MELAMINE ETHOXYLATES: NOVEL FORMALDEHYDE FREE RESIN RE-TANNING AGENTS

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Abstract. Melamine urea formaldehyde condensates or resin re-tanning agents are commonly used in the leather industry. They give rise to homogeneous filling, are easily and widely applicable, but generally contribute to free formaldehyde, measurable in emission or extraction methods from leather. Many projects to resolve this issue have been carried out. The weakness of the resin re-tanning is the reversibility of the bond formation between formaldehyde and two amino groups. The formaldehyde forms a methylene group after condensation with two amino groups and releases water. This methylene group can be hydrolyzed under acidic conditions to release formaldehyde again.

Melamine ethoxylates were found to be a formaldehyde free, stable, and easily applicable alternative. Besides the facts that they are made without formaldehyde, it proved to be possible to incorporate renewable components into the synthesis, giving rise to an even more sustainable product. Another sustainable aspect of this chemistry is the delivery of the potential product as a concentrated liquid versus most resin re-tanning agents being placed into the market as spray dried powders to remove the water in which they are made, consuming significant amounts of energy.

Melamine ethoxylates show advantages in comparison to a classical resin re-tanning agent in application on leather. An insight into the scope of application will be given, showing that melamine ethoxylates can be considered a formaldehyde free replacement for resin re-tanning agents.

1 Introduction

Within the leather making process the re-tanning step has the role to determine main leather article properties like fullness, softness, grain tightness, fastness properties, and tear strength. Major classes of re-tanning agents are phenol formaldehyde condensates and melamine urea formaldehyde condensates. Depending on the chemistry, rest monomeric phenol, formaldehyde or bisphenol S can be a problem with the phenol formaldehyde condensates (1), also known as syntans. Besides melamine urea formaldehyde also urea formaldehyde condensates are applied in re-tanning agents, representing another class, commonly referred to as resins. Both, melamine urea formaldehyde and urea formaldehyde condensates have similar properties on leather and face the same problem: slow release of formaldehyde. This process will be closer described.

Melamine ethoxylates were developed as an alternative to melamine urea formaldehyde condensates, resolving this problem by avoiding the use of formaldehyde. In their formulation other sustainable aspects were incorporated like partially renewable components and moving away from the energy consuming spray drying process. Application results on a widespread of leather articles and details about fastness properties will be given.

2 Materials and Methods

2.1 Melamine urea formaldehyde condensates

Urea formaldehyde condensates were discovered in 1884 (2). Since the 1930'urea formaldehyde condensates were used as impregnating resins in the production of chipboards. This helped to make the wood industry far more sustainable, since the huge amounts of waste in sawing of trees could be converted to chipboards, which were considered products of value made from waste. Later melamine formaldehyde condensates and melamine urea formaldehyde were developed, giving additional characteristics to chipboards like fire resisting properties.
Melamine formaldehyde condensates we first applied on leather in 1942 as tanning agents in form of a formaldehyde releaser (3). For application as re-tanning agents in leather the water solubility had to be improved. This issue was the same for both melamine urea formaldehyde and urea formaldehyde condensates. We will focus on melamine urea formaldehyde condensates, keeping in mind that problems of these two similar chemistries and approaches to resolve these problems are parallel.
Melamine urea formaldehyde condensates are generally made under moderate basic or acidic conditions in water (5), as can be seen in figure 1. The chain length, reflected in the number "n", is depended mainly on the amount of formaldehyde, but also on other reaction conditions as time and temperature. The bonds deriving from formaldehyde are marked in red.

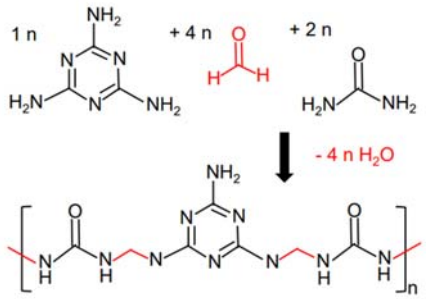

Fig. 1. Synthesis of melamine urea formaldehyde condensates

The issue of improving water solubility could be resolved by adding sulfites to the condensation (4), after having formed a poly condensate with more equivalents of formaldehyde. The sulfite condenses with amino methylol groups deriving from the excess of formaldehyde, releasing water and forming a sulfonic acid group attached to the poly condensate via a methylene group. The resulting structure is depicted in figure 2.

