



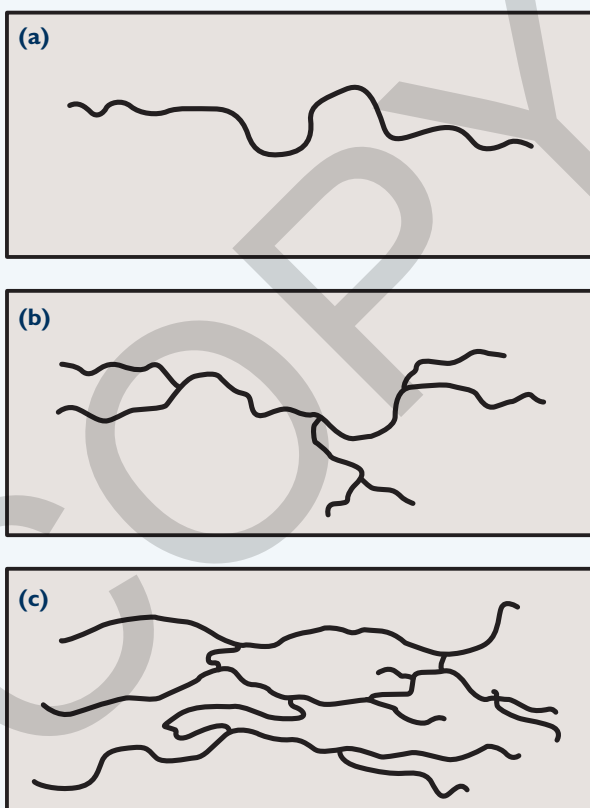
Adhesion and leather finishing

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Over and above the choice of binders, pigments and other finishing auxiliaries, the integrity of the finish is highly dependent upon the adhesion of the finish to the substrate, the coalescence of each finishing application within that film, and the inter-coat adhesion. Various mechanisms are involved in creating good adhesion at these critical stages, and these are described in detail in the following paper.

Panel 1: Polymers

Polymers are large macromolecules (e.g., chains) composed of monomers (repeating units) connected by covalent chemical bonds. The physical properties of a polymer depend on its size and the number and strength of the intra- and inter-molecular forces of attraction between the monomers.

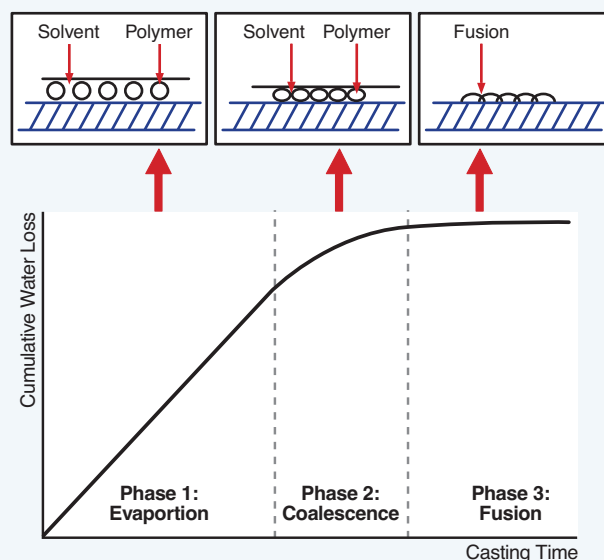


Polymer chains showing examples of:
a) linear structure (thermoplastic)
b) branched structure (thermoplastic polymer)
c) network structure (thermoset polymer)

Finishing is the final stage of leather manufacture where the crust leather is usually coated with a mixture of resins, pigments, and other auxiliaries. The function of the coating depends on the requirements for the end-use of the leather, be it shoe upper, upholstery or garment leather. Essentially, the finish protects the leather but may also be used to obtain a uniform colour, a glossy or matt appearance, waterproofing/water resistance, improved physical properties (e.g. *rub fastness*), the desired handle/touch, to hide defects (*upgrading*) and fashion effects/prints, etc.

Conventional leather finishes usually comprise from two to five application coats, each with a slightly different goal or function. Some applications may be designed to penetrate quite deeply into the grain fibre network to tighten the grain (e.g. impregnation coat) or create a specific finish effect (e.g. *oil pull-up* and other surface effects).

Panel 2: Three - phases of water loss from a polymer on drying





An interesting aspect of a conventional finishing operation that is frequently overlooked is that only one layer is required to adhere to the leather surface (*e.g. grounding coat, adhesion coat or base coat*). The other finish coats (*e.g. colour coat, season coat, top coat, etc.*) need to adhere to the underlying finish coat. The adhesion of each coat as an integral component to one another and to the leather is of vital importance to the leather manufacturer and, ultimately, their customers.

