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Making it stick

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Adhesives are used in a wide number of applications in the manufacture of footwear. The major ones, together with the most important types of adhesive used in each case, are shown in *Figure 1*. The two key areas in terms of volume of adhesive used are lasting and sole attaching, so this article will focus very much on these with especial attention given to the latter.

LASTING

The lasting of uppers (pull-over, toe, seat and side lasting) has been dominated for many decades by the use of hot melt adhesives and has become ever more productive with the development of specialised lasting machinery. This whole area was extensively covered in the article 'Developing the modern toe laster' in the July/August 2013 edition of *World Footwear*, including some of the latest

adhesive developments.

The most startling of these is the innovation by the Italian company Cerim of a water-based polyurethane adhesive that can be used on its lasting machines. It has developed systems that

can easily switch between hot-melt and water-based polyurethane as required by whatever means the footwear needs to be produced. This patented process is a first step away for the lasting process from the dominance of polyester and

FIGURE 1

APPLICATION	ADHESIVE
Topline folding	Hot melt polyamide
Fitting linings	Natural rubber latex, hot melt polyamide, EVA
Toe puff & counter bonding	Hot melt coating EVA
Lasting	Hot melt - polyamide, polyester; water-based polyurethane
Shank	Hot melt - EVA, polyamide
Sole attaching	Solvent or water-based polyurethane, polychloroprene primers
Heel covering	Solvent or water-based - polychloroprene
Insock insertion	Natural rubber latex, acrylates

polyamide hot melts. While it scores highly on points such as lower energy costs and the use of eco-friendly products, more important is that the use of a water-based polyurethane adhesive rather than a hot-melt results in a great improvement in the quality of the final product. Water-based polyurethane offers a thin, uniform and flexible film of adhesive rather than the thick inflexible bond produced by hot-melt. This greatly improves the flexibility of the shoe and also improves its overall shape.

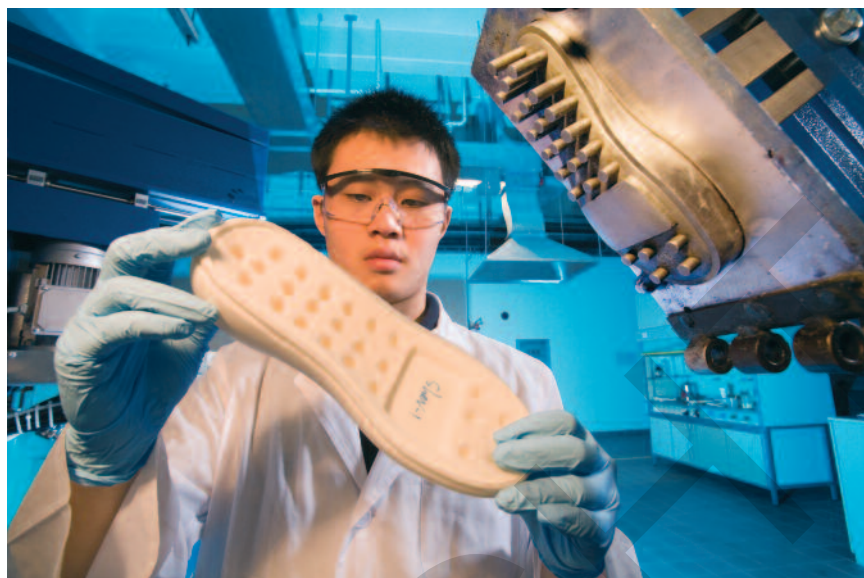
SOLE ATTACHING

Sole attaching has developed dramatically over the last 90-100 years closely linked to the development and commercial availability of new polymers for both soling and for adhesives. In the 1920s and 30s, the major soling materials were natural crepe, vulcanised rubber and leather. New methods to attach them were gradually developed using either solvent-based natural rubber or nitrocellulose adhesives until, by the mid 1940s in the US at least, a high proportion of women's soles was attached by adhesive, mainly solvent-based nitrocellulose.

