

HIGH EXHAUST ACRYLIC CHEMISTRY*

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INTRODUCTION

Mineral tanned leather has an affinity for natural and synthetic products. The tanner puts them in leather at different yet balanced proportions to meet the diverse and evolving requirements of the industry. These leather products include vegetable extracts, aromatic syntans, fatliquors, dyestuffs and synthetic polymers based on (meth)acrylic acid; to name a few. Their affinity to leather is strongly affected by their structure/composition. Poly(meth)acrylate retanning agents have one of the strongest physico-chemical attractions to chrome tanned leather. Their high degree of exhaustion, and specific structural features are factors that beneficially influence the performance of leather, and the handling of tannery waste water.

Polyacrylates have been used in the wet end processing of leather for the last 20 years. It is estimated that a yearly 100MM lbs of assorted polyacrylates are put in leather worldwide. Their persistence in our industry is a practical endorsement by tanners that they add value to their business. And so, why are polyacrylates so widely accepted in leather? The simple answer to this is in two parts. They have an agreeable balance between cost and performance and also a unique chemistry that enables their high exhaust onto leather. I will briefly speak about the balance between the cost and performance of polyacrylates. Next, I will detail their high exhaust chemistry and explain its beneficial influence on leather processing, waste water treatment, and leather performance. Please note that I will use the names

TABLE I
Cost-Performance Profiles

Cost	Performance	
• High	High	Fluorocarbons Silicones
• High	Low	Useless product
• Low	Low	Clay, Flour
• Low	High	Polyacrylates Fatliquors Aromatic Syntans, etc.

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polyacrylic and polyacrylate interchangeably to mean an acidic polymer that is derived from acrylic acids.

Cost/Performance of Polyacrylates

Table I shows the four profiles of cost-performance that are possible for a leather product or any other. A high cost and high performance is for a niche product like a stain repelling fluorocarbon or a waterproofing silicone. There is not a practical example for a high cost and low performance product because it is commercially useless and is grossly misaligned with any rational business objective. A low cost and low performance product is exemplified by clay and flour that are used as cheap leather fillers. The last group of low cost and high performance belongs to the majority of products in current use by tanners worldwide. These products are derived from different chemistries and seemingly compete with each other for use in leather. But note, each class gives leather a unique performance profile or signature that is only dependent on its structure and composition. Table II shows the principal design variables that directly affect the performance of polyacrylate products.¹

TABLE II
Design Variables of Polyacrylates

- **Composition of Matter**
Polyacrylic Acid e.g. 100 AA
Copolyacrylate e.g. 50 AA/50 EA
- **Molecular Size (Daltons)**
Low (2K), Medium (50K), High (100K)
- **Structure or Architecture**
- **Extent of Acid Neutralization**
0 - 100%

- **Composition of matter.** For example is the product a polyacrylic acid or a copolymer of acrylic acid?
- **Molecular size.** Is it low, medium, or high? A polyacrylate is normally bigger in size than for example a triglyceride oil component of a fatliquor.
- **Structure or architecture of the polymer.** It is the outcome of how a synthetic chemist put its monomers together.

- **Extent of neutralization** of the acidic component in the polyacrylate. It is optimized by application testing, and is usually in the range of zero to 100%

Experts on fatliquors or aromatic syntans for example, are also concerned with similar variables except that the raw materials they use are totally different from those of polyacrylates. My message is that the performance profile of a polyacrylate is inherently different from that of a fatliquor, a vegetable extract, or an aromatic syntan, etc. The practical consequence is to give tanners great latitude in making leather of varied performance and marketability.

What is the basis for the high exhaust of polyacrylates onto leather?

Mineral tanned leather has an affinity for a broad range of products that are derived from natural and synthetic origins. The tanner puts them in leather at different yet balanced proportions to meet the diverse and evolving requirements of the industry. Their affinity to the leather fiber and their ultimate retention in it, are strongly affected by their composition and structure. Polyacrylate retanning agents express one of the strongest attractions to chrome tanned leather. Elegant research by several investigators^{2,3,4} has shown the ability of carboxylic acid groups in polyacrylates to react with Cr^{3+} that is already in chrome tanned leather. I'd like to borrow examples from nature and from basic leather science to explain in simple terms this polyacrylate chemistry. Figure 1 is a schematic for chrome tanning that we have all seen as a supportive tool for understanding this phenomenon.^{5,6} This model will evolve further as researchers continue to explore and refine the mechanism of chrome tanning.⁶ For now it is

