

TOP-COATING OF LEATHER WITH AN EFFECTIVE UV-CURABLE WATERBORNE POLYURETHANE DISPERSION TECHNOLOGY.

Giovanni Dalla Valle¹, Massimo Cariolato², Giancarlo Lovato³

1. R&D, Corichem srl. Via Lago di Garda 16, 36040, Sarego (VI), Italy, ricerca@corichem.it
2. R&D, Corichem srl. Via Lago di Garda 16, 36040, Sarego (VI), Italy, ricerca.finishing@corichem.it
3. R&D, Corichem srl. Via Lago di Garda 16, 36040, Sarego (VI), Italy, giancarlo.lovato@corichem.it

ABSTRACT

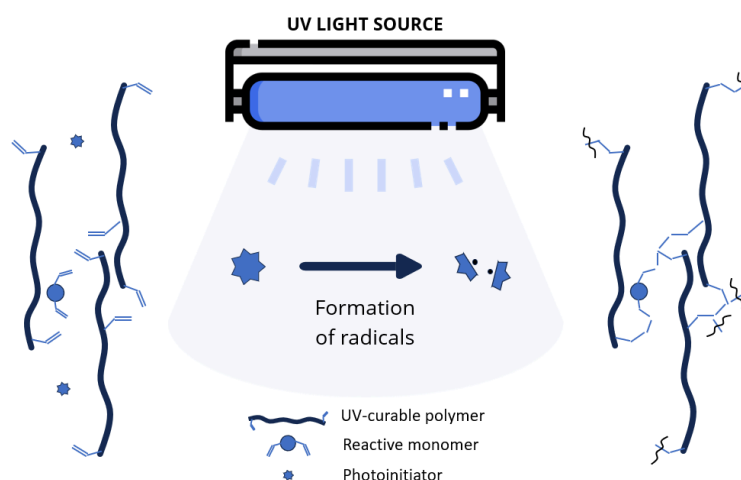
The synthesis and the characterization of a series of ultra violet photo-curable waterborne polyurethane dispersions (UV-PUD) for leather finishing was successfully conducted. The UV-PUDs obtained generate polyurethan films that reticulate under the exposition of UV light from 10 to 15 seconds without the necessity of the addition of any dangerous materials like polyisocyanate or polyaziridines. The obtained films show good values of elastic properties, resistance to repeated flection, rubbing resistance and chemicals resistance; results are discussed. The products obtained are suitable for the finishing of leather to obtain articles adapt for: footwear, leather goods and furniture. Formulation technique to obtain good results is discussed. The described top-coat technology does not require the manipulation of hazardous materials to achieve the optimal performance and do not suffer of pot-life problem because no external curing agent addition on the UV-PUD is required for the application. The application technique is very similar to the “state of the art” technology and it requires minimum modification of the common finishing facility for the installation of the UV equipment. Selection of raw materials, crucial for the obtainment of the required elasticity properties, is discussed. Also, bio-based raw materials are introduced in the project to obtain a bio-based carbon content up to 64%; biodegradability tests were conducted. Synthesis and formulation to get the correct merch properties are disclosed. The whole technological innovations presented are Patent pending.

Keywords: UV curing, One component, Bio-Based

1. Introduction

In the context of the leather finishing the use of water-borne polyurethane dispersions is well known. Due to the good elastomeric property, chemical and physical resistances and the great variety of different types of finishing that can be prepared, polyurethane coating systems are the best choice for the top coating of leather. Nowadays for sustainability issue the actual polyurethane coatings is designed as dispersions or emulsions of polymer particles in water. This type of technology allows to use water as liquid vehicle permitting to comply the sustainability issue that require to reduce the utilization of volatile organic compound. On the other hand, the more diffused waterborne dispersions in the leather industry are two-component systems that require the utilization of an external curing agent to reach sufficient performances. The goal is to covalently bond each other the various polymer