These early developments depended upon the presence of solvents in the adhesive at sole attachment for the adhesive films on the sole and upper to coalesce. This was achieved either by limiting the drying of the adhesive or by deliberately adding solvent just before sole pressing to reactivate the previously dried films. These nitrocellulose solvent-based adhesives were only suitable for bonding fibrous materials and their bond strengths were all below those accepted as normal today. Natural rubber adhesive bonds also lacked the stability of present day synthetic polymers and were prone to break down under the effects of heat, grease, flexing and copper contamination. Their main usage was therefore restricted to attaching crepe soles. Indeed, prior to 1940, available adhesives lacked the necessary versatility to bond the range of different materials which were to be found in stitched-on constructions.

POLYCHLOROPRENE ADHESIVES

The Second World War stimulated commercial production of synthetic polymers that soon found use as soling



Polyurethane adhesives have been highly successful as they can be used with such a wide range of soling materials. CREDIT: GFCC

materials. Until about 1950, solvent-based nitrocellulose remained the only option for stuck-on sole attachment. By then, solvent-based nitrile and polychloroprene adhesives were also starting to be used, with the latter the more popular because of their superior coalescing ability and ease of activation. The rapid growth of the stuck-on process during the period 1950-65 and based on vulcanised rubber followed by plasticised PVC sole units, was linked to the parallel development of excellent solvent-based polychloroprene adhesives capable of heat reactivation. The ability to reactivate pre-coated components days or even weeks later, gave the stuck-on process a degree of flexibility which made it highly attractive to shoe manufacturers.

The development of isocyanate solutions was another important step during this period as these could be added to the adhesive just prior to application. The combination provided greater heat, grease and solvent resistance, and frequently improved adhesion qualities. However, its addition also had the adverse effect of decreasing pot-life of the adhesive.

Solvent-based polychloroprene adhesives can be adversely affected by the grease content in leather whereby free fatty acid combines with minerals in the adhesive to form metal soaps that prevent good coalescence. These substances can also be found on the surface of many vulcanised rubbers and

may again lead to bad adhesion with solvent-based polychloroprene adhesives. Special primers, such as SATRA's Lacsol, were developed to remove this 'soap' and so improve adhesion.

POLYURETHANE ADHESIVES

By the mid 1960s the footwear industry was increasingly focused on the use of plasticised PVC for soling and upper materials and the limitations of solvent-based polychloroprene as an adhesive became more apparent. It did not have a good affinity to PVC and was susceptible to the softening action of the plasticisers used. Primers were developed for coating the lasted margin of PVC uppers prior to applying the adhesive and which made it possible to bond vulcanised rubber soles but not PVC.

Solvent-based polyurethane adhesives first appeared in the mid 1960s with excellent adhesion to plasticised PVC. These early polyurethane adhesives were expensive due to polymer and solvent costs. They also lacked the easy spotting tack of solvent-based polychloroprene adhesives and their inherent ability to stick to synthetic vulcanised rubbers. They did however show excellent resistance to grease and plasticisers. Furthermore, the addition of isocyanates was found particularly useful in modifying their heat resistance and adhesion to vulcanised rubber.

By the end of the 1960s, solvent-

based polyurethane adhesives were increasingly used on resin rubber soling either as a two-component adhesive with the isocyanate mixed into the adhesive just before application or with it used as a primer on the resin rubber before application of the adhesive.

Different approaches were taken to solve the problems of obtaining good adhesion between the sole unit and upper, especially when using vulcanised rubber. Certain countries favoured the use of two component adhesives with the isocyanate component being added just before use. Others preferred one-component adhesives with improved heat resistance and good adhesion to rubber obtained by compounding additives into the formulation together with isocyanates, although the latter were inhibited from reacting fully until the adhesive dried.

