

Finishing waterproof leather

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Interest in waterproof leather originated from the military. Soldiers are required to be active in all kinds of terrain and weather conditions and so the boots they wear must be sufficiently waterproof to protect their feet even in the wettest of environments. Wet feet in these circumstances can lead to serious problems.

More recently the production of specialised footwear for outdoor work, sports and leisure activities has given rise to a similar interest. Such footwear is often worn under similar conditions to its military counterparts. For this reason there is an obvious benefit from an ability of the leather uppers and the sole units used in the construction to withstand water. Golf shoes are one of the most prominent examples of this type of footwear, along with football, hiking and climbing boots. Waterproof leather is also used in sport gloves and high quality leather sports clothing.

The current demand for waterproof footwear has expanded well beyond these two markets. Waterproof leathers are now found in high performance applications of both high quality casual footwear and mainstream fashion shoes. The waterproof features satisfy practical concerns and differentiate the product from other brands. Although these shoes are not usually subjected to the rigours of other footwear, wear conditions may be experienced where water resistance is considered to be of value.

Taken together, these have led to an increasing pressure on the leather industry to produce waterproof leathers made to very specific and stringent standards of performance. The need for waterproof leathers will continue to rise in the future and one very important impact will be the effect of increasingly stringent environmental legislation. This is forcing tanneries to use more and more aqueous finishes rather than those with even low volatile organic compound or solvent content. This leads directly to an anomaly whereby hydrophobic leather will have to be coated with water-based finishes.

Laying the foundation

Developing finishes for waterproof leather is a complex task. The finisher and the tanner need to work closely together to ensure compatibility between the waterproofing process techniques, selection of finishing products, and application methods.

Hydrophobic characteristics are imparted to leather by various means. Hydrocarbon oils and waxes, silicones, fluorocarbons, specialised fatliquors and chrome stearate are the main products likely to be used. Often a combination of these materials is adopted to impart the desired effect and to obtain a uniform resistance through the cut of the leather rather than just on the surface. Whichever treatment is adopted, the problems associated with finishing the crust with aqueous products remain the same:

- The finish should not adversely affect the crust in terms of its dynamic and static performance.

- The finish should possess good adhesion properties.

And these properties of wetting and adhesion are closely related.

The physics of wetting and adhesion

WETTING

A liquid will wet a surface only if its surface energy or surface tension is lower than that of the substrate. If the value is very much lower, spontaneous spreading occurs. If it is higher then the liquid will not spread but will form distinct beads as illustrated in *Figure 1*.

When a droplet of a liquid resting on a surface has a contact angle of less than 90° then the liquid will wet the surface.

If the contact is greater than 90° then there will be no wetting. A contact angle of 0° results in both wetting and spontaneous spreading as illustrated in *Figure 2*.

In addition to wetting, surface penetration into the leather pores is also required. This is related to both wetting and viscous flow, the rate of penetration being related to the combination of surface tension, viscosity and contact angle.

The lower the viscosity of the finish and the more porous the leather, the quicker penetration occurs. However, capillary action is also dependent upon surface tension which affects both wetting and penetration. A balance therefore needs to be struck between surface tension, good wetting and good penetration.

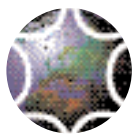
ADHESION

For one substance to adhere to another, good mutual wetting is necessary. So too is chemical reaction or attraction of functional groups in the coating onto the substrate. A good example is the way in which an isocyanate group will chemically react with a suitable coreactive hydroxyl or amino functionality.

Not only must the finish mixture wet the surface of the leather and penetrate the finish polymer that remains on the surface, as the water evaporates it must also be able to wet the substrate to ensure a secure bond.