chains or create an interpenetrating network for the purpose to enhance the crosslinking degree, obtaining a reduction of the swelling effect of solvents, resistance to hydrolysis and an upgrading of the mechanical properties (Noble 1997). Unfortunately, the most of these curing agents present problems regarding the toxicological profile. Another issue that affects the two-component polyurethane systems is the pot-life; some curing agents hydrolyze in water and others can variate the viscosity of the resins and eventually cause the gelling of the dispersion. This means that, after a period of time, the dispersion becomes useless and the product must be wasted or the curing agent must be reintegrated, with problems of environmental and economical sustainability and reproducibility of the application. To avoid these two problems the coating industry had developed some one-component systems. These types of coating do not necessitate the addition of a curing agent for the crosslinking of the film, so this type of finishing system overcame the problem of manipulate harmful materials and do not suffer of pot-life problem, because no crosslinking or hydrolysis take



place before the application. These types of finishings are quite common in many industrial sectors. In the field of the one-component coating system one of the most common routes is the UV-curing. This type of technology is based on the activation, by ultraviolet light, of some functional groups present in the backbone of the polymer chains. Once they are activated, the functional groups form each other a covalent bond making a connection between different polymer chains, creating a crosslinked network (Dall Agnol et al. 2021). These can be done via two major technologies that require to append on the polymer chain (meth)acrylates or epoxide functionalities. Once the coating is dry it is exposed to an UV source. A substance presents in the formulation, called photoinitiator, generate in this stage: free radicals in the case of (meth)acrylate functionalization or super-acids in the case of epoxy.

Figure 1. Schematic representation of the UV photocuring process for acrylated polymers.

These species initiate the polymerization between a polymer chain with another chain or between chains and monomers that can be added to the formulations (Decker 2001). A systematic description of this mechanism is discussed in much more detail elsewhere and it is beyond the scope of this article (Christian Decker 1992; Mark D. Soucek, Xiaofeng Ren 2014). In the context of leather finishing, a lot of work has been done to introduce this type of technology into the sector, but unfortunately without producing a proposal that could fully replace the current two-component technology. The main problem that was observed is the poor elastomeric property that these kinds of finishing systems manifest. We think that one of the main reasons for the lack of positive results is that, as noted in the literature, most of the efforts to introduce this type of technology in leather have been directed towards the formulation of already existing UV-curable resins designed for other sectors, in particular: plastic, wood and metal (Ali Khan, Islam 1997; Khan Khan, et al. 2002; Baysal, Kalav, Kayaoğlu 2019; Khan,

Rahman, Bhuiyan 2002; Uddin, Khan, Ali 1996; Khan, Rahman, et al. 2002). Products such as these, designed to be effective on rigid supports, are not suitable for the types of stresses that leather products undergo during their manufacturing and uses, particularly with regard to resistance to repeated bending. In this work we prepare UV-curable polymers that are designed to have the right flexibility and chemical-physical resistances to be effective in the leather finishing. In compliance with current sustainability regulations, bio-based versions of UV top coatings prepared with renewable raw materials have also been developed. All the materials shown in this paper are patent pending.

2. Materials and Methods

UV curing was performed on a conveyor belt UV lamps oven GST UVPlus (Giardina) equipped with an Hg and a Ga lamps. ATR FT-IR was performed on a Nicolet iZ10 (Thermo); traction experiment was conducted on an Instron 3345. Acetone, dimethylolpropionic acid DMPA, 2-hydroxyethyl acrylate 2-HEA, triethylamine, glycerol monomethacrylate (GMA), ethylenediamine EDA, polyhexamethylenediisocyanate and photoinitiators were purchased from Merck; ADICROL BIO SPD 56, ADICROL AIE 56 and ADICROL B 56 were offered by Nord Composites Italia, IRGANOX 1135 was purchased from Basf, IPDI (Minwo) was offered by Milano Colori, PTMEG 220 and 2000 were offered by Gantrade. Common laboratory equipment was used for the experimental set up. Polycarbonate based PUD and all other additives and resins that were used in this work have been selected from the Corichem portfolio. The NCO content was determined via colorimetric back-titration following the ASTM D2572-97 method.

