# A NOVEL RANGE OF PUDs FROM RENEWABLE SOURCES

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## ABSTRACT:

Like any other leather finishing product, a PU water dispersion (PUD) may be produced from ingredients that are, to some extent, obtained from renewable sources.
In fact, the "polyol" component (polyester or polyether), which traditionally comes from petroleum, may be obtained by an alternative chemistry.
Typical examples are the polyether-polyols produced by enzymatic transformation from corn starch, or the polyester-polyols obtained from the synthesis of diols and acids sourced from vegetal or animal oils.
In both cases the polyurethane obtained by poly-addition between a diisocyanate and one of these polyols will have a partial bio-material content and therefore it may be classified as a polymer from a partially renewable source.
From this assumption, a full range of polyurethane water dispersions with bio-content ranging from 50 to 75% on solids have been formulated, produced and tested for conventional leather finishing and for transfer finishing by release papers as well. They proved to act as fine binders with high hydrolytic resistance and excellent physical-mechanical profiles.
These polyurethanes - when employed as main binders or co-binders in finishing recipes, specially if other components are choosen among the available bio-based materials like natural oils and waxes, proteins, etc. - may help the finisher to obtain finished leather articles with high bio-based content and, by this way, to contribute to the sustainable requirements that are nowadays important.

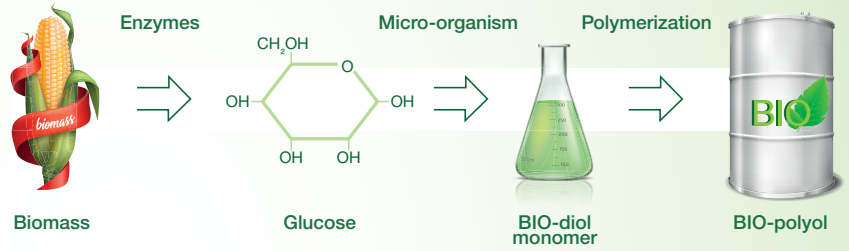
## MATERIALS AND METHODS:

Several poliols from renewable sources were selected, among the ones available in the market, and they were evaluated for the production of waterbased polyurethane dispersions:

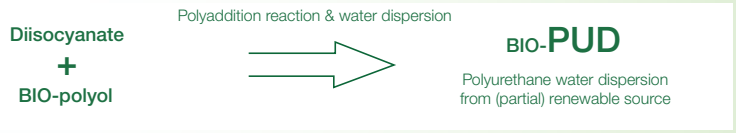
- polyether polyols produced from bio-1,3-propanediol (bio-PDO) and bio-1,4-butandiol (bio-PTMEG) obtained by fermentation processes of sugars derived from vegetal feedstocks
- polyester polyols from acids and/or glycols obtained from renewable sources

PUDs were produced via prepolymer method by reaction with both the common aliphatic diisocyanates typically used for leather coating binders (IPDI and H12MDI).
Water dispersion of the prepolymers was possible by using Dimethylolpropionic acid (DMPA) neutralized with Triethylamine (TEA) and/or Dimethylethanolamine (DMEA) and chain extension was carried out with Idrazine or Ethylendiamine.

### BIO-Polyol production




### BIO-PUD production




## RESULTS AND DISCUSSION:

Among the polyols evaluated, the final choice fell on polyether diols because they confer to the final polymers (listed on the below tables) better hydrolysis resistance, as theoretically expected, compared to polyesters.

| PRODUCT | POLYOL NATURE | DIISOCYANATE | SOLID CONTENT % | SOLVENT % | % BIO ON SOLIDS |
|---|---|---|---|---|---|
| PUD 1 | POLYETHER | IPDI | 35 | 2 | 58 * |
| PUD 2 | POLYETHER | IPDI | 35 | 2.4 | 75 * |
| PUD 3 | POLYETHER | H12MDI | 35 | 3 | 52 ** |
| PUD 4 | POLYETHER | H12MDI | 30 | 3 | 56 ** |

* ASTM D6866
** calculated

| PRODUCT | NATURE | HARDNESS (° Sh A) | MODULUS 100% (N/mm2) | % ELONGATION | POSSIBLE USE IN CONVENTIONAL FINISHING | POSSIBLE USE IN RANSFER FINISHING |
|---|---|---|---|---|---|---|
| PUD 1 | POLYETHER | 70 | 3.5 | 700 | BASECOATS | SKIN |
| PUD 2 | POLYETHER | 72 | 4.0 | 600 | BASECOATS | SKIN |
| PUD 3 | POLYETHER | 85 | 5.5 | 1100 | GENERAL PURPOSE | PRE-SKIN |
| PUD 4 | POLYETHER | 90 | 9.0 | 500 | TOPCOATS | PRE-SKIN |

## CONCLUSIONS:

Using PUDs produced from renewably sourced diols it's possible to finish leathers with a significant biobased content without compromising their performances, functionality and aesthetic aspects, which are basically the same obtained with conventional petroleum based raw materials.
The advantage is a sensible reduction of the environmental footprint of the final articles that will be more eco-sustainable, as requested by the current market trends.

**REFERENCES:** David De Smet, Madeleine Wèry, Willem Uyttendaele, Myriam Vanneste Bio-based waterborne PU for durable textile coatings - Polymers (Basel), 2021Dec; 13(23): 4229

Tenorio-Alfonso, A., Sánchez, M.C. & Franco, J.M. A Review of the sustainable approaches in the production of bio-based polyurethanes and their applications in the adhesive field. J Polym Environ 28, 749–774 (2020)

Ewa Glowinska, Wojciech Wolak, Janusz Datta Eco-friendly route for thermoplastic polyurethane elastomers with bio-based hard segments composed of bio-glycol and mixtures of aromatic–aliphatic and aliphatic–aliphatic diisocyanate. Journal of Polymers and the Environment 29, 2140-2149 (2021)