How to solve some of the problems that may occur when using adhesives and glues in the production of leather products

In the production of many leather goods, some auxiliary products that are widely used are adhesives – the glues.

According to the UNI EN 923 standard, the adhesive is a non-metallic substance capable of joining the same or different materials by surface fixing in such a way that the bond obtained is equipped with adequate internal strength. Surface fixation is called adhesion while the strength of the bond is called cohesion.

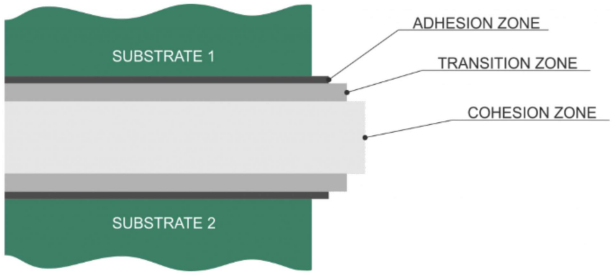
Sometimes it may happen that the use of these auxiliaries creates problems in the processed materials, especially with leathers. We will see how and why this can happen and how to avoid it.

Adhesion areas and adhesion theory

First of all we have to explain the tail happens when two or more materials are glued together. This part will be a bit long, so I ask you to be patient.

When bonding two materials (called substrates in technical jargon) with an adhesive it is necessary that the joint that is created has good technological resistance. In order for this to happen, a fundamental requirement that must be met is that an intimate contact is established between the substrates and the adhesive. The latter must therefore be able to distribute itself on the solid surface of the substrate. Using different words, let's say that the surface of the substrate must be wettable by the adhesive you have chosen to use. Now, in a junction of two or more substrates (also called adhesions), we distinguish three different zones:

- the adhesion area;
- the transition zone;
- the cohesion zone.



The adhesion areas are those areas that correspond to the points of intimate contact between the adhesive and the surface of the substrates. In this area, the adhesives bond with the substrates. The phenomenon of adhesion is due to the molecular interactions between substrate surfaces and adhesives. These interactions can be intermolecular interactions (which are weaker) and chemical bonds (which are stronger).

The transition areas are the areas in which one passes from the adhesion areas to the cohesion areas and, as the name implies, the properties of the adhesive are altered and are not very clear.

The cohesion areas are those areas that consist only of adhesive, which has an action that we can define as filling. In these areas the adhesives have the nominal properties that are reported in their technical data sheets because, here, the adhesives harden as they are, without their molecules having interactions with those of the substrates. The technological properties of these areas depend on the molecular forces that we call cohesion forces.

We can therefore understand how, when designing adhesives, it is necessary to consider all aspects concerning the three areas of adhesion.

Now let's focus on the true and priority adhesion area and let's see how the adhesion between adhesives and substrates occurs.

The first step is the creation of an intimate molecular contact between the two species, which must possess compatibility requirements.

Once this is done, the next step is to generate the adhesive forces between adhesives and substrates, according to what is called the adsorption adhesion mechanism. According to this theory, the cause of adhesion is the appearance of this type of forces which are responsible for both the true and prior adhesion and its technological characteristics. In fact, the mechanisms that have been proposed to explain membership are different and it seems they are all synergistic:

- mechanical
- interconnection;
- diffusion theory;
- electronic theory;
- the theory of adsorption;
- the theory of tacking.

The mechanism of adhesion by adsorption tells us that the materials adhere by virtue of the interatomic and intermolecular forces that are established between the atoms of the adhesives and substrates, the most common of which are those of Van der Waals and hydrogen bonds. In addition to them, chemical bonds can also be established through the interface that are defined as primary (such as covalent, ionic or metallic bonds), intermediate (donor-recipient interactions) and secondary depending on their relative strength.

As for the adhesion by adsorption, the materials adhere by virtue of the interatomic and intermolecular forces that are established between the atoms of the adhesive and the substrates. The most common forces are van der Waals forces and hydrogen bonds. In addition to them, chemical bonds can also be established through the interface. These bonds are called secondary bonds.

The formation of ionic, covalent and metallic interfacial bonds is also possible; which are called primary bonds.

The terms primary bonds and secondary bonds must be considered in a sense as the measure (although sometimes arbitrary) of the relative strength of the bonds.

As a final clarification, some believe that donor-recipient interactions can occur through the interface, the resistance of which is intermediate between that of primary and secondary bonds.

Different types of bonding

Gluing are not all the same and there are three main types:

- adhesive bonding;
- sealing;
- elastic bonding.

