



EFFECT OF ISOCYANATE AS CROSS-LINKER TO REDUCE DELAMINATION OF FINISHED LEATHER FOR AUTOMOTIVE SEAT COVER

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EFFECT OF ISOCYANATE AS CROSS-LINKER TO REDUCE DELAMINATION OF FINISHED LEATHER FOR AUTOMOTIVE SEAT COVER

ABSTRACT. This study aims to improve the quality of finished leather for seat covers by knowing the effect of isocyanate as a cross-linker to reduce delamination on the finished leather. Delamination is a condition where the three layers of finish (base coat, medium coat, and top coat) do not stick together, resulting in the lifting of the top coat during the adhesion test. The raw material used in the trial is C60 quality crust dyed cowhide, 1.1 mm to 1.4 mm thick with an area of ± 3 sqft. The stages of the finishing process include semi-finished selection, stacking, spraying (base coat), rest, stacking, roller embossing, rest, milling, stacking, spraying (medium coat, top coat), rest, stacking, laboratory, and measuring. The formulation of the improved seat cover article was carried out by increasing the percentage of cross-linker in the base coat mixture. The production formulation used 2% cross-linker, trial 1 used 3% cross-linker, and trial 2 used 4% cross-linker. The best results are with the addition of 4% cross-linker to reduce delamination and have an adhesion resistance value of 24.5 N. The conclusion is that the greater the addition of cross-linker as much as 4% in the base coat of the article seat cover will reduce delamination, increase thickness from 1.1 mm to 1.2 mm, improve color fastness resistance to a value of 4, and reduce softness value from 3.92 mm to 3.42 mm.

KEY WORDS: leather, cross-linker, delamination, adhesion

INFLUENȚA IZOCIANATULUI CA RETICULANT ÎN VEDEREA REDUCERII EXFOLIERII PIEILOR FINISATE DESTINATE TAPIȚERIEI AUTO

REZUMAT. Acest studiu își propune să îmbunătățească calitatea finisajului pieilor pentru tapițerie auto prin determinarea efectului izocianatului ca agent de reticulare în vederea reducerii exfolierii pielii finisate. Exfolierea este un fenomen în care cele trei straturi de finisaj (strat de bază, strat intermediar și strat superior) nu rămân lipite, ceea ce duce la desprinderea stratului superior în timpul testului de aderență. În studiu s-a folosit ca materie primă pielea bovină crust vopsită de calitate C60, cu o grosime de 1,1 mm până la 1,4 mm, cu o suprafață de ± 3 m². Etapele procesului de finisare includ selecția semifabricatelor, stivuire, pulverizare (strat de bază), repaus, stivuire, imprimare model, repaus, vâlcuire, stivuire, pulverizare (strat intermediar, strat superior), repaus, stivuire, testare de laborator și măsurare. Formula pentru produsul îmbunătățit de finisare a pielii pentru tapițerie auto a fost realizată prin creșterea procentului de agent de reticulare din amestecul pentru stratul de bază. Pentru formula de bază s-a folosit 2% agent de reticulare, pentru varianta 1 s-a folosit 3% agent de reticulare, iar pentru varianta 2 s-a folosit 4% agent de reticulare. Cele mai bune rezultate au fost obținute la adăugarea de 4% reticulant pentru a reduce exfolierea, variantă pentru care s-a determinat o valoare a rezistenței aderenței de 24,5 N. În concluzie, cantitatea de reticulant mai mare, de 4%, în stratul de bază al produsului pentru finisarea pielii destinate tapițeriei auto reduce exfolierea pielii, crește grosimea de la 1,1 mm la 1,2 mm, îmbunătățește rezistența culorii la o valoare de 4 și reduce valoarea moliciunii de la 3,92 mm la 3,42 mm.