Synthesis of the bio-based UV-PUD 1

A 4-neck 1000 ml jacketed reactor was equipped with a syringe stirrer, a condenser, a thermometer and a system to obtain inert atmosphere with nitrogen gas. 543.30 g of ADICROL BIO SPD 56, 35.73 g of DMPA, 178.03 g of IPDI and 150.00 g of acetone were introduced into the reactor. The solution was heated to 60°C and 0.8041 g of bismuth octoate catalyst were added. The reaction is quite exothermic. After 1 hour the temperature has been increased up to 75°C and 31.60 g of 2-HEA, 6.70 g of Irganox 1135 and 21.31 g of GMA were added. Temperature and stirring were maintained until a constant NCO value was obtained. The product was cooled down to 40°C and 28.30 g of TEA and 41.30 g of photoinitiator were added. After 10 minutes the prepolymer is slowly transferred in a beaker containing 2542.31 g of water maintained under vigorous stirring. The stirring was maintained for 30 minutes and then the product was filtered under a 40 µm filter.

Synthesis of the bio-based UV-PUD 2

A 4-neck 500 ml round bottomed flask was equipped with a syringe stirrer, a condenser, a thermometer and a system to obtain inert atmosphere with nitrogen gas. 81.00 g of acetone, 7.89 g of DMPA and 7.89 g of IPDI were introduced into the reactor. The temperature was set to 60°C until constant NCO value was obtained. Then in the reactor was introduced 24.79 g of PTMEG 220 and the temperature was set to 70°C until constant NCO value was obtained. Then 78.26 g of Adicrol Bio SPD 56, 42.67 g of IPDI, 21.06 g of 2-HEA and 0.076 g of Irganox 1135 were introduced into the reactor and the reaction was conducted until a constant NCO value. 7.12 g of TEA and 5.03 g of photoinitiator were added and the reaction mixture was cooled down to 40°C. After 10 minutes the prepolymer was slowly transferred in a beaker containing 503.20 g of water maintained under vigorous stirring. The stirring was maintained for 30 minutes and then the acetone was removed via vacuum distillation. The product was filtered under a 40 µm filter.

Synthesis of the UV-PUD 3

Experimental setup was the same as UV-PUD 2. In the reactor were introduced 183.34 g of ADICROL AIE 56, 12.51 g of DMPA, 62.51 g of IPDI, 89.00 g of acetone and 0.2864 g of bismuth octoate catalyst and the temperature was set to 70°C until a constant NCO value was obtained. 0.087g of Irganox 1135, 10.90 g of 2-HEA and 7.51 g of GMMA were added. The reaction was conducted until NCO value was less than 0.05%. The reaction mixture was cooled to 40°C and 9.94 g of TEA and 10.40 g of photoinitiator were added. After 10 minutes the prepolymer was slowly transferred in a beaker containing 557.90 g of water maintained under vigorous stirring. The stirring was maintained for 30 minutes and then the acetone was removed via vacuum distillation. The product was filtered under a 40 µm filter.

Synthesis of the UV-PUD 4

Experimental setup was the same as UV-PUD 2. In the reactor were introduced 119.16 g of Adicrol B 55, 8.21 g of DMPA, 40.73 g of IPDI, 78.00 g of acetone and 0,1356 g of bismuth octoate catalyst and the temperature was set to 70°C until a constant NCO value was obtained. Then we introduced 6.54 g of 2-HEA and we waited until constant NCO. Then 4.50 g of GMMA was introduced. The reaction was conducted until NCO value was less than 0.05%. The reaction mixture was cooled to 40°C and 5.52 g of TEA and 8.90 g of photoinitiator were added. After 10 minutes the prepolymer was slowly transferred in a beaker containing 579.02 g of water maintained under vigorous stirring. The stirring was maintained for 30 minutes and then the acetone was removed via vacuum distillation. The product was filtered under a 40 µm filter.

Synthesis of the UV-PUD 5

Experimental setup was the same as UV-PUD 2. In the reactor were introduced: 173.45 g of PTMEG 2000, 10.60 g of DMPA, 59.80 g of IPDI, 2.56 g of GMMA, 3.71 g of 2-HEA; the temperature was set to 70°C until a constant NCO value was obtained. The reaction mixture was cooled to 40°C and 6.46 g of TEA and 10.40 g of photoinitiator were added. A beaker containing 385.00 g of water was cooled to 10°C and 233.03 g of the prepolymer was slowly added to the water under moderate stirring. After 5 minutes from the end of the addition, 20.15 g of a 20% solution of EDA in water was slowly added in 5 minutes. The stirring was maintained for 30 minutes and then the product was filtered under a 40 µm filter.