Adhesive bonding is a process in which two materials, the same or different, are assembled in a solid and permanent way by means of adhesive substances, which bridge the surfaces or substrates to be joined. This results in a high uniformity in the distribution of stress over the entire joint surface which has a very positive effect on the static and dynamic forces that can be achieved. The adhesive joint achieves uniform distribution and absorption of pressure loads.

In sealing, sealing substances are used to block the passage of fluids through the surfaces of the joints or through the openings of the materials, creating real mechanical seals of the parts. These are not actual adhesives but many of them have adhesive qualities and are called adhesive sealants or structural sealants. The main difference between adhesives and sealants is that sealants generally have lower mechanical strengths, but higher elongation capabilities. Since the main objective of a sealant is to seal similar or different substrates, they must have sufficient adhesion to the substrates and good resistance to the environmental conditions in which sealing is required.

In elastic bonding, adhesives are used that are able to combine the advantages of sealing and bonding in a single operation. Elastic adhesives are mainly preferred for their ability to absorb and / or compensate for dynamic stresses in an elastic way and offer the possibility of transmitting loads. Many elastic adhesives have a high cohesive strength and a relatively high modulus of elasticity which allows them to create strong joints that have elastic properties at the same time.

Adhesives used in the production of footwear and leather goods

There are many methods of classifying adhesives. The method we have preferred to use concerns the polymerization-hardening mechanism of the polymers they are made of, or if the bonding occurs through a physical mechanism or through a chemical mechanism:

ADESIVI CHE INDURISCONO PER PROCESSO FISICO	ADESIVI CHE INDURISCONO PER PROCESSO CHIMICO		
	ADESIVI A POLIMERIZZAZIONE (RADICALICA, ANIONICA, CATIONICA)	ADESIVI A POLICONDENSAZIONE	ADESIVI A POLIADDIZIONE
Adesivi termofusibili	Cianoacrilati	Resine fenoliche	Resine epossidiche
Adesivi a solvente	Metilmetacrilati (MMA)	Siliconi	Poliuretani
Adesivi a contatto	Poliesteri insaturi	Poliammidi	
Adesivi in dispersione acquosa	Adesivi anaerobici	Bismalenimmidi	
Adesivi per l'acqua	Adesivi che polimerizzano per effetto di radiazioni	Polimeri MS	
Autoadesivi			
Plastisol			

The adhesives that harden through a physical process are those that, at the time of application, are already in the final chemical state. There is no crosslinking. This category

includes those polymers that can be reduced to the fluid state, that is thermoplastic resins that can melt or soluble or emulsifiable thermoplastic resins.

The adhesives that harden by chemical process are the so-called reactive adhesives and are divided into three categories according to the type of reaction they produce:

- Polymerization adhesives (radical, anionic, cationic);
- Polycondensation adhesives;
- Polyaddition adhesives.

These are the adhesives that are used in the production of products that use leathers and other similar materials, so now we are going to see specifically what it is.

The adhesives used in shoe factories and leather goods are still today, in most cases, made up of a solution of polymers in organic solvents, although other less toxic adhesives, such as hot-melt or water-based ones, have become increasingly popular. Organic solvent adhesives consist of a solid phase and a liquid phase. The most widely used are those based on natural rubber, neoprene and polyurethane adhesives, the use of which has become increasingly widespread in the last twenty years. Neoprene and polyurethane adhesives can also be used as two-component adhesives, ie by adding a certain amount of activator (which is usually a polyisocyanate) at the time of use, which activates its adhesive properties. The hot melt adhesives do not contain solvents and have the property of liquefying with heat to re-solidify with cooling, creating the junction of the parts to be glued. The use of these hot melt adhesives is spreading, implying a desirable improvement from the preventive point of view. As regards the additives of the basic substance, the plasticizers are mainly mentioned, among which the best known is tri-ortho-cresyl phosphate. Other additives are used such as terpene, phenolic resins, metal oxides (Mg, Zn), inert mineral fillers (amorphous silica), and others. Additives and thinners for glue are added up to the proportion of 5% of the weight of the glue to “stretch” the adhesive that is too dense. Solvents are also added, whose function is to allow the uniform distribution of the adhesive resin and, therefore, to evaporate to allow perfect adhesion between the parts to be glued. The choice of high volatility solvents allows you to speed up the gluing phases, but must be done very carefully to allow operators to apply the product.

