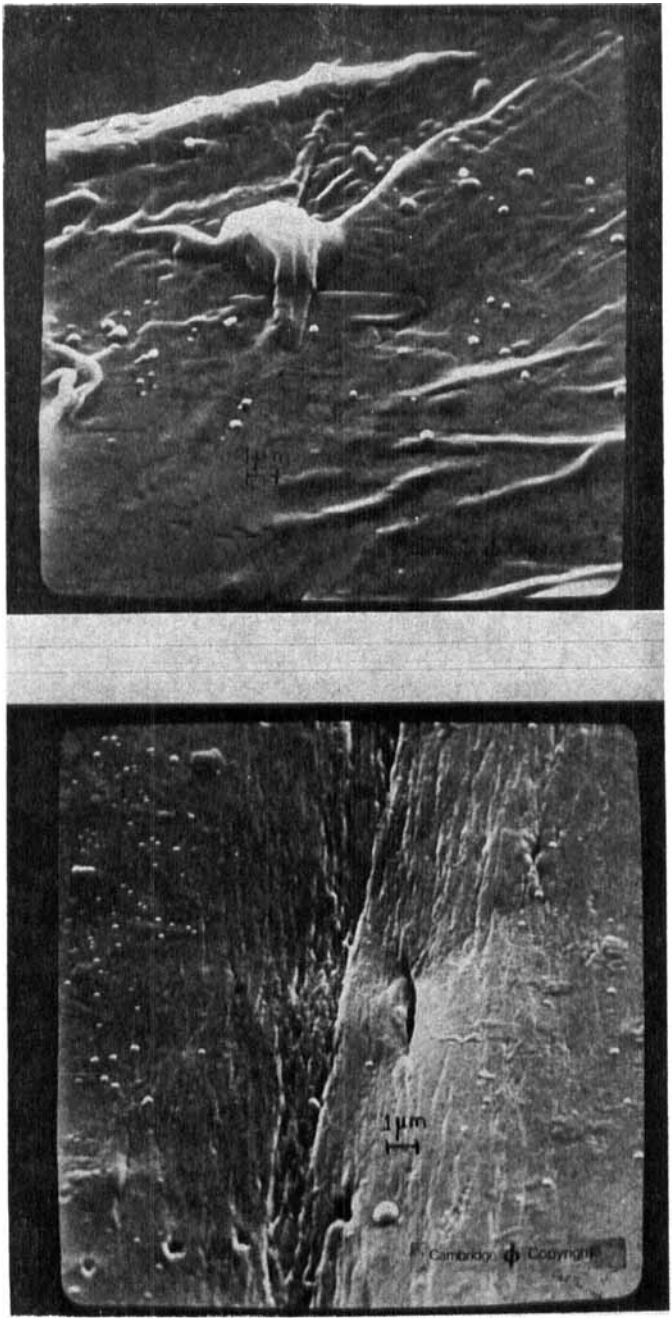

FIGURE 5 Stereoscan photomicrographs of thermoplastic rubber surfaces before (above) and after (below) chlorination by a 1 minute dip in 0.1 percent aqueous chlorine solution. The treatment has produced fine cracks in the surface.

producing some surface crazing. However, the degree of halogenation referred to above does not have an adverse effect on the flex crack resistance of the rubber.

Treatment of rubbers with gaseous chlorine can also be employed to effect an improvement in adhesion with a urethane adhesive. The conditions employed on the surfaces bonded to give the results in Table VII were storage for 5 minutes in a 0.1 percent wt/vol chlorine atmosphere. A saturated atmosphere of chlorine gas would contain 0.3 percent wt/vol of chlorine.

TABLE VII

Bonds to rubbers with a urethane adhesive after chlorine gas treatment

Rubber (original surface)	No treatment		Chlorine gas treated	
	Bond strength kgf/cm	Type of bond failure	Bond strength kgf/cm	Type of bond failure
SBR	1.1	100AR	8.1	90SR 5AR 5NC
Natural	0.2	100AR	3.5	100R
Thermoplastic	0.5	100AR	9.3	100R

AR = Adhesion to rubber failure
SR = Surface rubber failure
R = Rubber failure
AP = Failure of adhesion to upper plastic
NC = Non-coalescene failure

Using a gaseous chlorine treatment, the rubber surface requires no drying before adhesive application and this is therefore a practical advantage over the dip chlorination method. However gaseous chlorine treatment clearly involves greater capital costs.

The beneficial effect of the halogenation treatment on some rubber surfaces is maintained for greater than 6 months. Their life may be linked with the tendency of the rubber to produce a bloom.

As both of these treatments are a potential source of a toxic hazard, they could not be usefully employed in the footwear industry without very strict control on extraction procedures.