The majority of finishes are composed, primarily, of pigments and/or inert auxiliaries "trapped" within the resin coating and bound to the leather/polymer surface by the resins. Finishing resins are predominantly polyacrylic/acrylate and polyurethane polymers, but may include polybutadienes, nitrocelluloses (*cellulose nitrate*) or cellulose acetate butyrates (*CAB*), among others.

Film Formation

Finishing chemicals used in the leather industry are commonly applied as aqueous polymer dispersions. The finish coating/film forms as drying occurs and *because they are thermoplastic* may be completed and levelled by hot plating (*see Panel 5*).

After the aqueous based polymers are applied, film formation starts as indicated in *Panel 2*:

Drying Phase 1 - Evaporation: Water evaporates from the surface only, and the drying rate remains constant.

Drying Phase 2 - Coalescence: The rate of evaporation slows as some areas of the surface are no longer wet and moisture has to diffuse from within to the surface before evaporation may occur. This water loss from within the water-polymer mixture results in a reduction in volume and when contact between the polymer droplets occurs they begin to diffuse into one another and coalesce.

Drying Phase 3 - Fusion: There is no more water on the surface and the rate of evaporation slows further. Water reaches the surface by diffusing through the polymer or via interparticle channels before evaporating. The deformed polymer particles become homogeneous and the film achieves its mechanical properties.

Coalescence and fusion are important for the formation of a continuous film, i.e., the adhesion of the polymer to itself in a

horizontal direction (*autohesion*). Some stabilisers and surfactants may interfere with this process (*e.g., poor water resistance properties of aqueous polyurethane resins*), along with high drying temperatures and incorrect viscosities. Any additive that does not form a film will decrease the finishing resins ability to form film and adhesion properties. This in turn will decrease the physical integrity of the film or coat within a finish. This is why a resin:additive ratio of 2:1 or 3:1 is usually recommended.

A chain is often considered to be as strong as its weakest link and this also applies to leather finishes. Any area where the finish is not continuous will be a weak point where testing failures are more likely to occur.

The overall integrity of a leather finish is completely dependent on adhesion between and within each finish layer.

Adhesion of finish

There are four main classes of adhesion:

1. MECHANICAL ADHESION (BONDING)

This type of adhesion involves the physical interlocking of different materials, *e.g.*, stitching and Velcro. Leather finishing usually involves the application of a liquid borne polymer which is applied to the solid leather.

In order to achieve good mechanical adhesion the finish must wet the surface and be able to flow, or be drawn into the leather by capillary action. An increase or improvement in wetting will increase the contact surface area between coating (*finish*) and substrate (*leather*) and will also increase the opportunity for mechanical adhesion by "locking" the applied coat to the leather as indicated in *Panel 3*.

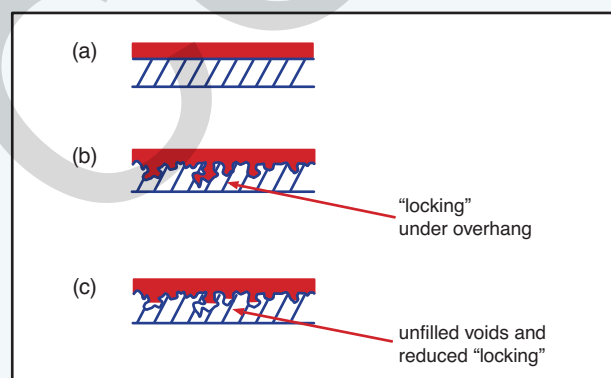
Another way to increase the contact surface area between the finish and leather, and improve adhesion, is to snuff/buff the grain. This process simply increases the total surface area of the leather and creates additional sites for mechanical adhesion. Wetting is equally important for adhesion under these circumstances (*see Panel 4*).

The degree of wetting is affected by the surface tension of the liquid-solid and gas-liquid interfaces and hence the contact angle.

2. CHEMICAL ADHESION (BONDING)

This type of adhesion [*Legend 1*] involves the formation of

Panel 3: Mechanical adhesion due to wetting



Indications of mechanical adhesion

(a) Smooth surface	(b) Rough surface	(c) Rough surface
• Small surface area • Adhesion limited to chemical interactions	• Large surface area • Good wetting • Good penetration • Good surface contact area • Good mechanical "locking" • Good adhesion	• Large surface area • Moderate wetting • Poor penetration • Poor surface contact area • Poor mechanical "locking" • Poor adhesion