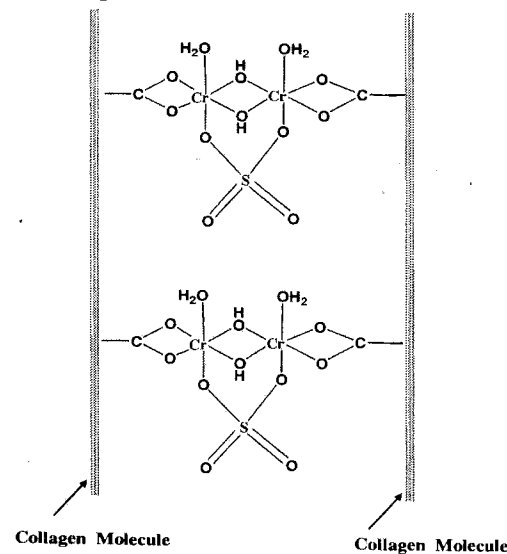


Figure 1. - Chrome Tanning Schematic

fully adequate to help us imagine the bonding of polyacrylates to Cr^{3+} . Collagen is a natural polymer that is derived from the condensation of amino acids. The vertical lines represent two collagen molecules. I deleted on purpose the amino groups which are naturally present on collagen so as to simplify this schematic. The two-collagen molecules have hanging carboxylic acid groups that emanate from glutamic and aspartic acids in their composition. This model shows that the carboxylic acid group is a chelating ligand. In a first reaction step with Cr^{3+} it makes two stable covalent bonds with it. As the system pH is raised, two spatially adjacent chrome complexes olate to make a stable cross link between the collagen molecules. The net effect is to immobilize the collagen molecules relative to each other and make them inseparable. This stabilizes the collagen super structure, and is a simple interpretation of the tanning phenomenon. A polymer strand of an acrylate is conceptually comparable to a collagen molecule. It has many hanging carboxylic acid groups that react with multiple chrome centers already on leather to make stable covalent bonds. This strong bonding is further augmented by additional ionic and hydrogen bonds with the fibers. The net outcome of these interactions qualifies polyacrylates as high exhaust and high uptake products onto chrome tanned leather.

Where is the polyacrylate in chrome-tanned leather? How far down the collagen hierarchy does it penetrate and ultimately reside? The short answer is that a polyacrylate was experimentally found by BLC to deposit on the fibrils.⁷ To help us visualize this, let us review the architecture of chrome-tanned leather.^{5,6,8} The sequence of steps which biosynthesize collagen from its amino acid constituents are:

- Amino acids make polypeptide strands
- Three polypeptide strands build a collagen molecule
- Five collagen molecules make a microfibril
- Many hundred microfibrils make a fibril
- Fibrils make fibril bundles
- Fibril bundles make fibers
- Fibers make fiber bundles

The amino acids glycine, proline and others are first condensed in a preset sequence to make a polypeptide strand. Three polypeptide strands aggregate in a triple helix configuration to make a collagen molecule. Five collagen molecules then assemble in a pentagonal structure to make a micro fibril. As I showed in Figure 1, the chrome cross links are formed between the collagen molecules of the micro fibrils. Thousands of micro fibrils then gather to make fibrils. In the limit of this structural build up, fibrils go to fibril bundles which go to fibers and lastly to fiber bundles. Let us model a micro fibril with a lead

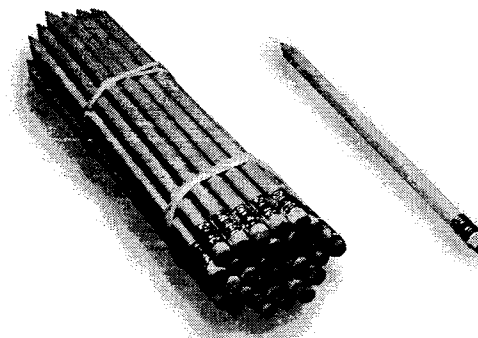


Figure 2. - Pencil Model of Fibril

pencil, and then aggregate many pencils to create a mock chrome tanned fibril. Figure 2 shows that the bundle of pencils is densely packed; but has a large surface area. The surface area of a fibril was experimentally determined by researchers to equal one square meter per gram.⁹ This surface attracts an assortment of products like polyacrylates. The outer surface of a fibril is made of collagen molecules that are spaced by many cross-links of chrome. These chrome centers are the anchoring sites for polyacrylates. For example, a strand of a low molecular weight polyacrylic acid has an average 28 carboxylic acid groups. Let 13 of them bind to spatially accessible chrome sites to make a combination of covalent, ionic and hydrogen bonds. It will be difficult to dislodge this attached polyacrylate even if 10 bonds are broken off by force. This multipoint bonding of a polyacrylate to the chrome tanned sites readily explains its affinity, and substantive abilities to this leather.