At this stage, we attempted to develop a halogenation treatment which could be safely used in a shoe factory. This work led to the development of Satreat which is a solution of an organic halogen donor in an organic solvent.[3] In parallel with this development, Larkhill Soling Company, familiar with the halogenation work done at SATRA, developed their own solvent halogenation wipe product.[4] Our preliminary work on halogenation also led our Dutch associate organisation, TNO, Waalwijk, to the development of Tenosol,[5] which is another similar product. At the present time, there are, therefore, at least three commercial products which fulfil similar functions and which can be used in a shoe factory, or other bonding operation.

The results in Table VIII show that Satreat is effective in improving the adhesion to the original surface of rubbers. It is normally applied by a brush and after treatment the adhesive application may be delayed up to a month. Besides improving the adhesion of urethane adhesives, halogenation improves the adhesion of polyester and polyamide hot melts to rubbers.

TABLE VIII

Bonds to rubbers with a urethane adhesive after the SATREAT wipe

	No treatment		SATREAT wipe	
Substrate (original surface)	Bond strength kgf/cm	Type of bond failure	Bond strength kgf/cm	Type of bond failure
SBR	0.1	100AR	6.4	100R
Natural rubber	0.4	100AR	5.9	100R
Thermoplastic rubber (TR)	0.5	100AR	12.9	100R

AR = Adhesion to rubber failure R = Rubber failure

Figure 6 shows stereoscan photographs of the surface of a vulcanized rubber before and after Satreat wiping and demonstrates that the wipe treatment is causing cracks to appear in the surface of the rubber. Experiments to introduce mechanically produced flaws, however, were unsuccessful in improving bonds with urethane adhesives.

V EFFECT OF HALOGENATION ON ADHESION

In considering the reasons for the improvement of the adhesion of urethanes to rubber surfaces brought about by halogenation one must take account of the following changes to the surface of the rubber bearing in mind that these are observed not with TR only but with unsaturated hydrocarbon rubbers generally. These include changes in surface morphology, polarity and surface free energy; insolubilization of an unvulcanized surface; an improvement in the bond strength shown by polyurethane, polyamide and polyester adhesives but much less improvement with polychloroprene adhesive. It is interesting to consider the relevance of current theories of adhesion in framing an explanation for the above observations.

It is obvious that the materials with which we are concerned are so heterogeneous that we have to be very careful in interpreting surface behaviour because of our uncertainty of what is present at or on the surface. This lack of absolute knowledge of the surfaces precludes any attempt at a rigorous approach but there is little doubt that the theoretical concepts, in