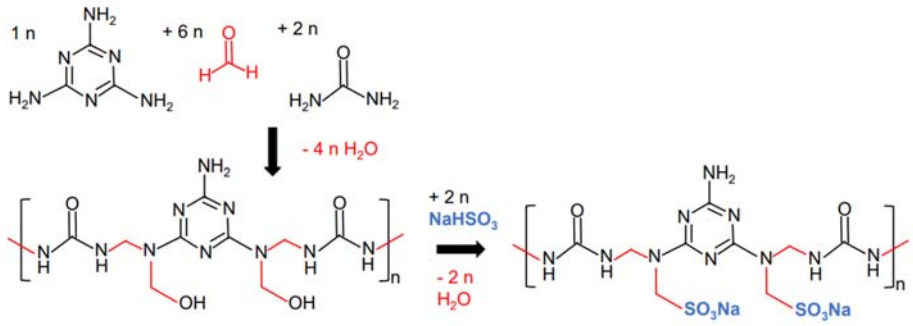

Fig. 2. Water soluble melamine urea formaldehyde condensates

In a basic pH-range the newly formed methylene bridges between two amino group deriving from formaldehyde are quite stable.
The re-tanning process is commonly carried out in floats at acidic pH ranging from pH = 3 to pH = 6. In this pH range the melamine urea formaldehyde condensates are not stable and slowly begin to hydrolyze the methylene, bridging two amino functionalities and releasing formaldehyde. This problem is inherent to this class of chemistry. The speed of hydrolysis is increased by lowering the pH, increasing the amount of acid or increasing the temperature (6). The hydrolysis is depicted in figure 3.

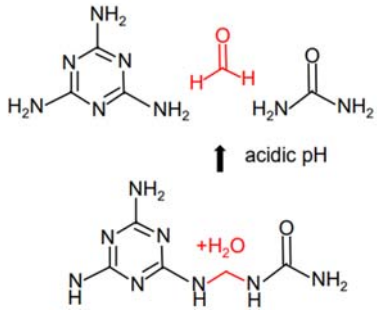

Fig. 3. Hydrolysis of a melamine urea formaldehyde condensate

The release of formaldehyde can be quantified in emission or extraction assays. In the emission test according to UNI EN 27587 a flow nitrogen is blown through a test tube with the pure product as powder product or liquid product. Emitted formaldehyde is carried with the nitrogen flow and directed into a cartridge where the formaldehyde is derivatized. The derivatized formaldehyde can be washed from the cartridge and quantified via High Pressure Liquid Chromatography (HPLC). This method is pH neutral. The pH of the test sample will not change during the test. If the melamine urea formaldehyde condensate is adjusted to a basic pH, low values of formaldehyde will be obtained with this method.
In the extraction assay UNI EN 17226 leathers samples can be analysed for formaldehyde. This is especially interesting for leathers made with formaldehyde condensates. The leathers are cut into pieces, extracted with warm water for a defined time. The aqueous solution is derivatized under acidic condition and the derivatized solution is submitted to High Pressure Liquid Chromatography for quantification. Due to the acidic pH in solution, the melamine urea formaldehyde condensates are prone to partially hydrolize. The acidity originates from strong acids, commonly used to establish the reaction conditions for derivatization with 2,4-di-nitro-phenyl-hydrazine (7).

Consequently, higher values of formaldehyde will be obtained with this method for melamine urea formaldehyde condensates.
From an application view in the leather industry the melamine urea formaldehyde condensates give rise to homogeneous filling, medium softness without compromising on grain tightness, if used in re-tanning.