UV top-coat (UV-TC) formulation

The top coats are formulated starting from the previous UV-PUDs, the processing is carried out at room temperature under moderate agitation with sawtooth impellers. The formulations compositions are reported in Tabel 1.

	UV-TC 1	UV-TC 2	UV-TC 3	UV-TC 4	UV-TC 5
Deionized water	39.90	42.72	40.70	13.40	42.65
DPM solvent		1.37		1.33	
Aminic acid neutralizing agent		0.07		0.07	
Silicone fluid					0.30
Fumed silica		1.03		1.00	
Acrylic resin thickener		0.34		0.33	
Standard PUD	8.00				
Waterborne waxes emulsion		2.06		2.00	
Amino silicone emulsion			3.00		3.00
Polycarbonate PUD	3.00		8.00		8.00

Silicone dispersion	0.30	1.51	0.30	1.33	
PUD matting agent		13.74		13.33	
Associative polyurethane thickener		2.06	1.00	1.67	1.00
Levelling agent	0.10		0.30	0.20	0.30
Acrylic monomer	0.70	0.62	0.70		0.75
Water soluble photoinitiator		1.17			
UV-PUD 1	48.00				
UV-PUD 2		33.31			
UV-PUD 3			46.00		
UV-PUD 4				65.34	
UV-PUD 5					44.00

Tabel 1. Components of the UV-TC formulations. Quantities are expressed as m/m percentage.

Instron experiment

The films were prepared by pouring the UV-TC onto silicone molds and letting them air dry. Various attempts were made to obtain films with a thickness of 2 ± 0.10 mm, 2 cm wide and 5 cm long. The films were irradiated under UV lamp for 15 sec. After one day of rest they were subjected to an Instron tensile test at a speed of 2 cm/min. Three experiments for each sample were conducted.

Biodegradability tests, carbon dioxide development in soil

The biodegradability of the UV-TC 1 and 2 in soil was determined by determining the release of carbon dioxide under aerobic conditions by microorganisms present in the soil. 100 g of moist soil were introduced into a specially modified flask (see Fig. 2). At half the height of the soil, in two separate apparatuses, samples of dry film of the two finishes were positioned, respectively with a mass of 282.80 mg for UV-TC1 and 236.70 mg for UV-TC 2. 10 ml of a 0.46 M KOH solution were introduced into the vial connected to the flask and the apparatus is hermetically sealed. The produced carbon dioxide is captured by the KOH solution and it is determined by titration of the excess base remaining with HCl in the presence of phenolphthalein. The apparatus is kept in the dark throughout the test and the amount of carbon dioxide is determined every 7 days for a total of 28 days of experiment. The KOH solution is replaced after each measurement.

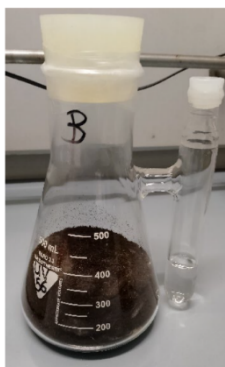


Figure 2. Apparatus for the determination of carbon dioxide evolved by the decomposition of UV-TC in soil.

Rubbing resistance

The leather was prepared with a standard primer and it was sprayed with UV-TC. After a short drying in the oven the leather was exposed to UV irradiation for 11 sec. Rubbing resistance was determined

according to IULTCS/IUF 450 method, using wet rubbing material, immediately after curing and after a day of rest.

Swelling test

Three films, like the one prepared for the Instron experiment, were prepared for each finishing. Each sample was weighted and immersed in a beaker containing ethanol for 2h or water for 16h or methyl acetate for 2 min. After the immersion time, the sample was removed from the solvent and its surface was rapidly and gently dried with paper. The samples were immediately exactly weighted. The percentage of swelling was determined. A film of a commercial polycarbonate based PUD was prepared adding an 8% of polyhexamethylenediisocyanate to the dispersion and curing the film at 80°C for 5 min. After one week of rest the film was submit to the same test.

Flex resistance

Flex resistance of finished leather, prepared as the one for rubbing test, was conducted in accordance to IULTCS/IUP 20 only on dry leather. The test is stopped after any damage is detected or after 100,000 cycles have been performed.