A practical finishing system must be effective within a number of constraints:

- The finish must be water-based for environmental and legislative reasons.
- The use of cosolvents to aid the wetting process is permitted, but must be kept to a minimum of volatile organic compound emissions, otherwise the formulation will be invalidated.
- The use of surfactants is not permitted because these will destroy the waterproof properties of the crust leather.
- The finish must exhibit good all-round physical performance. ➤



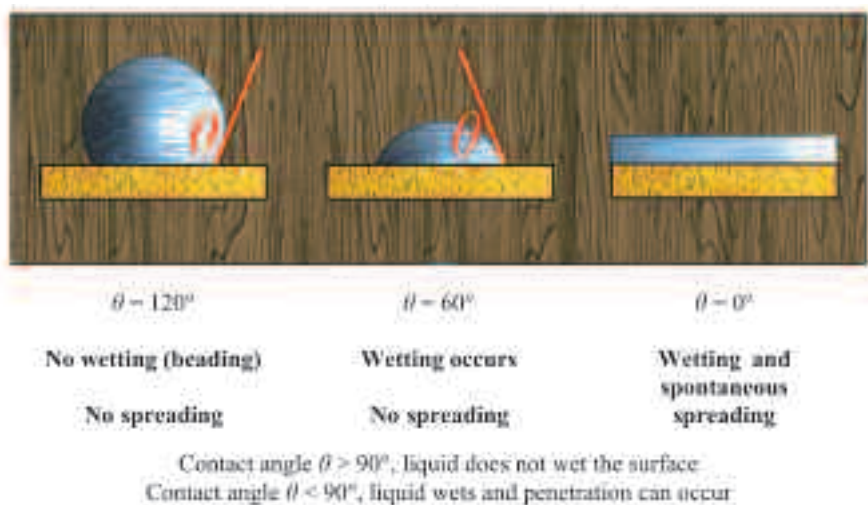
The key to finish performance

The first coat applied on any type of leather is critical to the success of a finish, and waterproof leathers are no exception. This initial coat (primer) bonds the rest of the finish system to the substrate and has a major influence not only on adhesion but also on other vital properties. These include flexibility, the ability to withstand scuffing and resistance to water penetration.

The finish must be specially formulated to perform appropriately on waterproof leather, but once this initial primer has been applied there is little difference between finishing conventional and waterproof leathers.

Adhesion is acknowledged to be the single most important attribute of any surface coating. Poor adhesion makes it virtually impossible to achieve a finish with a good balance of performance properties and, even more important, other properties become irrelevant. To achieve satisfactory adhesion to any leather is a challenge, but this is especially important when producing a finish for waterproof leather.

Figure 1: Wetting and contact angle



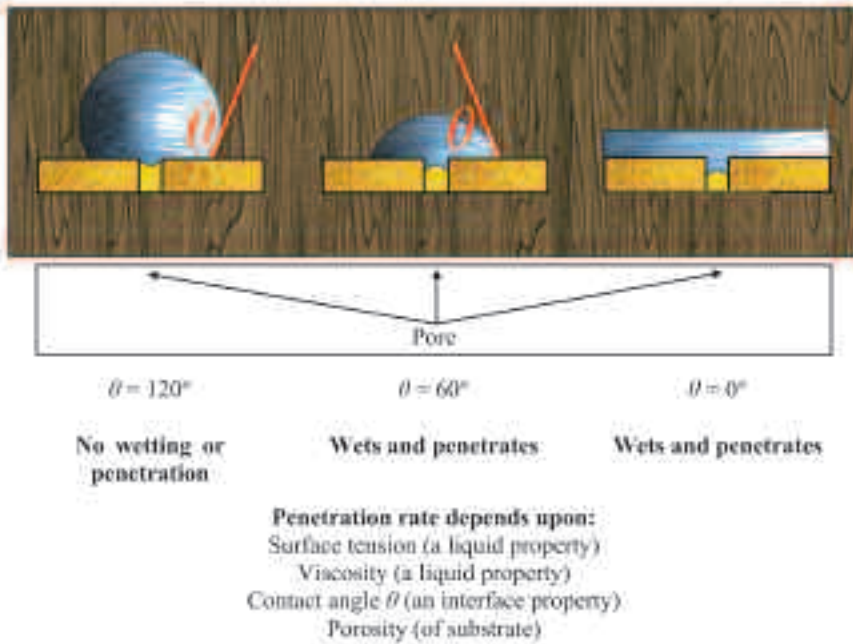
Fundamentals for finish adhesion

SURFACE WETTING

If a finish is to adhere well, it must be able to wet and penetrate the leather substrate. The use of certain solvents that act as adhesion promoters can therefore be beneficial. These tend to be



Figure 2: Penetration and penetration rate



very high boiling point products with an aggressive approach to assisting wetting and penetration, and have to be water miscible.