HALOGENATION

Polyurethane and thermoplastic rubber sole units were both introduced during the 1970s and, whilst there was no problem bonding the former using solvent-based polyurethane adhesive once the mould release had been removed using a solvent wipe, there were more problems with the latter. It was work by SATRA on the development of a halogenation wipe called Satreat that finally solved the problem and allowed thermoplastic rubber soles to be successfully bonded to uppers using solvent-based polyurethane adhesives.

This halogenation treatment was found to be equally effective on vulcanised rubber sole units and was made commercially practical by the development of low toxicity solvent halogenation solutions such as Satreat that made it possible to use them in the shoe factory. The advantages of halogenation in preparing vulcanised rubber surfaces for bonding with solvent-based polyurethane adhesive has led to the worldwide use of the system and to greater displacement of solvent-based polychloroprene adhesives by solvent-based polyurethane adhesives than might have otherwise been expected.

In the late 1970s special adhesives, both acrylic-modified polyurethanes and polychloroprenes, were developed for bonding thermoplastic rubber



SATREAT made it possible to use polyurethane adhesives on a wide range of soling materials.

CREDIT: SATRA

without halogenation. These are still used successfully but are less versatile than halogenation. Special polyurethanes for bonding PVC blends are also available. The appearance of other new polymers for solings such as EVA and POE has led to the developments of special primers enabling them also to be bonded with solvent-based polyurethane.

Thus solvent-based polyurethane adhesives gained ground rapidly through the 1970s and 1980s, becoming particularly dominant in the 1990s and far exceeding the use of solvent-based polychloroprenes. For over 50 years sole attaching adhesives were therefore almost exclusively solvent-based, although health and safety hazards linked with solvents—especially flammability and toxicity—had to be addressed in the workplace.

SEDS AND VOCs

The next great concern was the environmental pressure on air pollution which began in the 1990s. This led to the introduction of various SEDs (solvent emission directives) by developed countries. The European

Community act for instance was originally passed in 1999 as Directive 1999/13/EC, followed by Directive 2004/42/CE and then Directive 2008/112/EC. This imposed strict levels on the emission of VOC's (volatile organic compounds) due to the use of solvents. The purpose of an SED is to prevent or reduce the direct and indirect effects of emissions of volatile organic compounds into the atmosphere and potential risks to human health.

These SEDs obviously affect the type of adhesive that can be used by the footwear industry both in the country/region where the directive is enacted but also on the sourcing of footwear from elsewhere. For instance, back in the early 2000s it was surprising to find that the introduction of some of the early water-based polyurethane adhesives by HB Fuller was taking place in China. The explanation for this was twofold. First there was pressure from major brands such as Nike, Timberland and Clarks to be seen to be environmentally sound. Second, it was often easier to introduce the new equipment needed to handle water-based adhesives in the rapidly evolving

and growing production plants in China. It took longer to replace the solvent-based equipment then in use in the developed world's factories.

The amount of focus on the removal of VOCs is shown by the attitude of adidas which has issued figures for the changes in VOCs in its athletic shoes. In 1999, a pair of shoes contained on average 140 gram mostly from the adhesives involved. By 2010, it had been driven down to 25 gram. Quoting the figure as part of an 'individual roadmap' towards zero discharge of hazardous chemicals that it released in parallel with a joint statement made with five other companies in November 2011, the company said "We support in principle Greenpeace's aspiration for a world that is free of hazardous chemicals. However, while we are committed to being part of the solution, we have to acknowledge that the management of chemicals in multi-tiered supply chains is a complex challenge, requiring many actors to play a role in achieving this goal. The adidas group works with more than 1,200 contract factories in 69 countries around the world." It is therefore clear that major companies are serious about their environmental position and intention to reduce damage to the environment. Water-based adhesives will therefore soon dominate the footwear industry as they already do in so many others.