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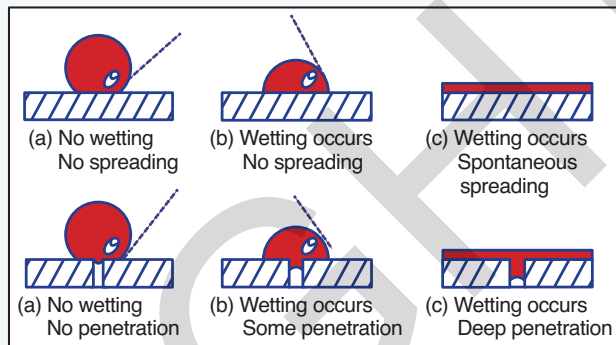


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Panel 4a:

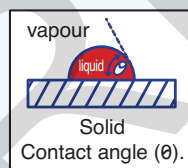
Wetting

When a liquid is in contact with a solid surface, wetting refers to the ability of the two phases to interact at the interface. The ability to interact is described by the contact angle. A contact angle of below 90° characterises a surface that is "wetting" and contact angles of 90° or greater as "non wettable". Liquid/solid interfaces which result in small contact angles tend to have large surface contact areas and vice versa for large contact angles.



Panel 4b:

Contact Angle



The angle at which a liquid/gas interface meets a solid surface is usually measured from inside the liquid.

Small contact angles result when interactions between the solid and liquid phases are favourable, e.g., if a surface is hydrophilic, water will produce a low contact angle, the surface will wet and the water may penetrate into the surface. A hydrophobic surface will produce a large contact angle when water is applied and will bead on the surface and will not wet.

A contact angle is fixed for a specific system and changes to the liquid or solid surface result in a new system. If the solid surface is kept constant, the contact angle can be changed by altering the surface tension of the liquid interacting with it.

Panel 4c:

Surface Tension²

Surface tension is important in the understanding of the physical and chemical behaviour of liquids. It is a result of the attraction between particles within a liquid. This attraction produces a layer of slightly more densely packed particles on the surface of a liquid which resembles an elastic sheet. Surface tension without interference will attempt to shape a liquid drop into a sphere, which has the smallest volume to surface area ratio possible. The introduction of a solid surface and gravity results in the tell-tale shapes we associate with water drops, and an increased volume to surface area ratio, relative to the degree of wetting and surface tension.

Item 4c⁽²⁾

Surface tensions of selected liquids.

Surface	Surface Tension (20°C) mN/m
mercury	425.4
water	72.8
glycerol	64.0
toluene	28.4
acetone	25.2
MEK	24.6
IPA	23.0
ethanol	22.1

Generally, surface tension decreases with increasing temperature. Alcohols (e.g., isopropyl alcohol - IPA, oxitol) and other organic molecules which are miscible with water (e.g., methyl ethyl ketone - MEK, acetone) help to lower surface tension of water, as do surfactants. This, in turn, would lower the contact angle, improve wetting, and promote adhesion. Inorganic salts can increase the surface tension of water.



chemical bonds between the applied coat and the layers below it, and the relative strength of the adhesion is dependent on the type/s and number of chemical bonds. The number of chemical bonds depends on the surface, liquid/polymer and the surface contact area (*also see section: mechanical adhesion (bonding)*). Chemical adhesion is not considered to be the major factor in the adhesion of leather finishes but does make some contribution to it.

Chemical bonding may be more conveniently separated into two classes representing:

Intermolecular forces of attraction: These include dispersion forces, dipole forces and hydrogen bonds.

- Dispersion forces are generally very weak forces and depend on the size, shape and polarity of molecules. They may be classified as non-polar bonds, as indicated in *Panel 6*.
- Dipole forces are slightly stronger and occur between molecules and chemical bonds, that have a permanent charge polarity.
- Hydrogen bonds are a particularly strong form of dipole force and generally the strongest example of an intermolecular force (*this accounts for the unexpectedly high boiling points for water and ammonia*).

These forces are often collectively referred to as secondary forces of attraction and are generally thought of as weak chemical bonds but, however, with shear numbers they can produce significantly strong interactions.

Panel 5: Polymers: the effect of heat

Thermoplastic polymers: These polymers may become soft when heated, they can melt and be remoulded.

Thermoset polymers: These polymers may become softer when heated but cannot melt or be remoulded. They tend to char and burn when heated sufficiently.

Once a thermoset polymer has been aged and cured it tends to show improved physical properties.