CUVINTE CHEIE: piele, reticulant, exfoliere, aderență

L'EFFET DE L'ISOCYANATE COMME RÉTICULANT POUR RÉDUIRE LE DÉLAMINAGE DU CUIR FINI DESTINÉ AU GARNISSAGE AUTOMOBILE

RÉSUMÉ. Cette étude vise à améliorer la qualité de finition des cuirs pour le garnissage automobile en déterminant l'effet de l'isocyanate en tant qu'agent de réticulation afin de réduire le délaminage du cuir fini. Le délaminage est un phénomène où les trois couches de la finition (couche de base, couche intermédiaire et couche de finition) ne restent pas collées, ce qui entraîne le décollement de la couche de finition lors du test d'adhérence. Une peau bovine en croûte teinte de qualité C60, de 1,1 mm à 1,4 mm d'épaisseur, d'une surface de ± 3 m² a été utilisée comme matière première dans l'étude. Les étapes du processus de finition comprennent la sélection des semi-fabriqués, l'empilement, la pulvérisation (couche de base), le repos, l'empilement, l'impression du motif, le repos, le foulage, l'empilement, la pulvérisation (couche intermédiaire, couche de finition), le repos, l'empilement, les tests et mesures en laboratoire. La formule de la finition améliorée du cuir pour le garnissage automobile a été réalisée en augmentant le pourcentage d'agent de réticulation dans le mélange de la couche de base. Pour la formule de base, 2 % d'agent de réticulation ont été utilisés, pour la variante 1, 3 % d'agent de réticulation ont été utilisés et pour la variante 2, 4 % d'agent de réticulation ont été utilisés. Les meilleurs résultats ont été obtenus avec l'ajout de 4 % d'agent de réticulation pour réduire le délaminage, pour lequel une valeur de force d'adhérence a été déterminée de 24,5 N. En conclusion, la plus grande quantité d'agent de réticulation, 4 %, dans la couche de base du produit de finition du cuir pour le garnissage automobile réduit le délaminage du cuir, augmente l'épaisseur de 1,1 mm à 1,2 mm, améliore la solidité des couleurs à une valeur de 4 et réduit la valeur d'assouplissement de 3,92 mm à 3,42 mm.

MOTS CLÉS : cuir, agent de réticulation, délaminage, adhérence

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INTRODUCTION

The quality testing of finished leather is important because consumer judgment heavily depends on it. Therefore, several things need to be considered in developing finished leather, namely the need to understand the skin's structure, the selection of raw materials and chemicals, and process control. The product development aims to improve quality so that consumers can accept it. According to Wiyodiningrat *et al.* (2012), the skin must have good quality, no defects due to insect/parasite bites, imperfections due to wounds/scratches, and others. The selling price has a high added value [1]. In the development of the leather processing industry, it is necessary to improve the basis of processing and testing technology to produce higher quality leather, and to be able to follow the development of fashion (fashionable), so that both local and international markets can accept it. One type of leather that can penetrate the global market is upholstery leather.

Upholstery leather is tanned using chrome tanning material, vegetable tanning material, or a combination of both with synthetic tanning materials (syntan) [1, 2]. They are made from whole cow and buffalo leather (whole hide).

Making quality upholstery leather requires a layer of granules [1]. Upholstery leather is usually used to make car seats and furniture-making materials, each of which has technical requirements according to its needs [1, 3]. Upholstery leather is very different from upper shoes regarding chemical properties and use. Upholstery leather is resistant to various temperatures, so it will not stick when hot or crack when the temperature is low. Currently, nitrocellulose has been replaced with a dispersed resin, which can be used as a binder in the finishing process [4].

Purnomo (2011) says that leather generally undergoes a stage called finishing, even though it is done very simply [5]. Efforts to improve the appearance of finished leather aim to increase its attractiveness and selling power. The repair process includes repairing existing defects caused by natural defects, storage (wounds, disease marks, and insects), and those that occur during the process. These defects include uneven and faded colors and do not match color standards. This needs to be repaired and perfected, even if only to adjust the hue, shading, and color tone. Finishing is also done for specific purposes, such as giving a different look, pattern, touch/feel/handle, softer, smoother, rougher, oily, waxy, silky, contrasting color, brilliant, pull-up, antique, two-tone, and others. The object of finishing is to give specific properties to the surface/grain and simultaneously highlight and maintain the natural properties of the leather. In general, there are three layers in the leather finishing stage: the base coat layer, the color coat layer, and the top coat layer.

