Priming without solvents

TOM BAYES investigates new ways of priming footwear components without resorting to solvent-based substances.

We are all familiar with phrases like 'sustainable production' and 'green credentials'. Many manufacturers and retailers are facing increasing pressure from the consumer to make clearer statements as to their environmental awareness and to provide evidence of their efforts to reduce the environmental footprint. SATRA has several projects under the general heading of 'sustainability'. The footwear industry still has some way to go in sustainable production, in particular regarding what happens at their products' end of life when compared to other industries – such as the car tyre and refrigerator sectors.

There is one aspect of footwear production that is often overlooked – the frequent requirement for adhesives to be used. For long life expectancy and durability, the adherends (the materials to be bonded) must be correctly prepared, which normally involves the use of priming chemicals. Adhesives and primers use carrier liquids to allow their effective application, and these are often very volatile organic solvents which assist with drying. Apart from a few, rare chemicals (for instance, acetone), most are subject to workplace exposure limits (WELs) and other environmental legislation. These are controlled by effective use of extraction, which vents them into the atmosphere and thus, seemingly out of harm's way.

Taking, as an example, a single production line producing each day some 3,000-4,000 pairs of footwear with a typical ethylene vinyl acetate/polyurethane (EVA/PU) midsole and a rubber outsole, total production for a year would be in the order of one million pairs. Typically, the total amount of adhesive and primer used per pair results in around 30 grams of 'volatile organic chemicals' (VOCs) vented to the atmosphere. This equates to 30 metric tonnes per year for just one production line. Reductions in emissions can be made by switching to water-based adhesives. Nevertheless, approximately 60 per cent of VOC emission will be as a result of priming solvents. SATRA has been evaluating alternatives to solvent-based priming and how to implement the technology.

Switching to a water-based adhesive is part of the solution, and this is relatively straightforward as long as certain rules are followed. It is important to have an effective application of the adhesive, effective drying and an understanding of the difference in 'green bond' strengths (when it gets to a state that can be safely handled without affecting the product) and the longer time required for full cure. It is often a case of removing one of the glue stations and drying for double the time.

Even with the implementation of water-based adhesives, the goal of solvent-free production still remains elusive, due to the need for correct priming. Water-based primers are available, as well as innovative technology, which is the subject of this article.

It is important to consider that priming serves several purposes. First and foremost, the chemicals are applied to modify the surface chemistry of the adherend and provide a much-improved key. This is particularly the case for PU-based adhesives. It is often the case that the two adherends will require completely different priming chemicals that are specific to that material in order to create a long-lasting bond. The majority of primers will consist of 98-99 per cent solvent carrier, with a relatively small amount of solids (the active ingredient). They are

Figure 1: As rubber has a low surface energy, the water droplet (left) is not wetting the surface due to its relatively high surface tension. By contrast, a solvent has a relatively low surface tension, and in this case easily wets the surface of the rubber (right)

designed to allow the active chemicals to come into direct contact with the materials to be primed. This is one of the reasons for using relatively strong solvents, as they are very good at wetting surfaces of materials that have low surface energies (figure 1). Wetting is an important property – both for the effectiveness of primer application and the effectiveness of the adhesive – and it is crucial when water-based adhesives are used.

Many solid materials that have 'covalent' bonds (those that involve the sharing of electron pairs between atoms) have a relatively low surface energy. This is true for polymers, which are the dominant materials used for solings. The covalent bond in a liquid results in higher surface tension – an obvious and observable property of water, as in small amounts it prefers to form droplets. These properties are in conflict when, for example, water-based adhesives are used on polymers such as rubber, as it is difficult to get the adhesive or primer to wet the surface of the rubber. To achieve good wetting, the surface energy of the solid material needs to be much higher than the surface tension of the liquid. Therefore, the primer incorporates powerful solvents as carriers, and the primer chemically modifies the surface of the material. This allows for better wetting and, in most cases, also provides chemical linkage sites for the polyurethane polymer in the adhesive.

However, priming also has other very useful benefits that add to the effectiveness, longevity and quality of the bond. Most primers are applied in a scrubbing action, and this has the advantage of cleaning the surface, effectively removing loose particles remaining from scouring and roughing, as well as soaps and release agents, all of which may act as contamination. This cleaning action is particularly true of rubber priming, which is also known as 'halogenation' or 'chlorination'. The importance of this advantage becomes very apparent when solvent-free technologies are introduced. Some polymers will need a pre-treatment prior to priming, and once again strong solvents are used to remove contaminates from the surface, including oily products that can migrate to the surface of compounds like vulcanised rubber. 'LACSOL' is a product developed by SATRA for this very purpose and, although not classed as a primer, it contains active ingredients that react chemically with these contaminants.