2.2 Melamine ethoxylates

Various attempts have been made in the past to overcome the formaldehyde release from melamine urea formaldehyde condensates. We developed melamine ethoxylates as a potential alternative to melamine urea formaldehyde condensates and urea formaldehyde condensates. One of the first decisions we had to make was to decide on the chemicals to use. Having had the choice between ethylene oxide and ethylene carbonate, we clearly favored ethylene oxide over ethylene carbonate for sustainability reasons, due to the fact that in a reaction with ethylene carbonate one equivalent of carbon dioxide is released. The first hurdle resulting from that decision was to enable the solid and quite unreactive melamine to react with gaseous ethylene oxide. This issue could be resolved by dissolving the melamine in a solvent of choice. In order to comply with sustainable principles, we decided for a renewable solvent and identified glycerine out of a screening. Glycerine is widely available for instance from the production of bio diesel. We then screened the reaction conditions of the ethoxylation (8). A typical example was carried out like this:

24 g of melamine were dissolved in 24 g glycerine in a 300 mL steel autoclave and warmed to 160°c under stirring. To this solution 192 g ethylene oxide were dosed within 6 hours. The reaction was allowed to proceed at this temperature for 3 hours until the pressure became constant. The pressure was released and a vacuum of 15 mbar was applied to the autoclave to remove volatile components. 235 g of a yellow liquid with low viscosity (935 m Pa s) was obtained.

The minimum requirement for a successful reaction was the complete reaction of the melamine in order to achieve a final product without toxic components, since melamine bears the hazardous label H 361 f, meaning it is suspected to have an impact on fertility. The melamine ethoxylate is a liquid with low viscosity that contains no water. It is readily soluble in water and therefore could be easily applied on leather. The synthesis of melamine ethoxylates is depicted in figure 3.

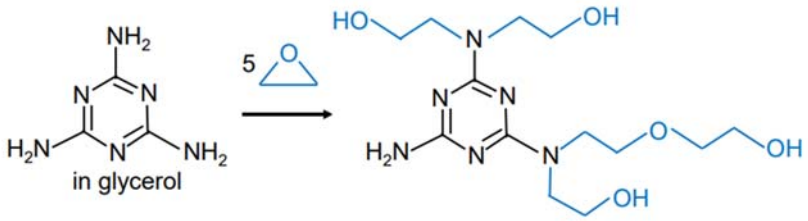

Fig. 3. Synthesis of melamine ethoxylates

2.3 Re-tanning of leather

The re-tanning was carried out on bovine wet blue or wet white with two millimeters strength after neutralization with eight percent active material in float lengths of hundred to two hundred percent, based on wet blue or wet white weight. Subsequently, the leathers were treated with one percent of a standard brown dye and with two percent of a standard fatliquor in a separate float. After re-tanning the leathers were dried and stacked. The comparison was run with a standard melamine urea formaldehyde resin and a poly ethylene glycol, subjected to the same procedure. The lightfastness was determined via Xeno test in a Suntester according to DIN EN ISO 105-B06. The softness can be quantified according to DIN EN ISO 17235, or via haptics. Grain tightness and fullness were evaluated via haptics.

3 Results and Discussion

The screening to identify optimized ethoxylation conditions for melamine is summarized in table 1:

Table 1. Results of re-tanning of bovine wet blue with melamine ethoxylates with varying chain length in comparison to a standard melamine urea formaldehyde condensate and a short chained poly ethylene glycol: + = better; 0 = similar; - = worse

Product	**Number of ethylene oxide equivalents / 1 equivalent of melamine**	**Leather properties compared to standard melamine urea formaldehyde**	**Leather properties compared to poly ethylene glycol (PEG)**
Melamine Ethoxylate 3 EO	3	-	+
Melamine Ethoxylate 5 EO	5	0	+
Melamine Ethoxylate 7 EO	7	-	+

Melamine Ethoxylate 10 EO	10	-	0

As can be seen in table 1, with a minimum of three equivalents of ethylene oxide per one equivalent of melamine, we were able to see a re-tanning effect. With five equivalents ethylene oxide we observed on optimum that did not improve raising the equivalents ethylene oxide to seven or more, if compared to a melamine urea formaldehyde resin. From ten equivalents ethylene oxide and onwards, we still saw a re-tanning effect, but this effect could also be achieved by re-tanning with poly ethylene glycol (PEG). Poly ethylene glycols are made from pure ethylene oxide, are widely available and show only weak re-tanning effects. Goal of our effort was to obtain superior results to re-tanning with poly ethylene glycol and similar effect to the standard melamine urea formaldehyde condensate. This was achieved with the sample deriving from five equivalents ethylene oxide. We scaled this composition up and tested this "pilot batch" in further application tests.