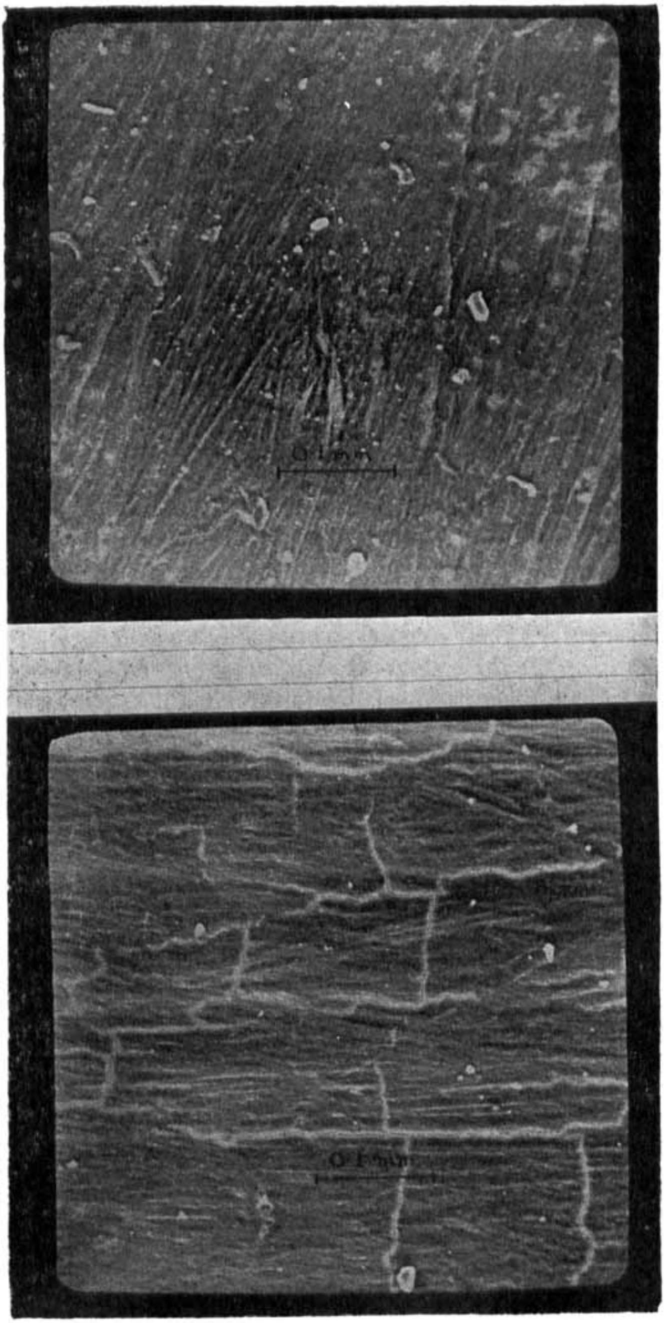

FIGURE 6 These stereoscan photomicrographs, showing a vulcanized rubber surface before (above) and after (below) wiping with Satreat (solvent halogenating treatment), illustrate the surface cracks caused by the treatment.

as far as they can be grasped in an empirical fashion, do serve us as a stimulus to investigation.

It seems widely accepted that given close enough contact between the molecules of adjacent surfaces, dispersion forces are more than adequate to explain the observed strength of a bond, and since urethane adhesive solutions appear to wet the rubber substrates even before halogenation one has the problem of explaining why they do not stick when dry.

The simplest explanation would be one involving weak surface layers such as mentioned earlier in respect of polychloroprene adhesives being rendered ineffectual by the presence of a zinc stearate layer. Indeed, dispersal of such blooms by Lacsol does improve the adhesion of some urethane adhesives to rubbers as must be expected. The contribution of another form of weak layer, that due to filler particles which tear out of the rubber surface and adhere to the adhesive layer, has been shown by stereoscan photographs of the separated surfaces. Again, this is only a partial reason for the failure of urethanes to stick to rubbers. If the particles are removed by acid treatment, adhesion is still bad. However, halogenation markedly improves the bond and demonstrates that the poor adhesion of urethanes to such rubbers is mainly the consequence of their failure to stick to the elastomer. To explain this one can consider the cohesive energy densities of the urethane and the rubber showing that they are far enough apart to imply incompatibility. However, the present authors favour an explanation involving the crystalline nature of urethane adhesives. It seems more reasonable that re-orientation of urethane molecules at the interface during the crystallization of the urethane adhesive film is sufficient to overcome weak adsorption forces and either create a condition of stress at the interface or to displace the molecules from attraction distances. Using this concept one need not necessarily invoke chemical bridges to explain the improvement in adhesion which isocyanates bring. Their function might be simply to disrupt the crystallization of the urethane elastomer at the interface and so reduce the stresses in that region.

The effects noted earlier of halogenation on the nature of rubber polymers are not helpful to any proposition that halogenation could promote molecular diffusion at the interface. Some of the rubbers are cross-linked and the changes in cohesive energy density expected with halogenation would not seem to be sufficiently large to cause it to be close enough to the cohesive energy density of a urethane to enable one to postulate that diffusion of the urethane into the treated rubber surface is likely.

The most acceptable explanation is one in which surface tension measurements were used to demonstrate a strong polar attraction between the halogenated surface and the urethane linkages of the adhesive.[6] The invocation of hydrogen bonding in these circumstances seems very appropriate and would suggest a high enough energy of adhesion between the rubber surface and the urethane molecules to resist subsequent dislocation by crystallization forces. We have, in fact, looked for some retardation of the crystallization of urethane adhesives on halogenated surfaces but have failed to detect this. However, it should be said that experimental determination of bond strength prior to crystallization did not unequivocally demonstrate that urethanes have better adhesion to rubber surfaces in the decrystallized state.

In 1971, Williams[7] in a lecture stressed the importance of shifting mechanical stresses away from the interface by modification of the surfaces and this seems appropriate to the case of halogenation. At that time it seemed possible that the "CASING treatment" of polyolefins[8] might also be improving adhesion by producing a crazed surface on the polymers. Although it is understood that this has been disproved, it was considered that crazing might be important in the improved bonds obtained on halogenated surfaces. It might be thought that in the case of treated thermoplastic rubber the strongly directional nature of the injected polymer could lead to better peel bonds when tested across the orientation than when tested parallel to the orientation, but this is not so. Generally speaking, one might expect that roughening of surfaces would give similar improvements in bonding with urethane adhesives on rubber if the influence of the crazed surface was a decisive factor. However, this is not so, but there is some evidence that the halogenated layer may be stripped off at lower loads than a non-halogenated surface. Another puzzling feature is the apparent failure of halogenation greatly to improve the bond of neoprene adhesives to moulded SBR surfaces. Here again the crazing shown by the stereoscan micrographs would have led one to expect that some improvement in bonding would have been brought about with polychloroprene adhesives. Although this is partially true on moulded surfaces the gain in bond strength is not approaching that found with urethane adhesives.