The method of applying the base coat and the way in which it dries can have either a positive or a negative impact on adhesion. Generally the application of wet coats ►

ADHESION-PROMOTING POLYMERS

As with conventional leathers, selected fine particle size polymers can be used to improve penetration and adhesion of base coats for application to waterproof leathers.

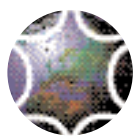
CROSSLINKING

Crosslinking does not generally improve adhesion. However, the use of a polyisocyanate crosslinking agent can yield benefits because it not only reacts with the polymer but also complexes with the -OH groups in the collagen fibre.

MAIN POLYMER SELECTION

Polymers that are selected as resin bonders in base coat formulations should possess a good balance of flex resistance and adhesion properties.

APPLICATION TECHNIQUE AND DRYING PROPERTIES

**Panel I****Performance evaluation****The Maeser test**

The Maeser dynamic water penetration resistance test (SATRA PM34) is the leather industry preferred method of evaluating performance as it represents the most accurate reproduction of the flexing action of uppers in wear. It is based on the American ASTM D2099 test.

The material under test is flexed with the outer surface in contact with water until penetration occurs. The flexing motion is designed to reproduce the action of the footwear upper during walking and involves flex, fatigue and pumping elements. This is a severe test for water penetration resistance and is believed to be more stringent and more informative about wear performance than tests which use a gentler flexing motion.

Because the test is severe, no sample pretreatment is recommended and leather is therefore normally tested "as received".

The Bally Penetrometer

The alternative test (SATRA PM171, BS 3144: Method 21, IUP 10) has been popular, particularly in Europe, for many years. It uses a more gentle flexing motion than the Maeser test and the adjustable degree of flexing is usually determined on the basis of leather stiffness. It is a useful test for ranking materials of low or medium water resistance.

As with the Maeser test, the sample of leather is flexed with the outer surface in contact with water until penetration occurs. Some versions of the test recommend that the grain surface of the leather should be lightly abraded before testing.

Whichever test is chosen, samples should be flexed in both

principal directions, in other words both parallel and perpendicular to the direction of the backbone.

Where no penetration occurs in the tests after 25,000 flexes (Maeser) or 500 minutes (Bally), the tests are continued up to 24 hours (equivalent to 150,000 Maeser flexes) to gauge more fully the water resistance of the leather. For footwear to be described as "waterproof" penetration must not occur until the later stages of this extended testing period, if at all.

Although routinely only the number of flexes to penetration is recorded, the mass of water absorbed by the leather under test can also be measured. For water absorption, SATRA has a guideline of no more than 30% by weight after 10,000 flexes or 200 minutes. Many users specify no more than 20% water uptake.

For specialist footwear such as golf shoes or hiking boots, leather is expected to reach at least the "very good" performance level. Leather that reaches the "moderate" level is considered to be suitable for everyday footwear where some degree of water resistance is expected.

Along with these specific tests, good all round performance including adhesion, flexes and rub fastness, are expected.

The Adhesive Peel test

This test (SATRA AM 16) may be used on both waterproof and heavily finished leathers such as patent, where the surface coating may possess greater film strength than the adhesive bond to the substrate. A tensile testing machine is used to measure the force required to continue peeling under wet and dry conditions. This property is very important for heavily finished waterproof leathers such as those used for white golf shoes.

that dry comparatively slowly generate improved adhesion. Thorough and vigorous padding in a multi-directional manner or alternatively by reverse roller coating seems to produce better adhesion than spray application of light coats.