Panel 6: Examples/Representations of adhesion bonds

Dispersion Forces	Dipole Force	Hydrogen Bonding	Covalent Bond	Ionic Bond
"Non polar bonds"				
Very Weak	Weak	Weak/moderate	Strong	Strong



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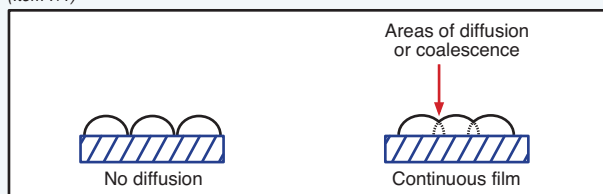
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**Panel 7:****Diffusion**

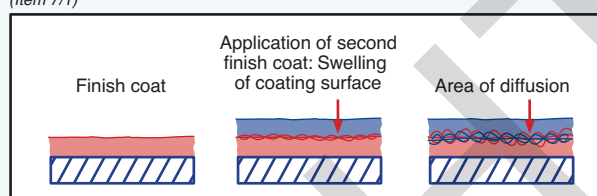
A natural process which describes how substances mix with one another. Fluids (liquids and gases) tend to move from an area of high concentration to an area of low concentration.

Example of autohesion diffusion

(Item 7/1)

**Example of intercoat diffusion**

(Item 7/1)



Discrete chemical bonds: These include covalent and ionic bonds.

- Covalent bonds are strong, formal chemical bonds between reactive sites (*functional groups*) and may exist between and within finish layers. Generally, covalent bonds contribute to adhesion but seldom play the major role. Covalent bonds are directly associated with crosslinking, and correctly selected crosslinking agents may be used to form covalent bridges between polymer chains, and possibly with the leather too. Crosslinking may contribute to the adhesion of finishing coats to one another and the leather, if sufficient wetting and diffusion have taken place prior to crosslinking. What crosslinking generally achieves is the conversion of thermoplastic linear and branched polymer chains to networked thermoset polymers with improved physical and waterproofing properties (see Panel 1 and 5). Crosslinking helps to seal the finish and if allowed to cure prior to the addition of following coats, may significantly hinder adhesion.
- Ionic bonding also contributes to adhesion and is a chemical electrostatic bond between a positively charged chemical site (*cation*) and a negatively charged chemical site (*anion*). This is similar in action but must not be confused with electrostatic adhesion.

Cationic finishing has been reintroduced relatively recently, and the cationic chemicals bind to the slightly anionic leather to produce an ionic bond. This difference in charge limits the penetration of the cationic chemicals into the leather and produces lighter finishes with good coverage and reduced chemical usage. The limited penetration, however, means that cationic finishes often suffer from poor adhesion and rub fastness properties.

3. ELECTROSTATIC ADHESION

This type of adhesion involves a physical attraction between two objects with a difference in electrical charge. An area which is rich in electrons will be negatively charged and an area which is electron deficient will be positively charged. Opposites attract and an electrostatic bond is formed. This type of bonding is usually restricted to electrically conductive materials, e.g., metals, etc and is not currently relevant to leather finishing.

4. DIFFUSIVE ADHESION

When two substances meet they may diffuse into one another if they are fluid (e.g., *liquid*) and are compatible, (i.e., *they are soluble with one another*) as indicated in Panel 7. Effectively, this combines/joins and therefore adheres substances together when they are dried as if they were one. This is particularly relevant to long chained particles, e.g., polymers/resins, in autohesion and film formation (*coalescence and fusion*).

If drying is performed at too high a temperature, the finish mixture is too viscous and/or the coat sprayed is too light, autohesion is compromised as there is no opportunity for diffusion and the formation of a continuous film. Diffusive autohesion may be further hindered by the presence of surfactants in aqueous finishing chemicals, particularly in polyurethanes.

The major factors in the adhesion of leather finishes are definitely mechanical and diffusive adhesion, and surface contact area. These factors are in turn are directly dependent on:

- The shape of the leather surface - a rough surface has a greater surface area and more opportunity for "locking".
- The wettability of the leather surface - this is subject to the contact angle and surface tension which, in turn affect the surface contact area, mechanical "locking" and diffusion.

Acknowledgements

(1) <http://www.initium.demon.co.uk/filmform.htm>

(2) <http://www.surface-tension.de>

Legend:

(1) Chemical adhesion operates in the same manner as chemical bonding and may be directly applied to tanning, retanning, dyeing and fatliquoring chemicals. Chrome tanning: starts as ionic attraction and then forms coordinate covalent bonds with carboxylate groups on collagen. Glutaraldehyde: forms covalent bonds with amino groups of collagen. Vegetable tannins: forms a vast array of intermolecular forces dominated by hydrogen bonds with peptide, carboxyl and amino groups on collagen. Some vegetable tannins may also form ionic and covalent bonds with collagen. Syntans, dyes, fatliquors: anionic syntans, dyes and fatliquor surfactants are attracted and initially bond to cationic sites on collagen. This is followed by a vast array of intermolecular forces after water is removed within first-time drying.