WATER-BASED ADHESIVES

The key background to water-based adhesives is that nowadays it is possible to disperse many polymers to form a latex or emulsion. A latex or emulsion is defined as 'a stable colloidal dispersion of polymer particles in an aqueous medium'. Polymer particles, each comprising thousands of tiny (100-200 nanometres diameter) individual molecules but still exceedingly small, are kept in suspension by the action of surfactants, stabilisers and other additives. Because these particles reflect light, the dispersion is usually milky white in appearance. Whereas solvent-based adhesives typically have a solids content of 20-25%, water-based products are normally in the range of 40-50%. This means that less adhesive has to be used and less carriage shipped from adhesive producer to end-user.

As with solvent-based adhesives,

water-based dispersions need to be dried after they have been applied so that the polymer particles are forced closer together until they coalesce into a film. The drying of water-based adhesives does take a little more energy than that required for solvent-based products but the higher solids content helps to reduce the amount.

Polyurethane dispersions (PUDs) suitable for formulating water-based polyurethane adhesives have now been available for over 20 years. Because they have molecules agglomerated as particles in water rather than individual molecules in solvent, their viscosity is inherently low, although it can be increased by thickeners if necessary. A big step forward was the development of isocyanate curing agents compatible with water-based polyurethane adhesives, enabling two-part systems to be offered. This is difficult to comprehend as it is well known that isocyanates react readily with water. However, chemists have played their part and developed isocyanates that 'like' PU polymers more than water and so prefer to act with them rather than the water content one would normally expect.

Polychloroprene dispersions are also well established, enabling water-based adhesives for many purposes to be formulated. Like their solvent-based counterparts these usually require the incorporation of a compatible tackifying resin. They are used in shoemaking for temporary sole attachment in welted footwear and other ancillary operations.

The formation of stable aqueous polymer dispersions requires good control of both formulation and process methodology. They are sensitive to various influences that can cause instability and irreversible coagulation of the polymer to form rubbery lumps. This means that water-based adhesives, both polyurethane and polychloroprene, should always be stored as recommended by the supplier and usually above 5°C to avoid freezing. Additions of chemicals, including water, should never be made unless these are specifically permitted.

FURTHER IMPROVEMENTS

Whilst these water-based adhesives dominated many aspects of footwear manufacturing during the 1990s, a fear of bond failure between the sole and

upper meant that many manufacturers preferred to continue using solvent-borne products for sole attachment. However, in recent years, water-based formulations suitable even for this demanding application have emerged through the addition of high ethylene-oxide content polyethers that help to ensure the desired high molecular weight structure of the polyurethane.

The resulting crystalline polymer backbone can create a one-component aqueous adhesive that forms bonds capable of supporting a 0.5 kg weight at temperatures above 100°C. After conditioning the bond at 80°C without a weight for 3 minutes and then loading it with 2.5 kg at 80°C for 5 minutes, the adhesive parted at speeds of less than 1 mm per minute compared with 14.5 mm/min for traditional water-based polyurethane formulations. Such properties makes the adhesive especially well suited for use in heat reactivation bonding of plasticised PVC, polyurethane or EVA soles to uppers made of either real or synthetic leather.

Another development has recently come from the Brazilian component and adhesive producer Gruppo FCC which has reported promising progress with a new water-based product for thermoplastic rubber (TR) soling materials which can be applied without the use of a primer. The company estimates that around 30% of the 900 million pairs of shoes made in Brazil each year have TR soles, so this is a significant step forward.

Early reaction has apparently been extremely positive and several manufacturers have already started to use it. They have reported savings in production costs as a result of a reduction in the amount of pre-work that needs to be performed as well as savings in protective equipment for operators. Naturally, VOC emissions are also down.

Thanks to currently available surface preparation and chemical technologies, solvent-free adhesives can now be reliably used throughout all traditional footwear production processes. But even though adhesive companies can now help shoemakers eliminate solvents completely, should they and will they? The data from adidas shows that one company at least is pursuing such an end and one can be sure they are not alone. 🍷