Melamine Ethoxylates as Novel Formaldehyde Free Replacements of Resin Re-Tanning Agents

by
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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. 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, reversing the synthesis.

Melamine ethoxylates were found to be a formaldehyde free, stable, and easily applicable alternative. Besides the fact that they are made without formaldehyde, it proved to be possible to incorporate renewable components into their 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, consuming significant amounts of energy in the process.

Melamine ethoxylates show advantages in application on leather in comparison with classical resin re-tanning agents. 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.

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 synthetic re-tanning agents are phenol formaldehyde condensates and melamine urea formaldehyde condensates. Depending on the chemistry, rest monomeric phenol, formaldehyde, bisphenol S and bisphenol F can be a problem with the phenol formaldehyde condensates,[1] also known as syntans. Besides melamine urea formaldehyde, urea formaldehyde condensates are also applied as re-tanning agents, both commonly referred to as resins. 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 closely 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.

Experimental

Chemicals were of reagent grade and obtained from commercial sources without further purification. Dynamic viscosity was determined according to DIN 51550.

Synthesis of the melamine ethoxylates were carried out in steel autoclaves connected to a vacuum pump and an ethylene oxide storage steel cylinder, positioned on a balance. A typical example was carried out like this: 24 g of melamine were dissolved in 24 g glycerin 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 mPa-s) was obtained.

Re-tanning was carried out with wet blue, obtained from the treatment of pickeled pelt with 6-8% chromium sulfate. In a typical example, 100 g of wet blue of southern German origin with a thickness of 1.7 mm was treated in a 3.5 L tanning drum with 100 g water, 1.2 g sodium formiate and 0.3 g sodium bicarbonate and the drum was turned for 90 minutes. The resulting float had a pH of 4.5. Eight grams of the retanning agent referring to active material were added and turning of the drum was continued for 90 minutes. The float was discharged and the leather washed with 200 g water.

Subsequently, the leathers were treated with one percent of a standard brown dye and with two percent of a standard fat liquor in 200 g water for 90 minutes, before the float was acidified with 0.7 g 85% concentrated formic acid and the drums were turned for 20

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minutes. The float was discharged and the leathers were dried via hang drying over night without vacuum at room temperature and stacked. The comparison was run with a standard melamine urea formaldehyde resin or a polyethylene glycol, subjected to the same procedure.

To evaluate the role of melamine ethoxylates in leather articles, the amount of melamine ethoxylates was reduced in the recipe and other products were added to the re-tanning float, like phenolic or sulfone syntans, polyacrylic re-tanning agents, vegetable tanning agents like Mimosa or Tara, or water proofing agents. Products and amounts depending upon need in the article.

The lightfastness and heat ageing properties were 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.

The free formaldehyde can be measured after derivatization with dinitrophenylhydrazine in solution after extraction of leather according to ISO 17226.

Results and Discussion

Melamine Urea Formaldehyde Condensates

Urea formaldehyde condensates were discovered in 1884.[2] Since the 1930's, 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 is a good example for how chemistry can help to convert waste into value. Later, melamine formaldehyde condensates and melamine urea formaldehyde were developed, giving additional characteristics to chipboards like fire resistance properties.

Melamine formaldehyde condensates were first applied on leather in 1942 as tanning agents in the form of a formaldehyde releaser.[3]

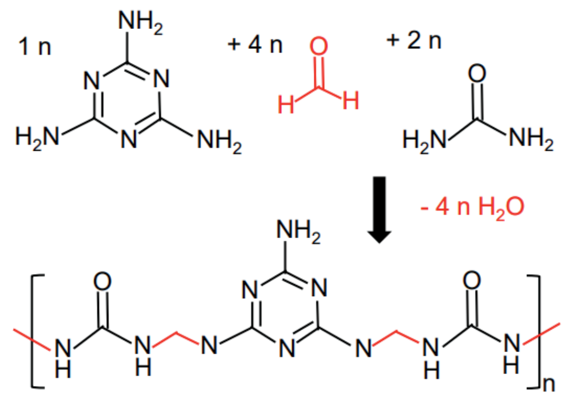

Figure 1. Synthesis of melamine urea formaldehyde condensates

For application as re-tanning agents in leather the water solubility had to be improved. This issue was the same for melamine urea formaldehyde, and urea formaldehyde condensates. This work will focus on melamine urea formaldehyde condensates, keeping in mind that problems of these 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.[4] The formula of the reaction can be seen in Figure 1. The chain length, reflected in the number "n", is dependent mainly on the amount of formaldehyde, but also on other reaction conditions such as time and temperature. The bonds deriving from formaldehyde are marked in red in the product.