OTHER SIGNIFICANT FACTORS

Adhesion may be the single most important factor in the success of base coats for waterproof leather, but it is not the only criterion. Minimising the use of hydrophilic materials in the base coat formulation is also essential.

Many additives that provide excellent benefits on conventional leather cannot be used on waterproof leather because they reduce the waterproof properties. Every component in a base coat formulation must be screened to ensure that the waterproof properties of the leather are not compromised in any way. Flow additives, levellers and penetrators must always be avoided because they may contain wetting agents based on surfactants. Also, many seemingly innocuous ingredients contain additives such as casein binders or waxes that may adversely affect water resistance.

Guideline formulations**ADHESION COAT**

Typically use a fine particle size resin, usually polyurethane based that has good adhesion properties. Dilute with water and combine with an aggressive, high boiling point solvent to facilitate wetting and penetration. Roller coater or hand padding

is the preferred means of application because the mechanical action helps overall adhesion. In general, avoid the use of light spray coats:

Polyurethane resin (fine particle size)	100 parts
Water	200 parts
High boiling point solvent	100 parts
<i>Apply using pad, roller coater or heavy spray</i>	

Apply an uncoloured sealer coat to allow the resin to perform its main function without having to carry pigments and other non-film forming particles. The correct formulation and application of the sealer coat is essential in order to establish a good bond between the leather surface and the subsequent finish coats. When this part of the system is well formulated then the whole finish is likely to work and perform as required.

BASE COAT

Use almost any typical available base coat products so long as they have been screened and tested beforehand to make sure they are appropriate and not detrimental to the performance of the crust leather:

Polyurethane or acrylic resin (fine particle size)	100 - 200 parts
Polyurethane or acrylic resin (general purpose)	100 parts
Colloidal filler	25 parts
Pigment	100 parts
Water	300 parts
High boiling point solvent	25 parts
<i>Apply using pad, roller coater or heavy spray</i>	



TOP COAT

A broad range of products can be used. Aqueous top coats are now preferred to the traditional solvent-based ones which commonly used products that contained high volatile organic compounds.

HANDLE AND FEEL MODIFIERS

These must be used sparingly and cautiously because these are typically based on oils, waxes, and silicones that contain significant levels of surfactant.

Key steps for finishing hydrophobic leathers

In order to maintain the waterproof properties of the crust and achieve adequate good all round physical performance of the finish, the following steps should be followed when finishing hydrophilic leathers:

- Screen all finishing products for suitability for use on waterproof leather by applying them individually onto crust leather and checking the Maeser or Bally performance against a control sample of unfinished crust.
- Use a clear (non-pigmented) primer coat formulated with fine particle size polyurethane or acrylic resins that adhere and bond effectively with the crust.
- Use a clear sealer coat that contains neither pigment nor colloidal filler to maximise the effectiveness of the resin.

- Use only an appropriate water miscible solvent to assist the flow, wetting and penetration of the primer coat. Avoid incorporating the same solvent into the base coat and, because of the high boiling point and long evaporation time involved, keep the amount of solvent to a minimum.
- Apply the first base coat and the primer coat by padding or roller coating, as this is preferable to an all-spray finish.
- Adhesion of the sealer coat and overall finish performance may be enhanced by the inclusion of an isocyanate crosslinker.
- Use good quality, high performance products throughout the finish to ensure acceptable physical properties are achieved.
- Avoid the use of surfactants and other wetting agents, and be careful to avoid contamination of the formulation.
- Where possible, use only light finishes to avoid generation of higher film strength compared to its adhesive bond.

Given that the wet end waterproofing treatment remains constant, and provided the products and procedures selected for the finishing operations are well-controlled with sufficient critical check points established, the coating of the waterproof crust material should be relatively trouble-free. Care should be taken, however, when more than one wet end waterproofing treatment is used because a difference in the surface rheology is known to influence the choice of finishing products and the applications employed. 