3. Results and Discussion

Fig. 3 shows the IR spectrum of UV-PUD 1. In addition to the typical signals of the urethane function and characteristic of the selected polyol, peaks appear around 1630 and 805 cm^{-1} , typical of the normal modes of the acrylic functionality. Once the polymer is subjected to UV light irradiation, these two peaks disappear. In the case of the UV-PUD 5 polymer, prepared by emulsion extension, the peak at 1630 cm^{-1} is covered by the shoulder given by the vibration modes of the urea functionality.

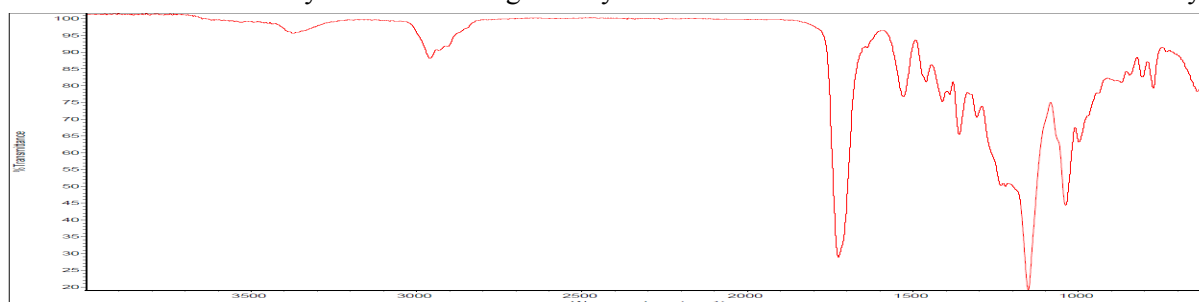


Figure 3. FT-IR ATR spectrum of the dry and uncured UV-PUD 1

The mechanical properties and rub resistance of the UV-TCs are reported in Tab. 2 and have proven to be suitable for leather finishing. Even the chemical properties of resistance to solvents and hydrolysis are good and in line with what is required by the market. They are also very satisfactory if compared with normal finishing resins once cross-linked.

The percentage content of biobased carbon for UV-PUD 1 and 2 was calculated on the basis of supplier declarations and are respectively: 64.08 and 35.99%.

Chemical resistances are reported in Tab. 3 and they are good if compared with common finishing cured with 6% of polyisocyanate.

The most significant result was the flex resistance experiment in which all the tested samples exceeded over 100,000 flex cycles. All commercial UV products that have been tested previously have in fact failed this test, presenting resistances even lower than 100 cycles. This type of product, designed

almost exclusively for rigid substrates, presents too glassy behaviours and ends up cracking after a few cycles (Cariolato, Tezza, Lovato).

	Elastic modulus [MPa]	Elongation at break [%]	Stress at break [MPa]	Rubbing cycles after curing	Rubbing cycles after one day
UV-TC 1	7.20	200.53	7.40	410	460
UV-TC 2	12.50	240.53	10.16	680	710
UV-TC 3	8.45	360.14	8.95	430	450
UV-TC 4	10.51	301.19	9.66	880	900
UV-TC 5	13.50	312.21	11.18	510	540

Tabel 2. Results of Instron experiments and rubbing tests

	Ethanol [%]	Water [%]	Methyl Acetate [%]
UV-TC 1	51.58	9.19	56.47
UV-TC 2	53.42	4.88	72.66
UV-TC 3	56.10	10.32	40.53
UV-TC 4	48.87	7.49	35.60
UV-TC 5	55.36	11.47	38.94
Commercial Polycarbonate PUD + Polyisocyanate	64.82	5.19	51.30

Tabel 3. Results of swelling tests

Biodegradability experiments were conducted only on biobased UV-TCs. The results show that UV-TC 1 can produce in 28 days 518.5 mg of carbon dioxide for every gram of film and is much more prone to biodegradation than UV-TC 2. This is explained by the fact that the first compound contains a higher percentage of polyester polyol than the second one. The results are shown in Fig. 4.