Table 2. Results of re-tanning of bovine wet blue or wet white with melamine ethoxylates in a mixed recipe compared to the same recipe with a standard melamine urea formaldehyde condensate: + = better; 0 = similar; - = worse

	Shoe Upper	**Shoe waterproof**	**Boot Nappa**	**Automotive Wet blue**	**Upholstery**	**Automotive wet white**
Colour strength	+	+	+	+	+	+
Filling	-	-	-	-	-	-
Softness	0	0	+	+	+	0
Grain tightness	0	0	0	0	0	0

As can be seen in table 2 in six different leather articles made with re-tanning recipies typical for these articles, the melamine ethoxylate gave superior results in colour strength compared to a standard melamine urea formaldehyde condensate. Three leather articles resulting from re-tanning with melamine ethoxylate showed superior softness. Grain tightness was similar for both chemistries. Observed fullness was less pronounces for leather articles made with the melamine ethoxylates.

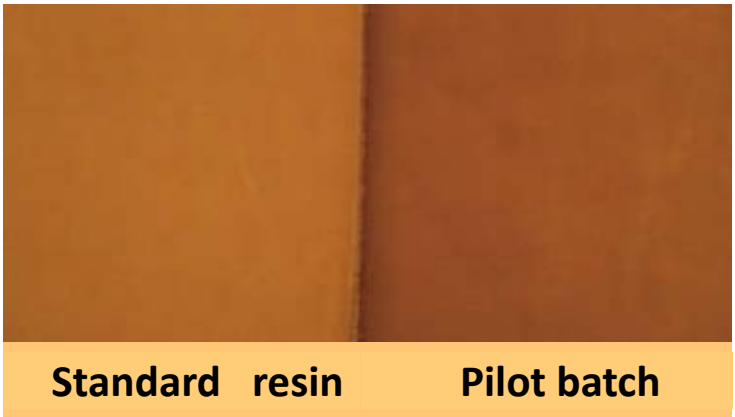

Fig. 4. Re-tanning example of melamine urea formaldehyde resin (left) compared to the pilot batch of melamine ethoxylates

An example of the colour strength advantage of the melamine ethoxylate is shown in figure 4. Results of lightfastness tests, determined via Xeno test in a Suntester according to DIN EN ISO 105-B06, gave clearly better results of the melamine ethoxylate than for the melamine urea formaldehyde condensate.

The melamine ethoxylate is a liquid with low viscosity that contains no water. It is readily mixable with water. This is a sustainable advantage over classical melamine urea formaldehyde condensates, which are made in water and are mostly subjected to spray drying, affording huge amounts of energy to remove the water in order to obtain a concentrated product. Another aspect of improved sustainability is the glycerine inside the product, giving rise to partially renewable starting materials, in contrast to entirely oil-based melamine urea formaldehyde condensates. Overall, we identified melamine ethoxylates as a sustainable alternative to melamine urea formaldehyde condensates.

References

1. *Ammenn, Jochen; Huebsch, Corinna; Schilling, Emil; Dannheim, Bernd;* ***Chemistry of Syntans and their Influence on Leather Quality****, JALCA, 110, 349–354, 2015.*
2. *Tollens, Bernhard;* ***Ueber einige Derivate des Formaldehydes****, Chem. Ber., 17, 653-659, 1884.*
3. *Dawson, William;* ***Tanning Agents****, US 2316741, 1943, 3p.*
4. *Lach, Dietrich; Streicher, Rolf; Bolz, Gerhard;* ***Verfahren zur Herstellung von wasserlöslichen oder selbstdispergierenden Harzgerbstoffen für die Nachgerbung von Leder und ihre Verwendung****, EP 0 063 319, 1982, 10p.*
5. *Shriver, Donald et al.;* ***Production of melamine-urea-formaldehyde concentrates****, US 3.458.464, 1969, 3p.*
6. *Liu, Ming; Wang, Yan; Wu, Yiang; Wan, Hui;* ***Hydrolysis and recycling of urea formaldehyde resin residues****, J. of Harzardous Materials, 355, 96-103, 2018.*
7. *Brady, Ocsar; Elsmie, Gladys;* ***The use of 2:4-dinitrophenylhydrazine as a reagent for aldehydes and ketones****, Analyst., 51(599), 77-78, 1926.*
8. *Ammenn, Jochen; Kunst, Andreas;* ***Process for producing leather****, WO 2011 158168, 13 p.*

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