The excellent adhesion of the initial and base coats greatly influences the following process. Therefore, the use of quality materials needs attention [6]. The ingredients' composition affects the leather surface's absorption properties and the finished leather's degree of penetration. Adhesion is also influenced by the mechanical application type, which is the drying method. The adhesion of the finished leather is tested by a quick reference test in which an adhesive tape is applied to the leather specimen. Quantitative measurement of adhesion is carried out in a tensile strength tester. The leather specimen is attached to a strong support surface using a two-component adhesive for a specified time.

Delamination is a type of layer deformation in a laminated material caused by stress and pressure on the material [7, 8]. Based on ISO 11644:2009, delamination is obtained by testing the grain of the leather strip that has been glued to the adhesive plate using an adhesive film. Delamination occurs if, during the test, the top layer or individual layers stick to the adhesive plate. One way to minimize the occurrence of delamination on the skin is usually done by cross-linking. Cross-linking is joining two polymer molecular chains by bridging between elements, groups, or compounds that are joined by carbon atoms in the main chain of chemical bonds [9].

Cross-linkers are chemical substances that react with various functional groups to make polymer binders through cross-linking. Binder polymers are polymers that are capable of forming upon drying the surface of the film layer. There are three types of polymer binders in leather

finishing: acrylic, butadiene, and polyurethane [10]. Each binder polymer has its properties and characteristics depending on the cross-linker used to form the cross-linking. The bond structure of the polyurethane binder has high strength and cohesion energy and produces more strong bond strength [11]. The formation of cross-linking will also result in the finished leather becoming more resistant to friction, to water and solvents, to adhesion, and to abrasion [12-14]. Therefore, the formation of cross-linking in polyurethane binders is very important [15]. Polyurethane binders are formed due to the reaction between isocyanate groups ($R - N = C = O$) with hydroxyl groups (OH). This study will use isocyanate compounds in the form of polyurethane binders as cross-linkers. Isocyanate compounds have an -NCO functional group that will interact with the hydroxyl group (-OH) of the binder, which occurs at low temperatures ($< 150\text{ }^{\circ}\text{C}$) [16, 17]. Variations in the use of isocyanate as a cross-linker are expected to provide optimum conditions in producing finished leather for automotive seat cover.

EXPERIMENTAL

Materials and Methods

Materials

The materials that have been used in the research are crust-dyed leather with quality: C60, thickness 1.1-1.4 mm, 3 sqft, isocyanate (cross-linker), Compound Manama DLH, polyurethane, silicon, wax, pasta color, H_2O . All materials are of technical grade.

Methods

The crust-dyed leather that has been used previously has gone through a conventional process consisting of soaking, liming, deliming, bating, pickling, tanning, retanning, dyeing, fat liquoring, fixing, and so on. At the finishing stage, the variation has been done by using isocyanate as a cross-linker on the base coat, medium coat, and top coat, according to Table 1. The finished leather is then analyzed for adhesion resistance, thickness, color-fastness, and softness. Analysis refers to ISO 11644:2009(E) IULTCS/IUF 470:2009(E).

Table 1: Formulation of Base, Medium, and Top Coat Finished Leather for Automotive Seat Cover

Parameters	Formulation		
	A1 (2%)	A2 (3%)	A3 (4%)
1. Base coat			
Compound Manama DLH	1000	1000	1000
Pasta color	100	100	100
Isocyanate	22	33	44
2. Medium coat			
Water		240	
Silicone		30	
Polyurethane		760	
Pasta color		100	
Isocyanate		79.03	
3. Top coat			
Water		235	
Silicone		102	
Wax		40	
Polyurethane		676	
Isocyanate		147.44	

RESULTS AND DISCUSSIONS

The process of forming cross-linking between the hydroxyl group (-OH) on the binder and the -NCO group on the isocyanate will result in strong cross-linking as shown in Figure 1. This interaction

occurs after the C=N double bond is broken to form a carbonyl (positive charge). The hydroxyl group will be free to attack the carbonyl by releasing hydrogen. So that cross-linking will be formed between isocyanate and hydroxyl groups to form polyurethane binders. The cross-linking is expected to reduce the delamination on finished leather for automotive seat cover so that high-quality products are produced.

