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PROBLEMS ARISING FROM THE USE OF ADHESIVES AND GLUES DURING THE PRODUCTION OF LEATHER ARTICLES AND POSSIBLE SOLUTIONS

In the production of leather goods, some widely used auxiliaries are adhesive substances (glues).

The UNI EN 923 standard defines an adhesive as

a non-metallic substance capable of joining equal or different materials by surface bonding in such a way that the resulting bond has adequate internal strength.

Surface bonding is called ADHESION while bond strength is called COHESION. It can sometimes happen that the use of these auxiliaries creates problems in the processed materials, and this can happen when the materials are skins. We will see how and why this happens and how to avoid it.

Adhesion zones and adhesion theory

First of all, we have to explain what happens when you glue two or more materials together. This part will be a little long, so I ask for your patience.

The materials that are glued together are called SUBSTRATES. When two or more substrates are bonded by means of an adhesive, the joint that is created must possess good technological strength. For this to happen, a requirement to be met is that intimate contact is created between the substrates and the adhesive. The latter must therefore be able to distribute itself over the solid surface of each substrate. In other words, the substrate surface must be wettable by the adhesive in use. Now, in a joint of two or more substrates, we distinguish three different zones:

1. Adhesion zone;
2. Transition zone;
3. Cohesion Zone.

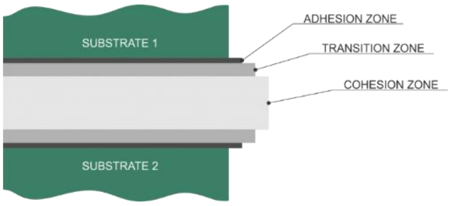

FIG. 1: EXAMPLE OF A JOINT

ADHESION ZONES correspond to the points of intimate contact between adhesive and substrate surfaces. In these zones, adhesives create bonds with the substrates and the phenomenon of adhesion is due to the molecular interactions that occur between the surfaces of these two substances. These interactions can be intermolecular interactions (weaker) and chemical bonds (stronger).

TRANSITION ZONES are the zones where there is a transition from adhesion to cohesion zones. In these zones, the properties of the adhesive are altered and unclear.

COHESION ZONES consist only of adhesive, which has a filling action. In these zones, the adhesives possess the nominal properties that are listed in their data sheets because, here, the adhesives harden as is, without their molecules having any interaction with those of the substrates. The technological properties of these areas depend on the molecular forces at play, which are the cohesion forces.

We can therefore understand how, when designing adhesives, it is necessary to consider all aspects concerning the three zones that will make up the joint.

Let's focus on the actual bonding zone and see what mechanisms are involved.

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

The next step is the generation of adhesive forces between adhesives and substrates, according to what is called the ADHESION MECHANISM BY ADSORPTION. According to this theory, the cause of adhesion is the appearance of these forces, which are responsible for both true and prior adhesion and its technological characteristics. In fact, the mechanisms that have been proposed to explain adhesion are diverse and all appear to be synergetic:

- Mechanical interconnection;
- Diffusion theory;
- Electronic theory;
- Adsorption theory;
- Tacking theory.

The adsorption adhesion mechanism says that 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 Van der Waals and hydrogen bonds. In addition to these, chemical bonds can also be established across the interface, which are termed primary (such as covalent, ionic or metallic bonds), intermediate (donor-recipient interactions) and secondary bonds depending on their relative strength.

The terms primary bonds and secondary bonds should be considered in a sense as a measure of their strength, although the distinction is arbitrary because the overall strength attributable to an interaction also depends on the number of interactions present.

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

Types of gluing

Three main types of bonding can be distinguished:

- Adhesive bonding;
- Sealing;
- Elastic bonding.

ADHESIVE GLUING is a process in which two materials, equal or different, are solidly and permanently assembled by means of adhesive substances, which bridge the surfaces or substrates to be joined. A high uniformity of stress distribution over the entire joined surface is achieved, which has a very positive effect on the static and dynamic forces that can be achieved. The adhesive joint achieves a uniform distribution and absorption of pressure loads.

In SEALING, sealing substances are used to block the passage of fluids across joint surfaces or through material openings, creating true mechanical seals of the parts. They are not true 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 purpose 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 the sealing is required.

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

Adhesives used in the production of leather goods

There are many methods for classifying adhesives. The method we have preferred to use concerns the polymerisation-curing mechanism of the polymers of which they are made, i.e. whether bonding occurs through a physical mechanism or through a chemical mechanism.

Adhesives that cure through a physical process are those that are already in their final chemical state at the time of application. There is no cross-linking. This category includes those polymers that can be reduced to a fluid state, i.e. thermoplastic resins that can melt or thermoplastic resins that are soluble or emulsifiable.

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

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

It is precisely these adhesives that are used in the manufacture of artefacts using leather and other similar materials, so we will now look specifically at what they are.

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			

FIG. 2: TYPES OF ADHESIVE FOR LEATHER PRODUCTS

Adhesives used in shoe and leather goods manufacturers are still, in most cases, made up of a solution of polymers in organic solvents or water, although the most common are hot-melt or water-based adhesives. 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 over the last two decades. Neoprene and polyurethane adhesives can also be used as two-component adhesives, i.e. by adding a certain amount of activator (which is usually a poly-isocyanate) at the time of use, which activates their adhesive properties.