The issue of improving water solubility could be resolved by adding sulfites to the condensation.[5] The sulfite condenses with amino methylol ($-CH_2OH$) groups, deriving from an excess of formaldehyde submitted to the poly condensation. The methylol group, by reacting with the sulfite, releases water and forms a sulfonic acid group attached to the poly condensate via a methylene group. The resulting structure is depicted in Figure 2.

In a basic pH-range the newly formed methylene bridges between two amino group deriving from formaldehyde are quite stable.

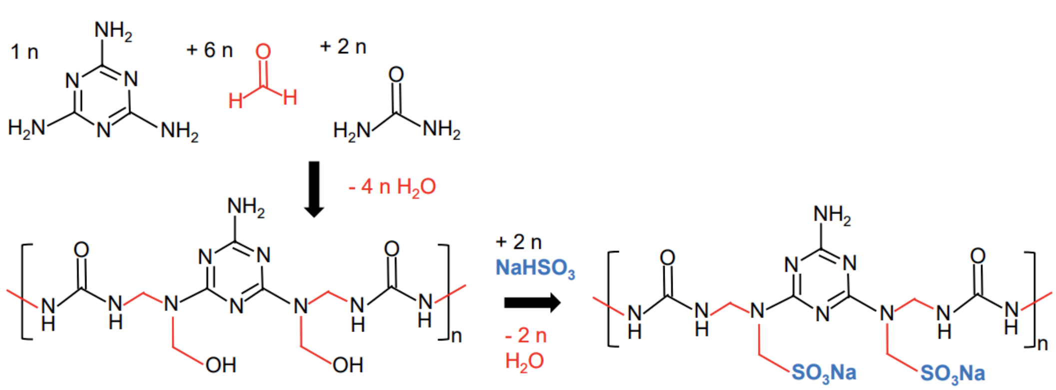

Figure 2. Water soluble melamine urea formaldehyde condensates

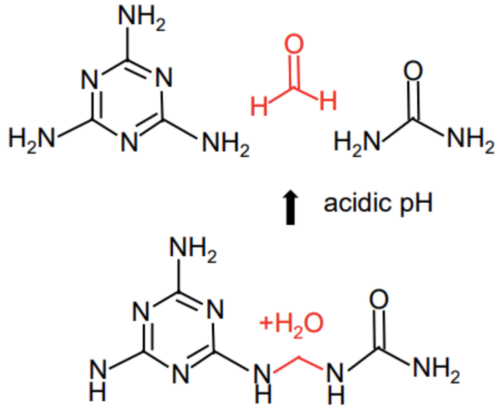

Figure 3. Hydrolysis of a melamine urea formaldehyde condensate

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 and requires both acidity and presence of water. 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.

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 or neutral pH, low values of formaldehyde will be obtained with this method.

In the extraction assay UNI EN 17226 leathers samples can be analyzed for formaldehyde. The leathers are cut into pieces, extracted with warm water for a defined time. The resulting 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 partial hydrolysis. The acidity originates from strong acids like phosphoric acid, commonly used to establish the reaction conditions for derivatization with 2,4-di-nitro-phenyl-hydrazins[7] and frequently present in derivatization product formulations. Consequently, higher values of formaldehyde will be obtained with this method for leathers made with 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.

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 to make within the project was to decide on the chemicals to use. Choices were gaseous ethylene oxide or liquid ethylene carbonate, with a clear favor for ethylene oxide for sustainability reasons: in a reaction with ethylene carbonate, one equivalent of carbon dioxide would be 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. To again comply with sustainable principles, we decided for a renewable solvent and identified glycerin out of a screening. The solvent will remain in the final product and can help to augment the penetration of the polymer. Glycerin is widely available for instance from the production of biodiesel. We then screened the reaction conditions of the ethoxylation.[8]

The minimum requirement for a successful reaction was the complete reaction of the melamine to achieve a final product without toxic components, since melamine bears the hazardous label H361f, meaning it was proven to have an impact on fertility of rodents. The resulting melamine ethoxylate is a liquid with low viscosity that contains no water. It is readily soluble in water and could be easily applied on leather. The synthesis of melamine ethoxylates is depicted in Figure 4.