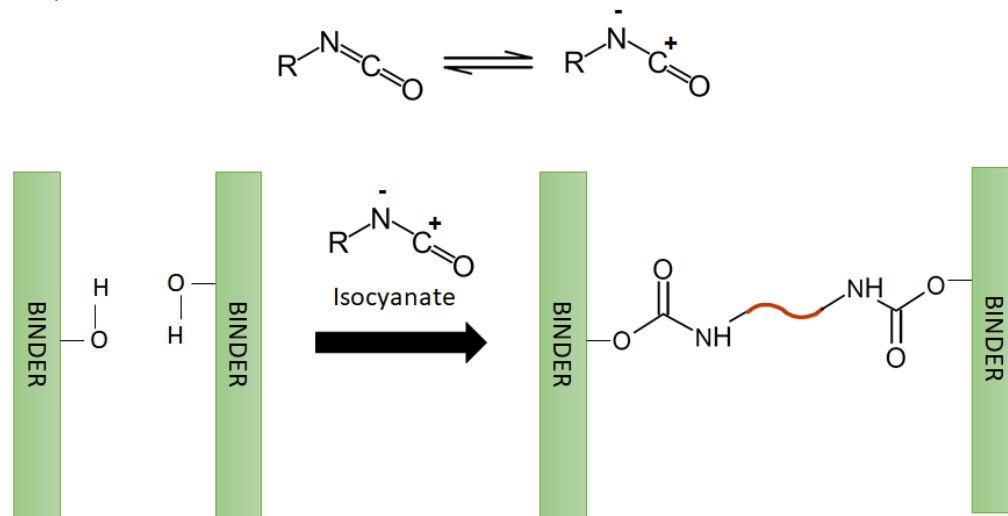


Figure 1. Interaction of hydroxyl group from the binder and isocyanate group as cross-linker

The adhesion resistance test is a test to measure the resistance of the finishing layer to be separated from the substrate (leather). The finishing formulation for finished leather for automotive seat cover uses 2% cross-linker isocyanates (A1) with an adhesion resistance value of 12.4 N. However, the A1 formulation has a delamination result that is not following the standard (ISO 11644:2009(E) IULTCS/IUF 470:2009(E)), namely peeling off the top coat without being followed by a base coat layer (Figure 2a). The adhesion resistance test for finished leather for automotive seat cover, which uses 3% cross-linker isocyanates (A2), has decreased by 11.9 N. This result still follows the standard, which is more than 3 N (Figure 2b). The results of the adhesion resistance test from finished leather for automotive seat cover with 4% cross-linker isocyanates (A3) also showed good delamination; namely, the three finishing layers (base coat, medium coat, and top coat) appeared to stick together and peel off so that the leather on the crust was visible at 24.5 N (Figure 2c).

The addition of a cross-linker in the base coat indicates an increase in the force required to separate the finishing layer from the leather. The results of the adhesion resistance test of the A3 formulation were more excellent than the A1 and A2 formulations of the adhesion resistance test. This indicates that the delamination process decreases in the A3 formulation. This shows that more use of cross-linker in the base coat can improve the inter-coat adhesion on the automotive seat cover finishing layer.

