Optimal Remedy for Bisphenol Obscurity from United Chemicals: Latest Acrylic Polymer Innovations

Leather production is a process based on chemical modification of collagen protein and in this process, a wide variety of chemicals with different properties are used in each different process step. The urgent call for a sustainable shift, a widely discussed global concern, has led to rigorous ecological scrutiny of the leather industry, mirroring the scrutiny in various other sectors. Each passing day witnesses a growing number of organizations meticulously investigating the environmental repercussions of chemicals utilized in the leather manufacturing process.

One of the most important problems voiced today is the problem of bisphenol in synthetic tannins used in pre-tanning, tanning and tanning processes. Synthetic tannins have been used for many years in leather production especially to fill the loose parts of leathers and to increase the performance of vegetable tannins. Depending on the type of syntans, they can provide fullness, grain tightness, elasticity, heat resistance, improved light fastness and some special effects to the leather. Due to the increase in demand for chrome-free leathers in recent years, the use of syntans in tanning has also increased significantly. The problem of bisphenol in the leather industry emerged after Bisphenol A was announced as an SVHC candidate substance and its use in plastic bottles was banned in Europe.

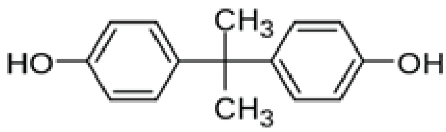

Figure 1. Structure of Bisphenol A

More recently, these activities have begun to extend to compounds with analogous compositions that serve as inputs Bisphenol S or are found as remnants Bisphenol F in synthetic tanning agents. Unfortunately, existing technologies provide only minimal opportunities to decrease Bisphenol S and Bisphenol F levels significantly lower than 100 ppm. As a consequence, these compounds and the resulting leather products will become subject to regulation and can no longer be marketed within the European Union. These anticipated restrictions have pushed tanneries and leather chemical manufacturers to search for new chemicals that can be used instead of synthetic tannins in retanning processes, which are one of the key stages of leather production.

Acrylic Polymers

Retanning process holds significance in the leather production, aiming to even out leather structures by filling in their loose and empty areas (Leafe, 1999). Over the past 15 years, a diverse range of retanning agents has emerged with the primary objective of enhancing leather's performance and structure. Among these agents, polymers have gained significant attention since the 2000s and have become widely adopted as retanning and filling agents in leather processing. These polymers serve a multifaceted purpose, including the filling of loose areas within leather while also imparting tanning effects by bolstering the thermal stability of the material. Depending on their chemical composition and molecular structure, these polymers can additionally offer enhanced elasticity, smoother grain, increased tensile strength, increased softness, improved light fastness for the leather goods.

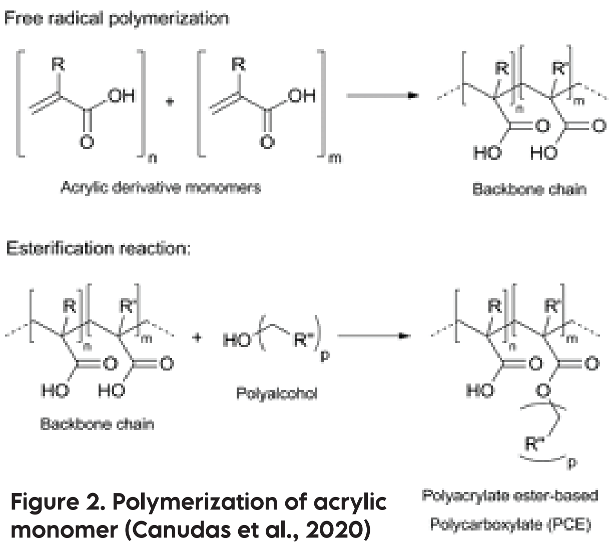

Figure 2. Polymerization of acrylic monomer (Canudas et al., 2020)

Typically, the acrylic polymers employed in retanning process consist of high molecular weight structures composed of recurring units referred to as monomers.

The characteristics imparted to the skin primarily hinge on both the monomer species utilized in the synthesis and the molecular weight of the resulting polymers. Primary monomers in widespread use encompass acrylic acid, acrylonitrile, styrene, and maleic acid. Typically, these substances manufactured through diverse polymerization methods involving acrylic or methacrylic acids, coupled with acrylic esters.

Acrylic polymers are extensively utilized during retanning due to its effective selective filling ability, enhancing the leather's cutting value. Moreover, it is free of phenol and formaldehyde.
The effectiveness of retanning with acrylic resin is widely acknowledged, and its performance hinges largely upon how deeply it penetrates and fills the leather's structure. Consequently, to enhance this retanning process, it's crucial to thoroughly comprehend the factors that impact acrylic resin's penetration and distribution within the leather. Notably, the molecular weight and functional groups of acrylic resins play a pivotal role in determining their penetration and distribution throughout the leather. Additionally, various retanning operation conditions, such as pH, temperature, and float ratio, exert a significant influence on the extent and uniformity of penetration and distribution.