Figure 3 is a scanning electron micrograph of chrome-tanned leather that was treated with a Lubricating Acrylic Syntan. This elegant work by BLC showed that this polyacrylate deposited as a sheath or a thick film around the fibrils. The natural diameter of the untreated fibrils increased from ~130 nm to ~180 nm. It is not clear from this picture whether the polyacrylate penetrated the fibrils and to what depth. On the macro scale, this picture illustrates that the



Figure 3. - Lubricating Acrylic Syntan Residing on Fibrils

product fills leather without plugging the natural voids in it. This open treatment is typical of polyacrylates and makes low density leathers that breathe for comfort in use.

What is the impact of the high exhaust of polyacrylates on the processing of leather?

The chrome sulfate complex in blue stock is a Lewis acid. It reacts with anionic products to make new complexes. And so, blue stock is a material that exchanges anions which also means that it has a cationic character. The sulfate group is weakly bound to chrome and is readily replaced during wet processing. For example, it is displaced by acetate during the neutralization of blue stock, and by a poly anionic acrylate in retanning, and by anionic dyestuffs, and by sulfated fatliquors etc. The affinity of blue stock to these anionic products is inversely related to the extent of its neutralization. A low extent of blue stock neutralization means a high affinity by its surfaces and hence a rapid uptake of the polyacrylate product. By contrast, a higher extent of blue stock neutralization allows the polyacrylate to penetrate deeper in this substrate relative to the former case and still bind to fibrils. Polyacrylates are exhausted in a reasonable amount of time during wet processing. Figure 4 shows the uptake profile of a polyacrylate that was offered at 6% solids to a neutralized blue stock. The lower graph shows that 98% of the polyacrylate solids offered were taken up in one hour by this high affinity substrate. By comparison, the upper graph shows that 86% of the polyacrylate solids were exhausted in one hour by the relatively lower affinity or the higher neutralized blue stock. The residual polyacrylate in either float can be further lowered to immeasurable levels by extending the processing time a bit longer and by applying the polyacrylate at a higher bath temperature. The spent bath from this process step is relatively pure and contains sulfate salts. In principle, it can be reused as the floating medium for the next process product without a detriment to the final leather. This suggested practice will save water and diminish the overall cost of processing. My message is that the high exhaust of a polyacrylate onto the leather is money well spent. The polyacrylate is in the leather where it needs to be and not in the effluent water.

What is the effect of the high exhaust of polyacrylate on the treatment of tannery effluent?

Suppliers of consumer products who use polyacrylates in laundry detergents have extensively studied their effect and fate in the environment.^{10,11} The polyacrylates are called in this application anti soil re-deposition agents. They remove the particulate soil during the laundering of clothes and keep

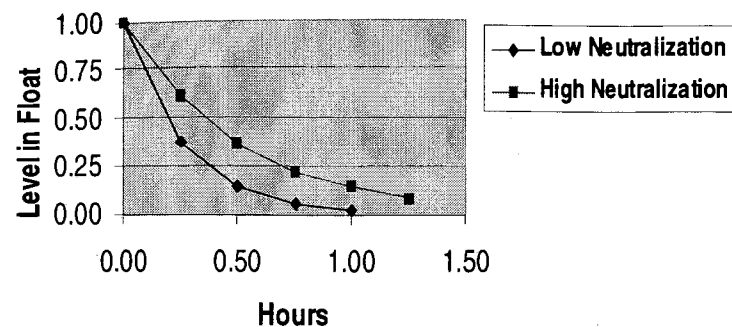


Figure 4. - Uptake of Polyacrylate by Neutralized Blue Stock

it dispersed in the wash float. Polyacrylates are stable to heat and light. They are not readily degraded by the mild chemical and biological conditions in the environment. Fortunately, they have a low toxicity to organisms that live in water and on land. Polyacrylates are removed from bodies of water by two routes. First, they are coagulated by calcium and magnesium cations that are naturally found in hard water. They are also precipitated by trivalent iron that is added on purpose to the wastewater so as to sludge all of the dissolved anionic materials for disposal in landfills. Second, polyacrylates strongly adhere to precipitated solids, and hence become immobilized on them. My message is that polyacrylates are inert, they are treatable in wastewater, and are gentle to the environment.