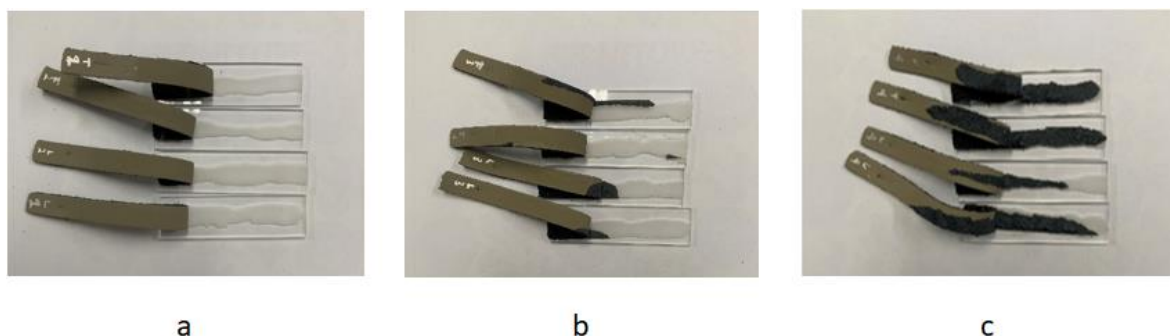


Figure 2. Adhesion test on Finished Leather for Automotive Seat Cover Using Isocyanate (a) 2%, 12.4 N adhesion resistance (b) 3%, 11.9 N adhesion resistance; and (c) 4%, 24.5 N adhesion resistance

One of the parameters to determine the quality of finished leather for automotive seat cover is the thickness test. The thickness test on the finished leather for automotive seat cover is a combination of the thickness of the crust leather and the finishing layer or the total of the finished leather. The higher the ratio between (NCO):(OH), the faster the finishing layer will dry [18-20]. The faster the finishing layer dries, the less absorption it will have on the leather, so it will cause the finishing layer on the leather surface to be thicker. The standard thickness of finished leather for automotive seat cover is usually in the range of 1.0-1.4 mm. The thickness of the finished leather for the sample formulations A1, A2, and A3 was 1.1; 1.2; and 1.2 mm (Table 2).

Table 2: Test result for Finished Leather for Automotive Seat Cover

Parameters	Cross-linker variation formulation		
	A1 (2%)	A2 (3%)	A3 (4%)
Adhesion Resistance (N)	12.4	11.9	24.5
Thickness (mm)	1.1	1.2	1.2
Color-fastness to Dry Rubbing	-	-	4
Color-fastness to Wet Rubbing	-	-	4
Color-fastness to Rubbing with Benzine	-	-	4
Softness (mm)	3.92	3.60	3.42

The color fastness test for finished leather for automotive seat cover was carried out with 3 types of tests using dry felt, wet felt with water, and wet felt with petrol/benzine. The color fastness test on dry felt was carried out for 2000 cycles with a minimum value of 4 (good). The color fastness test standard for wet felt with water is carried out for 1000 cycles per minute with a minimum value of 4 (good). The standard for color fastness testing for wet felt with petrol/benzine is carried out for 10 cycles per minute with a minimum value of 4 (good). The higher the color fastness value, the better the color fastness test of finished leather [7]. This can also indicate that the more cross-linkers are added, the more cross-linking is formed. This can increase the bond strength between layers (base, medium, and top coat) on the finished leather. The more cross-linking that is formed will increase the value of the color fastness of a material [21].

The color fastness test was only carried out on automotive seat covers using the A3 formulation because only the A3 formulation had results without delamination. The color fastness test results of A3 were obtained with a value of 4 (following the standard). The results of the color fastness test can be seen in Figure 3.