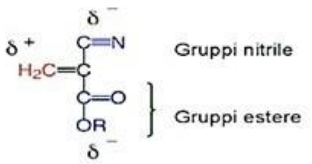

FIG. 3

Hot melt adhesives do not contain solvents and have the property of liquefying with heat and re-solidifying with cooling, creating the joint of the parts to be bonded. The use of these hot-melt products is becoming more widespread, implying a desirable improvement from a preventive point of view. As far as additives to the base substance are concerned, plasticisers, such as tri-ortho-cresylphosphate, are mainly mentioned. Other additives are used such as terpenic and phenolic resins, metal oxides (Mg, Zn), inert mineral fillers (amorphous silica), and others. Additives and glue thinners are added up to a proportion of 5% of the weight of the adhesive to 'stretch' the excessively dense adhesive. Solvents are also added, whose function is to allow the adhesive resin to be evenly distributed and then evaporate to allow perfect adhesion between the parts to be bonded. The choice of highly volatile solvents allows the bonding phases to be accelerated, but must be done very carefully to allow the operators to apply the product.

In recent years, efforts have been made to reduce the use of solvent adhesives in favour of those in aqueous solution. The technological advantage of their use is due to the possibility of maintaining a high percentage of the solid component in relation to the volatile part, in contrast to solvent-based adhesives (40% versus 20% respectively). The formulation of water-based products allows both liquid and pasty compounds to be obtained, depending on their intended use (brush, spray or spreader application).

Problems occurring when using adhesives

When working with leather and hides, it can happen that these materials are attacked by the adhesives used. Very often, shoe manufacturers, decorators and leather goods manufacturers point the finger at the tanneries, claiming that the materials they deliver are of poor quality, but I would like to explain to you that this is not the case and help you solve this type of problem.

Unpleasant situations can occur after laminating leather with linings or synthetic materials. The leather wrinkles and an unsightly orange-peel effect appears, especially when the materials are intended for the production of rigid products that must have a smooth look. This problem occurs when using so-called superglues, which are cyanoacrylate adhesives whose main characteristic is that they form very strong bonds in a matter of 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 that favours the attack by nucleophilic substances, such as hydroxyls, and stabilises the resulting carbanion.

The hydroxyl ions often originate from the dissociation of water, can perform the attack and trigger the anionic polymerisation reaction that leads to curing:

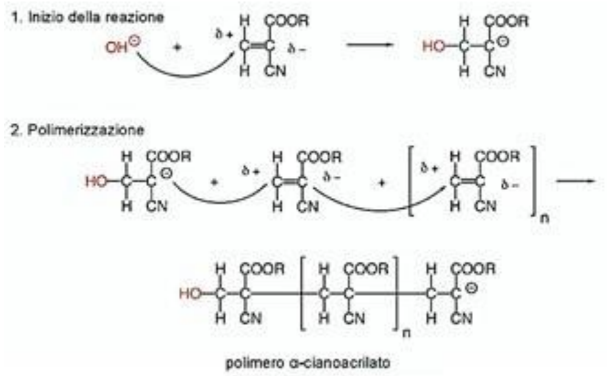

FIG. 4: CYANOACRYLATE BONDING MECHANISM

The polymerisation of this type of adhesives is triggered by absorbing the humidity of the environment, if this is between approximately 50% and 70%, or, if this is not the case, by absorbing the humidity contained in the surface of the substrate we are gluing. Leather and hides are natural materials which, as such, are characterised by dynamic moisture content, i.e. which can vary depending on the situations and environments in which they are found.

When these materials are glued, the adhesive will draw the moisture required for curing from both the environment and the materials being glued. When the environment is not accessible, the necessary moisture will be withdrawn from the leather. If the action of the adhesive is abrupt, the subtraction of moisture is also abrupt, and this creates strong imbalances in the internal humidity of the leather. In such a situation, it is very easy for Type I moisture, i.e. structural water, to be subtracted from the leather.

The reaction is so sudden that Type I and Type II Moisture do not have time to bring themselves back into equilibrium, resulting in severe local stress and an attack on the protein structure (secondary and tertiary structure) of the skins' protein. This is why hides and skins can give problems of wrinkling or even discolouration.

To solve this problem, it may be useful to cut the quadrants of skins you need, spray a light amount of water on the flesh side and leave them to stand for several hours, covered with nylon and with the flesh sides in contact. This slight surplus of moisture will be absorbed by the adhesive during curing. I also recommend trying the use of different adhesives, most likely this advice alone will help you solve the problem.

A second problem concerns the use of adhesives containing high percentages of solvents. Grease solvents are used to soften leather. There are many different types of fatliquors and their mechanisms of action are twofold: the establishment of a chemical bond with the leathers and physical deposition on the fibres. Physical deposition is the fattening mechanism that allows us to have greater softness and flexibility because it increases the mutual smoothness of the fibres, increasing all their technological properties. The fatliquors that are chemically bonded to the leather do not have a high softening power, but become non-removable by means of solvents. This type of fatliquor is used in the production of special articles, such as water-repellent leathers, in most cases the fatliquors form very mild chemical bonds and bind to the CYANOACRYLATE BONDING MECHANISM leather by means of post-drying hydrophobic interactions. If we use adhesives with a high solvent content on leathers that have not been prepared for use with this type of adhesive, we run the risk that the solvent in the adhesive will migrate some of the fat deposited on the fibres, making the distribution of the softener uneven and drying areas drier than others. We must also remember that the higher the solvent content in an adhesive, the longer the curing (and therefore extraction) time. I always advise you to inform the tanneries when you need to use adhesives of this type, so that they will be equipped to adapt their processing formulations.

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Dear reader, thank you for reading!

If the article was useful to you, if you would like to exchange some information about it or if you need my help, please leave a comment or contact me at:

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