What is the impact of the high exhaust of polyacrylate on the performance of leather?

Leather is a composite or a blend of natural and synthetic materials. Its performance is the sum contribution of each product residing in it. Table III shows some attributes of polyacrylates. For example, a high molecular weight polyacrylic acid fills leather. This performance is quantified by the thickness ratio of the crust to the starting blue stock. In this case this ratio equals 1.2, and signifies a 20% plumping factor. By contrast, a low molecular weight polyacrylic acid gives a flat piece of leather; but does a better job at leveling

TABLE III

Leather Performance Due to Polyacrylates

<u>Polyacid Syntan</u>	<u>Lubricating Acrylic Syntan</u>
Full/Plump	Full/Plump
Level Dye Color	Soft, Strong
Firm/Tight Grain	Low Fog
	Waterproof
	Washable

the color of anionic dyestuffs. Leather that is made with a polyacrylate has a constant performance as it ages in use. This is because the product is chemically stable and is physically immobilized during the service conditions. For example, let a tanner make soft and low fog automotive upholstery with a combination of a high quality classical fatliquor and a Lubricating Acrylic Syntan. During normal use, this leather is subjected to wide-ranging conditions of temperature, humidity, and radiant energy. It is likely that oily components in the fatliquor have olefinic or double bonds of natural and synthetic origins. These double bonds will oxidize under the influence of heat and light, and so change the fatliquor. Yet another component of the fatliquor may be a simple hydrocarbon. It will evaporate from the leather in hot weather and leave a fog on the windshield. In the final analysis, this leather has changed chemically and physically. Its current softness and strength are no longer those that were measured initially. By contrast to the classical fatliquor, the Lubricating Acrylic Syntan in this leather has not changed during all this; because it is chemically and physically inert. And so, this attribute will extend the longevity of the automotive leather.

The structure and composition of a polyacrylate plus its high exhaust onto chrome stock, do not fully communicate its performance potential. A polyacrylate like any other leather product used in the wet end must penetrate the cross section of the substrate to express its performance in the crust. Its penetration and fixation must be facilitated by using the right neutralization of the blue stock as I mentioned earlier. Figure 5 shows the distribution of a polyacrylate in the cross section of crust leather that is fully acceptable. This depth profile was determined experimentally by using the technique of Photoacoustic Spectroscopy. First, the grain surface is irradiated with infrared energy that selectively couples to the carboxyl groups in the polyacrylate. In response, the leather emits a sound of a certain frequency and intensity. This acoustic output is measured and decoded as a number that is proportional to the polymer concentration. The analyst then removes a ~0.25 mm. thick layer with a sharp razor, and tests the newly exposed area.

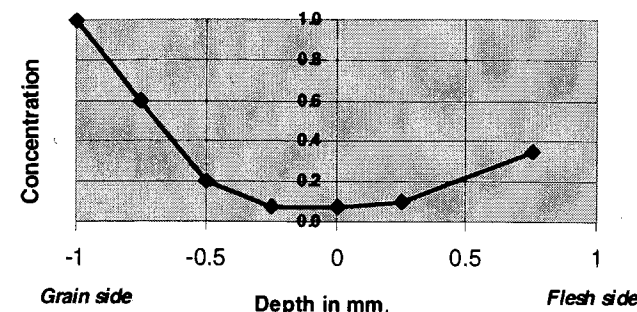


Figure 5. - Distribution of Polyacrylate in Chrome Tanned Leather. This process is repeated to generate the shown graph. My message is that the proper penetration and fixation of a polyacrylate in the cross section of leather are a must to fully express its performance. This same message applies equally well to all other wet-end products.

CONCLUSION

In conclusion, the principle factors that continue to make polyacrylate products successful in our business are:

- they provide an agreeable balance between cost and performance,
- they are highly exhausted by mineral tanned leather,
- they are chemically inert during their service life, and
- they are friendly to the environment.

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