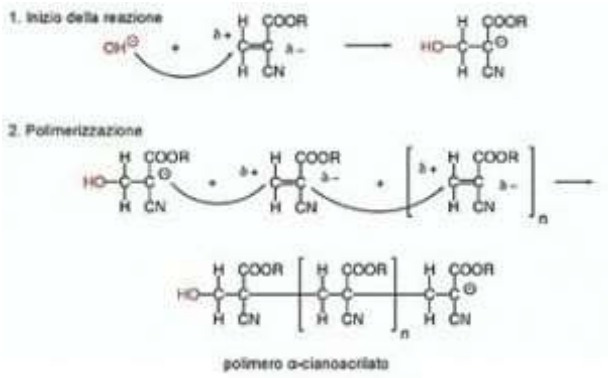
In recent years, efforts have been made to reduce the use of solvent adhesives in favor of adhesives in aqueous solution. These adhesives, like adhesives in organic solvent, are made up of the solution of certain substances (polymers and elastomers) in a solvent liquid, with the possible addition of appropriate additives but the technological advantage of their use is represented by the possibility of maintaining a high level of percentage of the solid component with respect to the volatile part, contrary to solvent-based adhesives (respectively 40% versus 20%). The formulation of water-based products allows to obtain both liquid and pasty compounds, according to their intended use (application by brush, spray or spreaders).

Problems that occur when using the adhesives

When working with hides and skins, problems may occur that are due to the aggression of the materials by the adhesives. Very often shoe factories, interior designers and leather workers point the finger at the tanneries, stating that the materials they deliver are of poor quality. With this article I would like to explain to you why, very often, this is not the case and to help you solve problems of this type.

Some very nasty problems can occur after laminating leathers and leathers with linings or synthetic materials. The skin wrinkles and an ugly effect appears to be seen, especially

because the couplings are performed on rigid products that often have a smooth look. This problem occurs when the so-called super glues are used, which are cyanoacrylates whose main characteristic is to give rise to very strong bonds within a few seconds. Chemically they are single-component adhesives that have a special chemical structure, in which the nitrile and ester groups exert a strong electrophilic effect which favors the attack by nucleophilic substances, such as hydroxyls, and stabilizes the resulting carbanion. The hydroxyl ions obtained from the dissociation of water can attack and trigger an anionic polymerization reaction that leads to rapid hardening:



The polymerization of this type of adhesives is triggered by absorbing the humidity of the environment, if this is between values of about 50% and 70%, or, otherwise, by absorbing the moisture contained in the surface of the substrate. Hides and leather are natural materials and, as such, are characterized by moisture contents that depend on the humidity of the environments in which they are immersed. When these types of materials are glued, the adhesive will draw the moisture necessary for its polymerization from the environment or from the material. In the case of lamination, the moisture will inevitably be recalled by the hides and, when the action of the adhesive is sudden, the removal of moisture is just as sudden. This is the reason why hides and skins can cause wrinkling or even detachment problems.

To solve this problem, it may be useful to cut the quadrants of the skins you need and spray a light amount of water on the flesh side of the skins, leaving them for one or two hours to rest with the flesh sides in contact and covered with a nylon. This surplus of water will be used by the adhesive for polymerization. In addition, I also recommend that you try using different adhesives, most likely this advice alone will help you solve the problem.

A second problem concerns the use of solvent-based adhesives, in all types of leathers and skins but especially in those intended for particular productions. The greasing substances are used to soften the leathers. There are many different types of greasers and their main mechanisms of action are two: the establishment of a chemical bond with the skins and the physical deposit on the fibers. The physical deposit is the fattening mechanism that allows us to have greater softness and flexibility because it increases the reciprocal smoothness of the fibers, increasing all their technological properties. Fatliquors that bind with chemical bond to the skin do not have a high softening power, but become non-extractable fatliquors by means of solvents. This type of fatliquors is used in the production of particular items, such as water-repellent leathers. If we use solvent adhesives on leathers that have not been prepared to be used together with this type of adhesives, we risk that the solvent present in the adhesive will migrate part of the fatliquor deposited on the fibers, making the distribution of the softener uneven and making it dry. leather areas. Furthermore, we must also remember that the hardening times of solvent-based adhesives are much higher than those of water-based

adhesives. Personally, I always recommend that you inform the tanneries if you prefer to use adhesives of this type, so that they are equipped to use non-removable greasing substances.

If the article was useful to you or if you need my help, feel free to leave a comment!

Daniele Pistorio