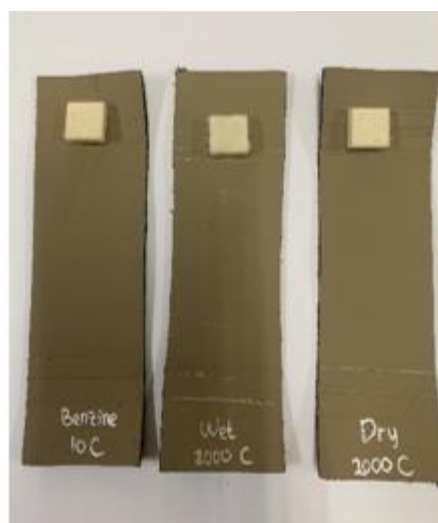


Figure 3. Test Results for Color fastness Formulation A2 with 4% cross-linker

Softness testing of finished leather for automotive seat cover has a standard of 3-4 mm. The results of testing the sample formulations A1, A2, and A3 obtained 3.92, 3.60, and 3.42 mm, respectively. Then the addition of a cross-linker results in a reduction in the softness of the finished leather. This could be due to the cross-linker isocyanates being very easily dispersed into a dilute mixture. These materials have high reactivity and can be used on the base and top coats. Polyisocyanates are used to harden polyurethanes through crosslinking reactions (Fig. 1) and are related to previous research [22, 23]. Softness testing of finished leather for automotive seat cover has a standard of 3-4 mm. If the thickness of the finished leather for automotive Seat cover is <3 mm, it will increase the air permeability but can also decrease the dimensional stability of the leather, so it is not suitable for finished leather for automotive seat cover [24].

CONCLUSIONS

The addition of isocyanate as a cross-linker by 4% in the automotive seat cover base coat can reduce delamination, increase the thickness from 1.1 mm to 1.2 mm, improve the color fastness resistance to a value of 4, and reduce the softness value from 3.92 mm to 3.42 mm. The greater the addition of isocyanate as a cross-linker can improve the quality of finished leather for automotive seat cover.

REFERENCES

1. Wiyodiningrat, S., Setyamurti, R., Pahlawan, I.F., Research on Making Environmentally Friendly Upholstery Leather / Carseat for Automotive, *Majalah Kulit, Karet Dan Plastik*, **2012**, 28, 1, 09-17, <https://doi.org/10.20543/mkpp.v28i1.200>.
2. Gaoming, C., Bingzhang, L., Bo, L., *A Study of Cattle Hide Automobile Upholstery*, Beijing: China Leather Industry Research Institute, **2011**.
3. Cech, P. and Stadnik, J., VOC Emissions from Natural Upholstery Leathers, *Polish Journal of Environmental Studies*, **2021**, 30, 6, 4945-4955, <https://doi.org/10.15244/pjoes/134851>.
4. Thorstensen, T., *Practical Leather Tehnology*, 4th edition. Florida. New York: Robert E. Keiger Publishing Company Malabar, **1993**.
5. Purnomo, E., *Softy Leather*. Yogyakarta: Politeknik ATK Yogyakarta, **2011**.
6. John, G., *Possible Defects in Leather Production*. Hemsbach: Lampertheim, **1997**.
7. Suriani, M.J., Rapi, H.Z., Ilyas, R.A., Petru, M., Sapuan, S.M., Delamination and Manufacturing Defects in Natural Fiber-Reinforced Hybrid Composite: A Review, *Polymers*, **2021**, 13, 1323, <https://doi.org/10.3390/polym13081323>.
8. Patten, E.W., Atwood, S.A., Van Citters, D.W., Jewett, B.A., Pruitt, L.A., Ries, M.D., Delamination of a Highly Cross-Linked Polyethylene Liner Associated with Titanium Deposits on the Cobalt-Chromium Modular Femoral Head Following Dislocation, *J Bone It Surg (Br)*, **2010**, 92-B, 9, 1306-1311, <https://doi.org/10.1302/0301-620X.92B9.24290>.
9. Musa, B.H., Hameed, N.J., Effect of Crosslinking Agent (Glutaraldehyde) on the Mechanical Properties of (PVA/Starch) Blend and (PVA/PEG) Binary Blend Films, *J Phys Conf Ser*, **2021**, 1795, 1, 012064, <https://doi.org/10.1088/1742-6596/1795/1/012064>.
10. Olle, L., Bacardit, A., Morera, J.M., Bartoli, E., Argelich, J., Cross-linked Polymers for Aqueous Finishing. Binders Crosslinked with Polyaziridine. Part I: Behaviour of Polyurethane, *J Soc Leather Technol Chem*, **2008**, 92, 3, 96-102.
11. Sun, M., Bi, Y., Zhuang, W., Chen, S., Zhao, P., Pang, D., Zhang, W., Mechanism of Polyurethane Binder Curing Reaction and Evaluation of Polyurethane Mixture Properties, *Coatings*, **2021**, 11, 1454, <https://doi.org/10.3390/coatings11121454>.
12. Sarkar, K., *Theory and Practice of Leather Manufacture*, Mahatma Gandhi road. Madras: Second Avenue, **1995**.
13. Bacardit, A., Shendrik, A., Combalia, F., Jorge, J., Olle, L., Study of Cross-Linking Reactions on Butadiene Binders in Aqueous Finishing, *J Soc Leather Technol Chem*, **2010**, 94, 248-253.

