

# The role of acrylic amphoteric

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A tanner learns that the difference between a tanning agent and an agent that does not tan is that a tanning agent will change the shrinkage temperature when added to untanned collagen. Another piece of jargon that needs to be understood is the difference between a resin and a polymer. A resin is a product that, when dried, gives a resinous residue while a polymer will not. A polymer is a molecule that is the product of an assemblage of smaller monomers with the help of a chemical that can link them together, or through its own self assembly. Many synthetic tanning agents (syntans) and resins are also polymers in that they consist of monomeric materials that are joined together. To add one more complication, modern chemical demand has required that the chemist use combinations of monomers to produce co-polymers. Homopolymers that use one type of monomer are a little rarer at present, while a tanner is much more used to seeing heteropolymers that have a mix of monomeric units.

Synthetic tanning agents have been a valuable contributor to the development of versatile, high performing leathers that are not subject to the natural limitations of vegetable tanning extracts (veg tans). Classical syntans rely on the use of phenol, cresol, or naphthalene as monomers in polymer preparations that include further treatments such as formaldehyde or sulphone condensations. By treating the monomers or polymers with bisulphite the solubility and later reactivity of the polymers is improved. The molecular weight, co-polymer selection, and degree of solubility are chosen by the chemist and the product's attributes are then marketed. The classical syntans are generally anionic (in charge) and bind electrostatically to the collagen. The larger replacement syntans can hydrogen bond through their phenol groups to the peptide groups on the collagen. Classical syntans will struggle to bind electrostatically to chromium-free leathers due to the leathers lack of cationic groups.

Later developments in resins/polymers included condensation products of urea-formaldehyde, melamine, and amino-functional products. Styrene-maleic anhydride, dicyandiamide, and poly vinyl alcohol technologies have more recently provided alternatives to the formaldehyde-based

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products. In general, the retanning agents (retans) mentioned are anionic in charge and react well to cationic tannages. They do not, however, react well with chromium-free or vegetable tanning materials. Dicyandiamides and amino resins have amine groups that can become cationic, which lends themselves to more dual function application. Dye intensity can be boosted or unchanged by the inclusion of these products. Polyurethanes (PU) can also be used in the retanning of leathers and the wide range of PU functionality means that most applications can be tailored when a PU is formulated.

#### Vegetable tannins and chromium-free

The intention to use chromium-free tanning materials is a high priority for many tanneries trying to satisfy an increasing number of brands asking for it. When a vegetable tanning agent or aldehydic system is used the cationic nature of the leather is reduced. The vegetable tanning agents bind electrostatically and through hydrogen bonding to the collagen. While the hydrogen bonding does not reduce the available cationic groups, the anionic charge on the veg tans will reduce amino groups available for anionic retans, dyes, and fatliquors to bind to. The reactions of the subsequent post tannage are then reduced, resulting in a higher chemical oxygen demand (COD) in the effluent and leaves the tanner shaking their head at the wasted chemical cost.

Aldehydics have a similar property, in that they too will



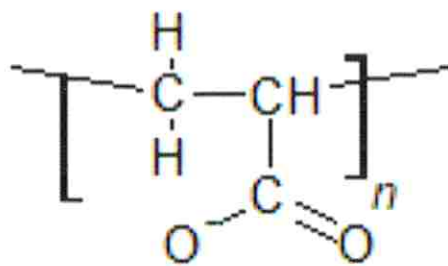
interact with the amine groups of the collagen. The interaction is not electrostatic in that the pH of the leather, if high enough, will cause the amino groups to flip into their amine form and this enables their nucleophilic nature. That nucleophile is an excellent group that can attack carbonyls, for instance, the carbonyl on an aldehyde (or a methylol group). These covalent linkages will change the amino groups available for dye interest.

Polycarbamoyl sulfonates (PCMS) are also cationic group hungry in that the carbonyl group that lies next to the sulfonate group on the PCMS is a target for the nucleophilic collagen amine. Triazine chemistry has a halogen leaving group, that again allows a substitution reaction between the collagen and the nucleophilic amine. The tanning material interactions mentioned so far reduce the cationic groups available for the dye/retan/fatliquor and the result is a leather that will not have the same level of property that a chromium leather would have unless the tanner adjusts the process.

**Amphoterics**

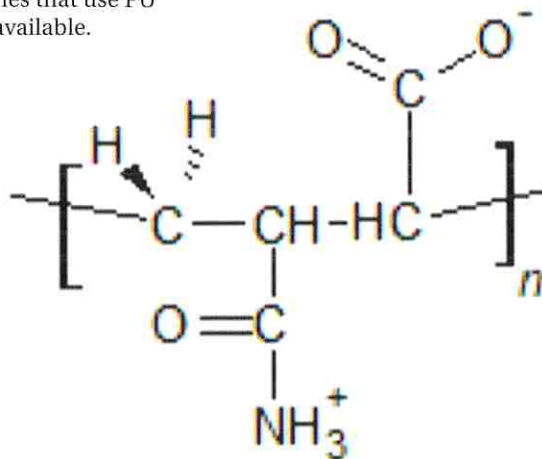
One way in which tanners have adjusted their post tanning wet end recipes has been to use amphoteric products or zwitterions that can provide both a cationic and an anionic charge to the collagen. The general result is an improvement of anionic retan uptake, better leather properties, while reducing COD and cost. This is no more relevant than the use of this technology on chromium-free and vegetable tannages. Tanners will also always make use of cationic products to help with uptake, but the selection of cationic products is becoming restricted if the end user also stipulates that the leather should be metal free as well.