To return again to the effect of free isocyanates on the urethane-to-rubber bond, we observed that the bond strength of premixed urethane adhesives containing free isocyanates to dry rubber surfaces could be quite substantial. But after immersion in water there was a very marked decline in bond strength with mainly failure at rubber surface. When the same premixed urethane adhesive containing isocyanate groups was used on halogenated resin rubber surfaces, the resultant bonds were hardly affected by water under the same conditions. This suggested that the free isocyanate in the modified adhesive had not achieved true chemical bridges with the surface whereas there is a much stronger polar attraction between the same adhesive and a halogenated surface. This polar interaction is sufficient to resist the ingress of water.

The improvements in adhesion obtained with urethane adhesives are not exclusive, in fact similar increases in bond strength are to be found on halogenating a rubber surface to be used with polyester or polyamide hot melts. Once again in the case of the polyamide adhesive one is able to postulate some form of hydrogen bonding at the interface, however, this is more difficult in the case of the polyester. Here one may use the fact that most polyesters have terminal hydroxyl groups in order to explain the improvement in bond strength. In a lecture to a Gottwaldov Symposium on hot melt adhesives, Adcock[9] demonstrated the possible role of crystallization in explaining the poor bonding of polyester adhesives to rubber surfaces. He produced a graph showing a very close relationship between the loss of bond strength with time and the increase in crystallization of the polyester adhesive with time.

An attempt was made at SATRA to use ethyl acetate as a model liquid for polyester adhesives to show whether there was an increase in attraction between this substance and halogenated surface. However, it was not possible to set up a model system which was close enough to practical conditions to give any convincing proof.

It would probably be fair to summarise our attempts to relate practical effects to theories as stimulating if not satisfying.

VI BONDING ETHYLENE-PROPYLENE TERPOLYMER RUBBER (EPDM)

Recently the EPDM rubbers have become of some interest to the footwear industry and it has been shown[10] that by subjecting the rubber to ultra violet radiation and following this with polyisocyanate wipe an improvement in adhesion is obtained.

In SATRA work, on NORDEL EPDM (Du Pont (U.K.) Limited) rubber formulations supplied by the manufacturers, it was found that a double

TABLE IX

Adhesion of EPDM rubber

	Scoured surface no treatment		Scoured surface dual prime treatment	
Adhesive	Bond strength kgf/cm	Type of bond failure	Bond strength kgf/cm	Type of bond failure
Polyurethane	0.4	100AR	6.4	100R
Polychloroprene	0.7	100AR	6.8	95R 5NC

AR = Failure of adhesion to rubber R = Rubber failure
NC = Non-coalescene failure

priming treatment derived from halogenation can produce acceptable bonds to the rubber and failure occurs within the rubber with both urethane and polychloroprene adhesives. This system, the results of which are shown in Table IX, is a halogenation step followed by an isocyanate treatment and the IR spectra at first suggested that unsaturation had been removed. However, it was later shown that the "unsaturation" indicated by the 970 cm^{-1} peak was removed by solvent extraction and what we had further taken to be absorption bands of new $-OH$ groups were probably due to surface water introduced during the treatment.

VII CONCLUSIONS

In the work described in this paper, it is clear that SATRA has concentrated on modifying the rubber surface to improve adhesion rather than developing adhesives specifically for rubber. There are two main reasons for this approach:

i) The adhesives available in the footwear industry have been developed by the adhesive manufacturers to bond to the wide range of substrates used in the industry. The footwear manufacturer would prefer not to use special adhesives for each material but would certainly prefer a general purpose adhesive so there was no chance of confusion.

ii) By modifying an adhesive to bond to rubber, it is quite likely that the other critical properties of the adhesive would deteriorate (such as tack retention, shelf life, open time, heat resistance, etc.).

References

1. E. F. Hall, *Aspects of Adhesion*, **5**, Ed., D. J. Alner (Univ. Lond. Press. London 1969), p. 105.
3. N. B. Stokes, *JBBSI* **14**, 196 (1967).
3. Satreat, Registered Trade Mark (U.K.) 963193.
4. Larkhill Soling Co., Private Communication (1972).
5. J. S. A. Langerwerf, *Proceedings of International Conference on Shoemaking Technology*, Evian, June 1972.
6. W. C. Wake, *Adhésion des Élastomères*, (Assoc. Francaise Ing. du Caout. Plastiques, Paris, 1970), p. 19.
7. M. L. Williams, *Aspects of Adhesion*, 7, Ed., D. J. Alner and K. W. Allen. In the press.
8. H. Schonhorn, in *Adhesion, Fundamentals and Practice*, (Maclaren, London, 1969), p. 18.
9. S. A. Adcock, Int. Symp. of the Central Council Czechoslovak Scientific and Tech. Soc., held at Gottwaldov, Czechoslovakia, September 1968.
10. United Shoe Machinery Corp,, U.S. Patent 3,600,289, priority, August 31, 1967.