14. Cheaburu-Yilmaz, C.N., Ozkan, C.K., Yilmaz, O., Synthesis and Application of Reactive Acrylic Latexes: Effect of Particle Morphology, *Polymers (Basel)*, **2022**, 14, 11, 2187, <https://doi.org/10.3390/polym14112187>.
15. Olle, L., Frias, A., Sorolla, S., Cuadros, R., Bacardit, A., Study of the Impact on Occupational Health of the Use of Polyaziridine in Leather Finishing Compared with a New Epoxy Acrylic Self-Crosslinking Polymer, *Prog Org Coat*, **2021**, 105, 106162, <https://doi.org/10.1016/j.porgcoat.2021.106162>.
16. June, Y.-G., Jung, K.I., Choi, M., Lee, T.H., Noh, S.M., Jung, H.W., Effect of Urethane Crosslinking by Blocked Isocyanates with Pyrazole-Based Blocking Agents on Rheological and Mechanical Performance of Clearcoats, *Coatings*, **2020**, 10, 961, <https://doi.org/10.3390/coatings10100961>.
17. Panwiriyarat, W., Tanrattanakul, V., Pillard, J.-F., Pasetto, P., Khaokong, C., Effect of the Diisocyanate Structure and the Molecular Weight of Diols on Bio-Based Polyurethanes, *J Appl Polym Sci*, **2013**, 130, 1, 453-462, <https://doi.org/10.1002/app.39170>.
18. Liow, K.S., Sipaut, C.S., Mansa, R.F., Ung, M.C., Ebrahimi, S., Effect of PEG Molecular Weight on the Polyurethane-Based Quasi-Solid-State Electrolyte for Dye-Sensitized Solar Cells, *Polymers*, **2022**, 14, 3603, <https://doi.org/10.3390/polym14173603>.
19. Gogoi, R., Alam, M., Khandal, R., Effect of Increasing NCO/OH Molar Ratio on the Physicomechanical and Thermal Properties of Isocyanate Terminated Polyurethane Prepolymer, *Int J Basic Appl Sci*, **2014**, 3, 2, 118-123, <https://doi.org/10.14419/ijbas.v3i2.2416>.
20. Sebenik, U., Krajnc, M., Influence of the Soft Segment Length and Content on the Synthesis and Properties of Isocyanate-Terminated Urethane Prepolymers, *Int J Adhes Adhes*, **2006**, 27, 7, 527-535, <https://doi.org/10.1016/j.ijadhadh.2006.10.001>.
21. Lv, Z., Tan, T., Hussain, M., Zhou, W., Ma, M., Effects of Crosslinking Sericin on the Color Fastness and Antioxidant Activity of Naturally Colored Silk, *Fibers Polym*, **2022**, 23, 658-665, <https://doi.org/10.1007/s12221-022-3082-y>.
22. Ahmed, S., Zohra, F.-T., Ecological Aspects of Cross Linking Agents and Their Role in Leather Finishing for the Production of Finished Leather, *LeatherAge*, **2011**, XXXIII, 2, 67-71.
23. Rosita, G., Changes in the Formation Characteristics of Polyurethane Based on HTPB and TDI Reaction Composition, *Jurnal Teknologi Dirgantara*, **2016**, 14, 2, 159-170, <https://doi.org/10.30536/j.jtd.2016.v14.a2420>.
24. Roh, E.K., Effect of Punching on Physical and Mechanical Properties of Leathers: Focus on Car Seat Covers, *Journal of Engineered Fibers and Fabrics*, **2019**, 14, <https://doi.org/10.1177/1558925019890569>.

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