The main difference between an amphoteric and a zwitterion is that the zwitterion is dependent on the pH of the solution that it is found. Zwitterions are commonly proteins and they can also be amphoteric if the pH allows. Zwitterions will always be amphoteric at their iso-electric point. Amphoteric products generally have both anionic and cationic charges at their usual working pH which makes them versatile for use on chromium-free leathers. The main benefit, of course, is generally increasing the cationic groups available, especially if the amphoteric has more cationic charges than anionic charge as the increase will then be additive. Polyurethanes are commonly sold as amphoteric because the wide range of industries that use PU polymers is large and the products are readily available.



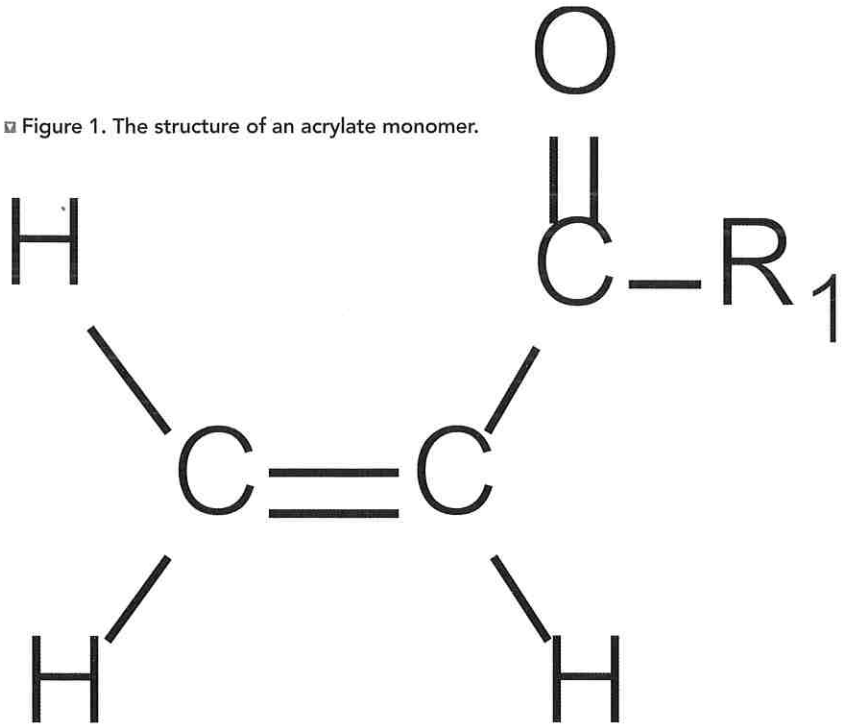
**A.**

Figure 2. A hypothetical structure of how an amphoteric acrylate polymer could look.



**B.**

Figure 1. The structure of an acrylate monomer.



**Acrylate**

When speaking about syntans/resins/polymers, no mention was made of the huge chemical family - the acrylates (propenoates). These polymers are generally manufactured as homopolymers but, for specific application, they are co-polymerised. The copolymers can be made of a mixture of acrylates, but they can be hybridised with urethanes or even siloxanes to produce interesting materials. Figure 1 shows the general structure of an acrylate.

The R-group can be substituted with a range of chemistries. Alcohols, amines, and cyano-groups are quite commonly used, but the most popular additions are short or long chain attached to the structure shown in Figure 1 using an ester linkage. The longer the ester, the more lubricating the product will be. The ester chain will tend to be quite hydrophobic so can bind to the collagen through hydrophobic bonding, but it will allow "smearing" with other fatty substances. If the polymer is predominantly a homopolymer of long chain acrylic esters, then the polymer may have water resistance properties that can then be imparted into the leather.

In general, the manufacturer will co-polymerise the acrylate monomers with acrylic acids that can ionise to provide an electrostatic group that can also bind to the amino groups in the leather. This means the acrylics could suffer from the same problem that other anionic retanning materials face; retan/dye/

fatliquor uptake problems. Industries outside of the leather industry have used amphoteric polymers for some time and the chemistries have been a mixture of siloxanes, acrylates, and polyurethanes (and even hybrids of the chemistries).

As mentioned above the use of an amphoteric provides an outstanding amount of options when it comes to providing a range of binding sites to leather chemicals. In chromium-free leathers the tanner will need to increase the number of cationic groups available if the correct level of property and chemical exhaustion is required. ■