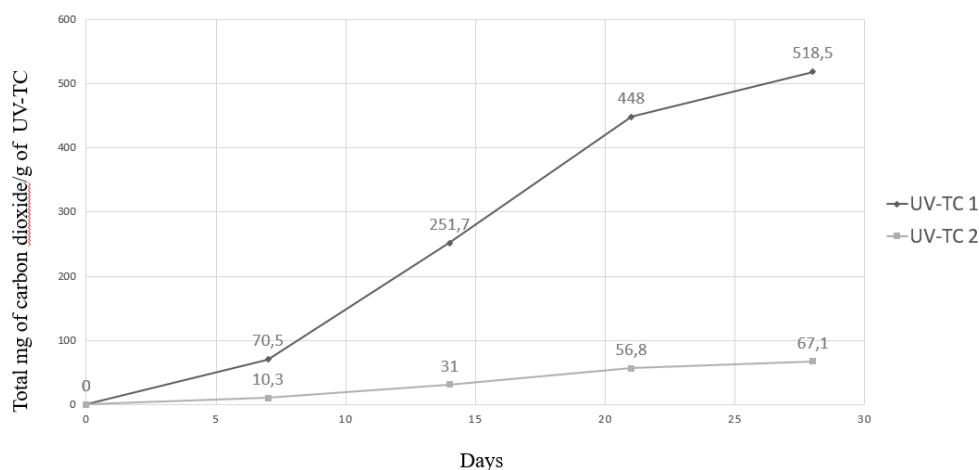


Figure 4. Results of the biodegradability test.

No particular problems were highlighted in the preparation of UV-TCs since the various UV-PUDs developed demonstrated the same characteristics in the formulation phase as common PUDs.

Given the use of ultraviolet radiation for the curing it was decided to use aliphatic isocyanates in order to avoid absorption interferences that depress the formation of radicals. The production of UV-curable

aromatic polyurethane acrylates is possible but it is done on much more reactive systems than those described here. The choice fell on IPDI for two reasons: the different reactivity of the two isocyanic groups which prevents the formation of undesirable substances during the preparation phases of the UV curable prepolymer and the good flexibility imparted to the films produced by the polyurethane dispersions prepared with it (Ono Jones, Pappas 1985; Dall Agnol et al. 2021).

In order to obtain a good elongation at break, it is necessary to reduce the degree of cross-linking of the cured polymer (Maurya et al. 2018). The goal, in fact, is not to cross-link a still-fluid finish. Rather, the aim is only to increase performance, as it is done with classic curing agents. To do this it is necessary to construct UV curable prepolymers that are linear and possess a low molar density of double bonds. In this manner it is possible to obtain cured polymers with high elongation at break (Chen et al. 2024; Weikard et al. 2004). The resins developed in this project in fact have double bond densities between 0.18 and 0.80 mmol/g. Looking at the technical material provided by the manufacturers, we find that this value, in the currently commercially available raw materials, is usually between 4 and 8, in some cases it drops below 2.5, while values lower than 1 are very rare and for niche applications. On the other hand, however, UV-curable polymers with such a low density of double bonds can suffer of poor tensile strength and scratch resistance because of poor reticulation. Therefore, a good balance between mechanical properties and elasticity is crucial for the success of the project. We found two promising ways to achieve the goal. The first is to construct polyurethane polyureas with a low density of double bonds, so that the formation of stronger hydrogen bonds in the hard domains provides higher mechanical strengths to the prepolymer. The second method is the careful selection of polyols and eventually combination with the previous one. A good choice to achieve good results can be using polyesters polyols. Indeed, the film that can be obtained have a higher Young's modulus compared with similar ones prepared with polyether polyols such as PPG or PTHF. This is due to the formation of hydrogen bonds between the soft segments resulting in improved mixing between hard and soft phases (Kim 1996). Both of these methods decrease the percentage of elongation at break, but a good compromise between percentage of elongation and resistance to elongation is in fact essential for these applications as top coats. A third option, already explored in the leather industry, would be the two-component dual curing using both UV and classic crosslinkers such as polyisocyanates. In this work this option has not been taken into consideration as our goal is to eliminate the use of external crosslinkers.

4. Conclusion

A series of one-component UV curable water-based products for leather finishing has been developed. The products have been prepared starting from aqueous dispersions of polyurethane acrylates developed in this work. The top coats, once applied, dried and crosslinked with a short irradiation under UV lamp have shown performances similar to the traditional bicomponent products already widespread in the leather industry. Bio-based versions of the UV-PUDs have been successfully prepared.