Unlocking the Enchantment of Acrylic Polymer Formulations: Innovations from United Chemicals R&D Laboratories

Today, as always, United Chemicals laboratories have carried out intensive research and R&D studies to solve the problems of the leather industry and have managed to bring the performance properties that synthetic tannins provide to leather during the retanning stage, with a series of innovations made in acrylic polymers.
As a result of intensive literature survey, preliminary trials, optimization studies in polymerization degrees, molecular weight, and functional groups in the chain, we were able to reach our final formulations. We offer four different latest generation acrylic polymers with specific properties for various types of leather.
UNISIN RE: It is an anionic polymer which has a unique selective filling property in the empty and loose areas of the hide or skin structures. UNISIN RE gives excellent fullness even in the flanks and bellies with tight grain and can be used for full grain and corrected grain leathers. With the use of the product in the retanning bath, the tensile strength values in the leather increase significantly while the apparent density values in the fibers also increase.
UNISIN RE100: It is an amphoteric polymer suitable for pretanning and retanning. UNISIN RE100 is suitable to be used in wide range of pH and has very distinctive filling effect. Leathers treated with UNISIN RE100 have very fine elastic grain with outstanding closed pores and significant increase of tear strength. UNISIN RE100 have high light fastness and can be used all kind of leather.
UNISIN EZN: It is an anionic polymer which has a good selective filling property in the empty and loose areas of fiber matrix. Leathers retanned with UNISIN EZN have high apparent density values. It also improves elasticity of leathers and ideal softy type of leathers without altering their typical properties.
UNISIN FX-40: It stands out as a versatile amphoteric polymer designed for both chrome retanning and general retanning processes. Its adaptability across a broad pH spectrum makes it a valuable choice for various types of leather. The application of UNISIN FX-40 results in leather with a notably tight grain and a substantial boost in tensile and tear strength. Furthermore, this polymer enhances light fastness.

Performance of Advanced Acrylic Polymer Formulations

After preparing the acrylic polymers, they were incorporated into the leather production recipe at a 5% ratio. The production recipe details are outlined in the table below. To effectively assess the impact of the polymers on the leather, the control group leathers were deliberately devoid of any acrylic polymers.

Process	%	Products	Time	Marks
Neutralization	150	Water 35 °C		
	1.0	HCOONa	20'	
	0.4	$NaHCO_3$	60'	pH 5.0
Washing	250	Water 35 °C	30'	
Retanning	150	Water 35 °C		
	5	**Acrylic polymers**	60'	
Fatliquoring	2	Blends of natural and synthetic oils	60'	Temperature 50°C
	2	Sulfited and sulphated fatliquor		
	2	Phosphoester based fatliquor		
	x	HCOOH	30'	
	x	HCOOH	60'	pH 3.5
Washing	200	Water 20 °C	20'	

In order to evaluate the retanning efficiency of the developed acrylic polymers, the wet thickness of the chrome-tanned samples before the retanning process (T1) and after fixation (T2) were measured from 8 different points in total, including each corner, edge midpoints and center. The average of the thickness values of the leather measured in this way was taken and the filling efficiency of acrylic polymers was calculated as a percentage using the formula below.

$$Filling\ Efficiency\ = \frac{(T_2 - T_1)}{T_1} x\ 100$$

The tensile strength and elongation at break of leather were determined following the TS 4119 EN ISO 3376 Standard. Tear strength of retanned leather was evaluated using the TS EN ISO 3377-2 method and the apparent density of treated fibers was measured in accordance with the TS EN ISO 2420 Standard.

	Filling efficiency (%)	Apparent density (g/cm^3)	Tensile strength (N/mm^2)	Elongation (%)	Tear strength (N)
Control	-	0.44	12.3	70	94
Unisin RE	16.81	0.58	18.3	60	99.5
Unisin RE100	19.04	0.51	14	67.3	109.2
Unisin EZN	13.68	0.57	10.3	59.2	91.7
Unisin FX40	11.61	0.53	13.6	65.4	116.4

Retanning is one of the most important factors in changing the physical properties of leather during the leather production. The amount and the type of retanning agent affect physical properties such as fullness, tensile and tear strength, elongation, and light fastness. Moreover, reactive groups of retanning agent can also make additional crosslinks between collagen fibers for increasing the thermal stability of collagen.

Filling efficiency, tensile strength, elongation at break, double edge tear load and apparent density results of treated leathers were shown in table above.From the results, it can be seen that the physical and mechanical properties of leather treated by all novel acrylic polymers were higher than control groups. Developed products improved the apparent density of leather compared to the control group leathers. From the Table, it was observed that the increase in the tensile strength of the leather with the application of UNISIN RE, UNISIN RE100 and UNISIN FX40 in the retanning process. The tensile strength value of the leathers was observed in control group leathers as 12.3 N/mm2, while the highest strength value was obtained in leathers treated with UNISIN RE with 18.3 N/mm2. When the double edge tear load results were examined, there was an important increase by 19.24% with the addition of UNISIN FX40 into the leather. Moreover, new generation acrylic polymer application improved the thickness of hide matrix up to 19.04% when compared to control samples with special filling effect.

Lasting Impressions

The global leather production landscape faces a substantial transformation due to the impending restrictions on bisphenol. This is particularly noteworthy because syntans, employed in leather retanning and pretanning since 2000, are now under scrutiny. It is essential to innovate additional alternatives that do not include the prohibited substances. These alternatives must maintain the existing quality and diverse range of leathers we appreciate today. The reduction in the usage of conventional retanning agents, known for their environmental unfriendliness, has led to an increased emphasis on acrylic polymers due to their favorable chemical properties and environmental advantages. For these purposes, United Chemicals declares adaptable and high-performance acrylic polymer retanning solutions for all kinds of leather types. The formulation for a syntan-free alternative and its resultant properties demonstrate the feasibility of creating a fully syntan-free product that meets all essential leather standards. As United Chemicals, we will always continue to offer you the best solutions for leather industry.

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