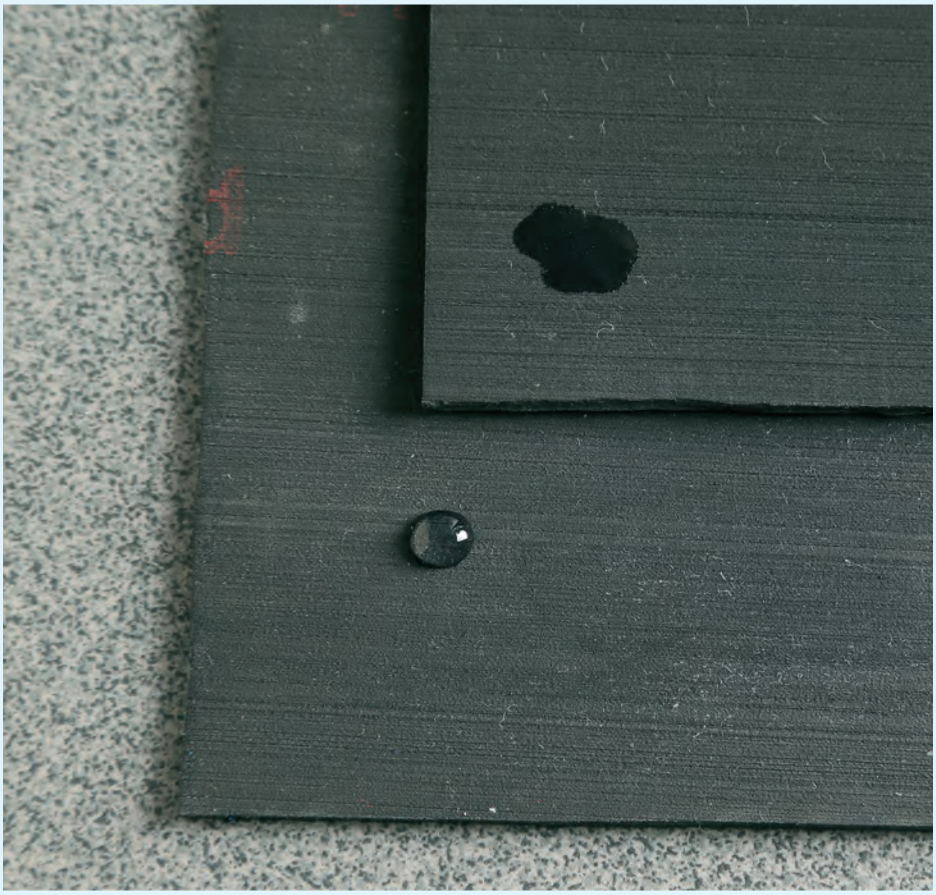

Figure 2: The rubber surface (bottom) is untreated, so the water remains as a droplet without wetting the surface. The other sample (upper right) has been primed using solvent-free technology and the effect on the water is very apparent – the water now freely wets the rubber surface, essential when using water-based adhesives

Apart from the impact on the environment and the need for effective ventilation for assembly workers, there are some technical disadvantages with the use of powerful solvents. Some commonly used polymers are susceptible to damage from solvent attack – thermoplastic rubber being one that can be damaged by the use of strong solvents. This risk is overcome by ensuring that the freshly primed units are allowed to dry flat and not under flexural stress, as failing to do this can result in cracking of the unit. Any cracks are likely to propagate during the life of the footwear, dramatically reducing the life of the soling – something we often see on finished footwear.

In the 1970s, SATRA developed a primer under its own brand known as 'SATREAT'. This is a two-part primer which can be made up on demand. It is a halogenation primer for use when rubber sole units are to be bonded using PU adhesives, and has been the industry standard ever since. Of course, it is vital that SATRA keeps abreast of new technologies and techniques, with scientific evaluation if possible. This is especially important for any practical alternatives offered to the heavy use of volatile organic compounds, as such a change can lead to safer working conditions and less impact on the environment.

New solvent-free priming

One solvent-free technology has been implemented by the Celtecnia company based near Alicante in Spain, and SATRA has had the opportunity to evaluate this interesting technology. Naturally, the technical detail is a trade secret, but the process is completely solvent-free. Powerful ultra-violet lamps are used along with ozone generation to prime mainly rubber compounds. The technique erodes the surface on a