5. Acknowledgement

Thanks to Prof. Mammi S. of the University of Padua and the doctors Honisch C. and Ruzza P. of the CNR for their contribution to the characterization of the materials. Thanks also to Dr. Mattia Fiorasi and Dr. Anna De Rossi for their support in the laboratory work.

6. References

1. Ali, K. M. Idriss, Mubarak A. Khan, e M. Niazul Islam «Upgrading of Wet Blue Leather Surface by UV Cured Coating». *Journal of Applied Polymer Science* **66**(1): 11–18, 1997.
2. Baysal, Gülçin, Berdan Kalav, e Burçak Karagüzel Kayaoğlu «Effect of Pigment Colour on the Printing Performance of Synthetic Leather Using a Ultraviolet-curable Water-borne Polyurethane Acrylate Binder». *Coloration Technology* **135**(4): 283–9, 2019.
3. Cariolato, Massimo, Diego Tezza, e Giancarlo Lovato, «Unpublished results, Corichem s.r.l.»
4. Chen, Lei, Yongchang He, Lu Dai, Wang Zhang, Hao Wang, e Peng Liu. «High-Stretchable and Transparent Ultraviolet-Curable Elastomer». *Polymers* **16**(24): 3464, 2024.
5. Christian Decker; Kinetic «Analysis and Performance of UV-Curable Coatings». In *Radiation Curing*, Boston, MA: Springer US, 135–79, 1992.
6. Dall Agnol, Lucas, Fernanda Trindade Gonzalez Dias, Heitor Luiz Ornaghi, Marco Sangermano, e Otávio Bianchi, «UV-Curable Waterborne Polyurethane Coatings: A State-of-the-Art and Recent Advances Review». *Progress in Organic Coatings* **154**: 106156, 2021.
7. Decker, Christian. «UV -radiation Curing Chemistry». *Pigment & Resin Technology* **30**(5): 278–86, 2001.
8. Khan, Mubarak A., Ruhul A. Khan, B. S. Aliya, e M. Niazul Islam, «Modification of wet blue leather surface by photo-curing with urethane acrylate containing dye». *Journal of Macromolecular Science, Part A* **39**(7): 723–44, 2002.
9. Khan, Mubarak A., M. Mizanur Rahman, e Z. R. Bhuiyan, «Effect of Co-Monomers on the Improvement of Crust Leather Surfaces Cured under UV Radiation». *Polymer-Plastics Technology and Engineering* **41**(3): 541–59, 2002.
10. Khan, Mubarak A., M. Mizanur Rahman, M. Z. R. Bhuyan, e M. U. Ahmad, «Curing of Crust Leather by Ultraviolet Radiation with Urethane Acrylate: Role of Pigment». *Journal of Applied Polymer Science* **86**(3): 692–97, 2002.
11. Kim, B. K., «Aqueous Polyurethane Dispersions». *Colloid & Polymer Science* **274**(7): 599–611, 1996.
12. Mark D. Soucek ; Xiaofeng Ren, «UV-Curable Coating Technologies», In *Photocured Materials*, The Royal Society of Chemistry, 15–48, 2014.
13. Maurya, Shyam Dev, S. K. Kurmvanshi, S. Mohanty, e Sanjay K. Nayak, «A Review on Acrylate-Terminated Urethane Oligomers and Polymers: Synthesis and Applications». *Polymer-Plastics Technology and Engineering* **57**(7): 625–56, 2018.
14. Noble, Karl-Ludwig, «Waterborne Polyurethanes». *Progress in Organic Coatings* **32**(1–4): 131–36, 1997.
15. Ono, Hiro-Kuni, Frank N. Jones, e S. Peter Pappas, «Relative Reactivity of Isocyanate Groups of Isophorone Diisocyanate. Unexpected High Reactivity of the Secondary Isocyanate Group». *Journal of Polymer Science: Polymer Letters Edition* **23**(10): 509–15, 1985.
16. Uddin, M. Khabir, Mubarak A. Khan, e K.M. Idriss Ali, «Development of Polymer Films and Its Application on Leather Surfaces». *Journal of Applied Polymer Science* **60**(6): 887–95, 1996.

17. Weikard, Jan, Erhard Fischer, Erhard Lühmann, e Diethelm Rappen. «UV-cured and elastomeric coatings - a contradiction?», *RadTech e|5 2004 Technical Proceedings*, 2004.