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

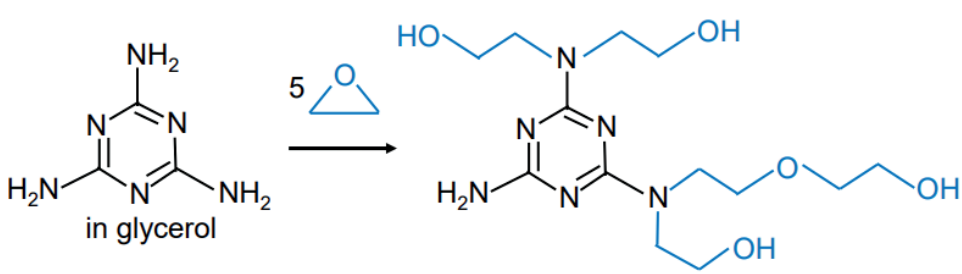

Figure 4. Synthesis of a melamine ethoxylate

Table I

Screening results of the re-tanning of bovine wet blue of different melamine ethoxylates against a standard melamine urea formaldehyde condensate and polyethylene 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 polyethylene 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 I, with a minimum of three equivalents of ethylene oxide per one equivalent of melamine we were able to see a re-tanning effect compared to a leather re-tanned with polyethylene glycol. 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. However, this effect could also be achieved by re-tanning with polyethylene glycol (PEG). Polyethylene glycols are made from pure ethylene oxide, are widely available and show only a weak re-tanning effect. Goal of our effort was to obtain superior re-tanning results compared to polyethylene glycol and similar effects 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 the resulting pilot batch in further application tests.

As depicted in Table II, leathers made with the pilot batch of the melamine ethoxylate performed better in fastness properties than leathers made with a standard melamine urea formaldehyde condensate. Lightfastness and heat ageing properties were determined according to DIN EN ISO 105-B06. Concerning filling properties, similar results were observed for both chemistries, while softness properties on leather was better with the melamine ethoxylate. Huge advantage on the side of the melamine ethoxylate is low free formaldehyde measured according to ISO 17226. The analysis on wet blue revealed free formaldehyde in the same range as after re-tanning with the melamine ethoxylate (< 10 ppm).

Table II

Re-tanning of bovine wet blue with the optimized melamine ethoxylate against a standard melamine urea formaldehyde condensate

+ = better; 0 = similar; - = worse

	Pilot batch melamine ethoxylate	Standard melamine urea formaldehyde condensate
Lightfastness	+	0
Heatfastness	+	0
Color strength	+	0
Filling	0	0
Softness	+	0
Grain tightness	0	0
Free Formaldehyde: ISO 17226	< 10 ppm (wet blue: < 10 ppm)	67 ppm (wet blue: < 10 ppm)

Table III

Results of re-tanning of bovine wet blue or wet white with melamine ethoxylates in a mixed recipe compared to a melamine urea formaldehyde condensate in the mixed recipe

+ = better; 0 = similar; – = worse

	Shoe upper based on wet blue	**Shoe water-proof based on wet blue**	**Boot Nappa based on wet blue**	**Automotive based on wet blue**	**Upholstery based on wet blue**	**Automotive based on wet white**
Other re-tanning agents	Phenolic syntan, Mimosa, Polyacrylic	Sulfone syntan waterproof agent	Phenolic syntan, Mimosa, Polyacrylic	Sulfone syntan, Tara	Phenolic syntan, Tara	Sulfone syntan, Tara
Color strength	+	+	+	+	+	+
Filling	–	–	–	–	–	-
Softness	0	0	+	+	+	0
Grain tightness	0	0	0	0	0	0

Two sets of six different leather articles were made with re-tanning recipes typical for these articles. In one set of leather articles the optimized melamine ethoxylate was used, in the other set same amount of a standard melamine urea formaldehyde condensate was applied. Differences between the two sets were noted in Table III; a "0" indicates same performance for both chemistries. Other re-tanning components required to make these leather articles are listed in the upper part of Table III. The melamine ethoxylate gave superior results in color strength in the leather articles, compared to leathers made with a standard melamine urea formaldehyde condensate. Three leather articles resulting from re-tanning with melamine ethoxylate showed superior softness. Observed fullness was less pronounces for all leather articles made with the melamine ethoxylate. Grain tightness on leather was similar for both chemistries.

An example of the color strength advantage of the melamine ethoxylate is shown in Figure 5. The same amount of melamine ethoxylate gives rise to darker shades than a standard melamine urea formaldehyde resin, reducing bleaching.

Conclusions

The melamine ethoxylate is a liquid product with low viscosity that contains no water. It can readily be diluted 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 obtain a concentrated product. Another aspect of improved sustainability is the glycerin inside the product, giving rise to partially renewable

Figure 5. Re-tanning example of a standard melamine urea formaldehyde resin (Standard, left) compared to the pilot batch of melamine ethoxylate

starting materials, in contrast to entirely oil-based melamine urea formaldehyde condensates. In performance on leather, the melamine ethoxylate gave superior results in color strength as well as in light fastness compared to a standard melamine urea formaldehyde condensate and partially better softness, while maintaining the grain tightness.

Overall, we identified melamine ethoxylates as a sustainable alternative to melamine urea formaldehyde condensates, resolving the issue of free formaldehyde.

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