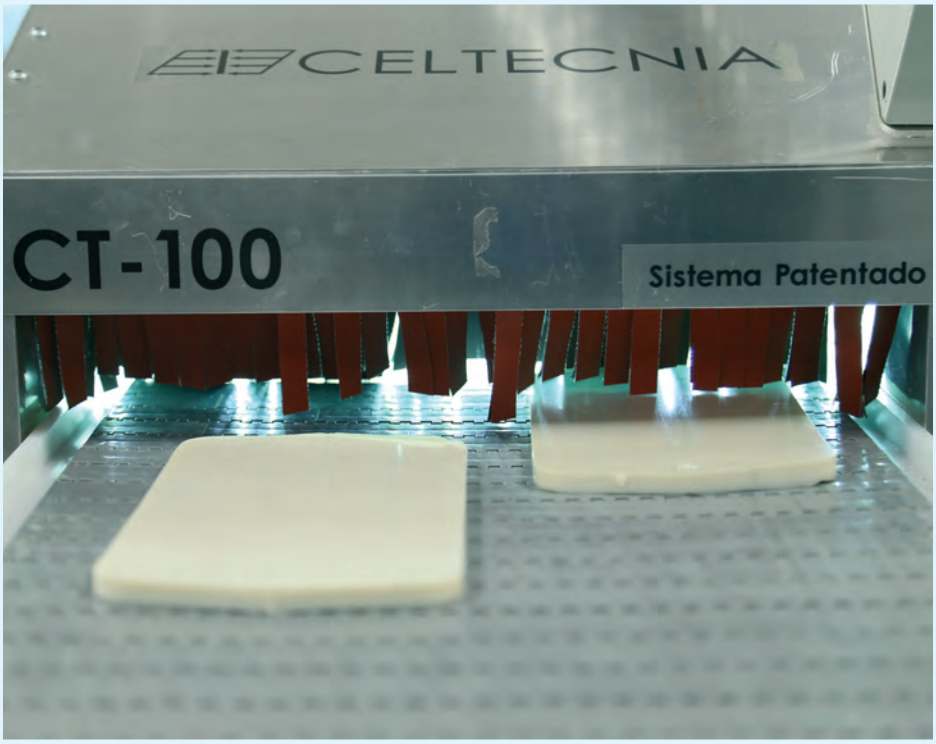

Figure 3: Moulded rubber slabs entering the Centecnia machine to prime the surface prior to the testing of bonds

microscopic scale, providing a greater surface area and an improved mechanical key for the adhesive. In addition, the technique causes certain surface bonds to break and provide linkage sites in a comparable fashion to halogenation. This effectively increases the surface energy of the material, allowing the water-based PU adhesive to very effectively wet and bond to the material (figure 2).

The waste product is a small amount of ozone, which can be extracted by a normal local exhaust ventilation (LEV) system to the atmosphere. Ozone, particularly at low altitudes in the atmosphere, is classed as a pollutant insofar as it is very reactive. In the atmosphere, it reacts with hydrocarbons which are responsible for photochemical smog. However, this process completely eliminates the production of the hydrocarbons themselves, which mostly come from volatile organic compounds. In addition, ozone has a short half-life and dissipates very quickly. In dry air, this takes place in approximately three days, and if the air is damp, this is reduced to around 11 hours. Considering the amounts of exhausted hydrocarbons that are eliminated in the process, the very small amount of ozone by-product has a little or no environmental impact.

For the evaluation, a selection of commonly-used shoemaking materials was sourced, mainly consisting of a selection of rubbers: styrene-butadiene (SBR), thermoplastic (TR) and ethylene propylene diene monomer (EPDM). Other common materials were also included in the trial, namely EVA, polyethylene (PE) foam, PU and polyvinyl chloride (PVC). Bonds were formed using recommended preparation methods and water-based PU adhesive. The resulting bond samples were then tested using SATRA TM401:2000 – 'Peel strength of adhesive bonds' to benchmark the bond strengths and mode of failure. This was repeated using the new priming technology (figure 3) with extremely favourable results.

As with water-based adhesives, the implementation of new technology rarely results in simply replacing a process. There will be other things to consider and take account of if technology is to be adopted effectively.

The previously-mentioned solvent-based primers have other useful benefits in terms of cleaning the surface. Many polymers have constituents that can migrate to the surface of the material and contaminate it, and roughing and scouring can leave fine granules on the surface that need to be removed. The scrubbing application of the primers achieves this very effectively.

SATRA investigated the additional use of solvent-free cleaners and their effect on bond strength. Again, the experiments were conducted using a variety of commonly used materials – various rubbers that would normally require halogenation, as well as EVA and PU. Divided into two equal groups, half were subjected to normal priming techniques, and the other identical set was prepared using a pre-wash with normal 'sugar soap' and then primed using the solvent-free technology. Sugar soap is a generic name for a non-toxic domestic cleaner available under several brand names. Several cleaners were tried, with sugar soap performing the best in terms of cleaning and its environmental credentials. Although it was a limited survey, the results showed that out of the common footwear materials chosen, 19 per cent of them had greater bond strengths, 63 per cent were comparable, and only 18 per cent were slightly poorer with a completely solvent-free process.

With careful selection of sole materials and correctly applied cleaning as a pre-treatment to remove contaminants, this new technology has been shown to be a very viable alternative for companies that want to completely eradicate the use of volatile organic solvents in production and dramatically enhance green credentials. It has shown to be not only a replacement for halogenation, but also be effective on EVA, PE foams and PU.

How can we help?

Members interested in the priming of footwear components without solvents can contact SATRA's footwear testing team for more information and assistance with the implementation of such a system.

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