# Water-based Anionic Sulfonated Melamine Formaldehyde Condensate Oligomer as Retanning Agent for Leather Processing

*by*

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## Abstract

This work deals with the synthesis of water-based anionic sulfonated melamine-formaldehyde condensate (SMFC) with very low free formaldehyde content by sequential formulation. The structure of the oligomeric SMFC has been confirmed using spectroscopic methods like FTIR and UV. Molecular weight of the condensates was determined by Gel permeation chromatography (GPC). These oligomers were then evaluated as retanning agents. Chrome tanned wet blue leathers were treated with SMFC in different proportions (1, 2 and 3% based on shaved weight) to optimize the use of the product for physical properties of leather including fullness and dye uptake. Further, the leathers were subjected to conventional dyeing and fatliquoring processes. Control experiments without SMFC were also undertaken to judge the efficacy of the product. The results showed that SMFC treated leather exhibited improved grain tightness, softness, fullness and dye uptake in the resultant leather. The most important aspect of the product was very low (<10 ppm) free formaldehyde content in the treated leather.

## Resumen

Este trabajo se ocupa de la síntesis del condensado aniónico de melamina sulfonada-formaldehído en base acuosa (SMFC), con muy bajo contenido de formaldehído libre por su formulación secuencial. La estructura de los oligómeros SMFC se ha confirmado mediante métodos espectroscópicos como FTIR y UV. El peso molecular de los condensados se determinó por cromatografía de permeación en gel (GPC). Estos oligómeros luego fueron evaluados como agentes de recurtido. Cueros wet blue curtidos al cromo fueron tratados con SMFC en diferentes proporciones (1, 2 y 3% sobre la base de peso rebajado) para optimizar el uso de los productos en las propiedades físicas incluidos el relleno y la absorción del colorante. Además, los cueros fueron sometidos a procesos convencionales de teñido y engrase. Experimentos de control sin SMFC se llevaron a cabo también para evaluar la eficacia del producto. Los resultados mostraron que el cuero tratado con SMFC mostró mejoras en la firmeza de flor, suavidad, llenura y en la absorción de colorante. El aspecto más importante del producto es un muy bajo (<10 ppm) contenido en formaldehído libre en el cuero así tratado.

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## Introduction

Leather making has been known from pre-historic times, where hides and skins were treated with natural materials. In recent times attempts have been made to make leather in a more scientific and organized manner using latest technologies and chemical inputs. Presently, chrome tanning is the most popular tanning methodology adopted worldwide. Nearly 80% of the total leather processing employs chrome tanning. Retanning is an important operation to impart organoleptic properties to chrome leather by reducing the short falls of the tanning process. There are several retanning agents available in literature.[1] Vegetable, formaldehyde and acrylic type of materials play a major role in the retanning process.[3] Many of the available products based on formaldehyde condensate do not conform to the required norm of formaldehyde content in leather (50-100 ppm), thus making the leather unsuitable for use. Tanning is the most important step in the production of leather. Raw hides obtained from ill-fed or fallen animals generally have a loose structure, which is caused by space between the collagen fiber bundles, in addition to the space required for free movement.[4] Examination of such hide a cross section clearly shows a non-homogeneous fiber structure. The fibers in the grain layer lie more parallel to the surface and are denser than the supporting reticular layer where the angle of weave is much higher.[5]

For footwear and other value-added applications, leathers must have necessary body, thickness and tightness of grain, improved cutting value and minimum or no looseness. This requirement is fulfilled by tanning agents, whose properties include uniform filling action in the voids between corium major and minor, thereby strengthening the grain. Thus, tanning is essentially the reaction of collagen fibers in the hide with vegetable tannins, chromium, alum, or other chemical agents thus converting the protein in the hides into the cross-linked leather material.[6] Tanning improves specific physical and chemical properties such as feel, handle, ability to resist wet heat and the ability to bind with other substances used during post-tanning operations.[7]

The common chrome tanning method has many advantages, but the lack of fullness, coarse nap, darkening of the leather on exposure to light, and the need to improve leather properties such as buffability, water repellency, cutting value, retention on embossing, demands the use of retanning agents.[8] Over the past few years, research work has been done on the process parameters in the retanning process and some new retanning mixtures have been studied.[9] Retanning agents such as resin syntans or polyacrylic acid[9] have become indispensable components in the tanning process. Modern retanning materials such as softening polymer resins are preferred over heavy vegetable retanning extracts. Also, polymeric, resin-based retanning agents have been found to give a good filling effect, plumpness, increase in compactness, especially in the belly and shank regions of low grade wet blue leathers.[10]

Earlier workers have also reported that by judicious incorporation of polymeric materials[9] during post-tanning operations, the physical properties such as leather break, grain tightness, etc., can be improved especially in the less-compact regions of leather.[11] Amino resins based on urea and melamine[12] have been reported to work well in these aspects.[13-14] Keeping this in view, water-based sulphonated melamine formaldehyde ionic condensate, which could be used as a retanning agent, was prepared and its effect on leather was studied. As the resin possesses functional methyl groups, it can react with amino groups of collagen thus serving as a good retanning agent.

## Experimental

### Materials

Melamine, paraformaldehyde (Polymeric form of formaldehyde n=100), and sodiumbisulphite, sulfuric acid, and sodium hydroxide. All the materials were received from Loba chemicals Private Ltd., India, and were used as received.

### Preparations of SMFC

Water-based sulfonated melamine formaldehyde condensate was prepared according to a four-step method.[15-18] In the first stage of the procedure 10g of paraformaldehyde dissolved in 250 ml of water in 50 ml of water is added maintaining the pH 6.0. 70g of paraformaldehyde are then added and further heated to 120˚C and continued at the same temperature for 120 minutes. In the second step, the pH is adjusted to 8-9 using 1N NaOH before sulfonation. 10g of sodium sulphite dissolved in 50 ml of water is added thus increasing the pH to 11; causing an increase in temperature while the salt is dissolving. The temperature of the solution is maintained 60 ˚C–120˚C and the reaction were continued for 60–120 min. In the third stage of the procedure, the solution is cooled rapidly to 50˚C pH of the solution is adjusted to 3.0 by the addition of 30% (w/w) sulfuric acid. In the fourth step, the NaOH is added to the solution, causing an increase in pH to 7–8. The solution is heated to 70˚C–100˚C and kept at that temperature for 60–120min. The reactants are stirred during the whole reaction time. The solution is finally cooled to room temperature, filtered to remove solid particulates, and treated with sodium hydroxide to adjust its pH to 11 yielding the condensate. Different trails were conducted with different process variables like temperature, pH, etc. The optimized products were used as a retanning agent in leather processing (See Table 1).

### Characterization of SMFC

FTIR (Nicolet Impact 400 Spectrophotometer) was used for structural characterization of the sulfonated melamine formaldehyde condensate as KBr pellets (sample:KBr = 1:80).

**TABLE 1**

**Leather processing details**

| Process | Control | Experiment |
|---|---|---|
| **Washing** | Water 200% 15' | Water 200% 15' |
| **Neutralization** | Water 100% Sodium Bicarbonate 0.5% 3*10'+30' | Water 100% Sodium Bicarbonate 0.5% 3*10'+30' |
| **Washing** | Water 200% 15' | Water 200% 15' |
| **Retanning, Dyeing And Fat Liquoring.** | Water 100% Run for 60' +Dye 1% Run for 30' +Synthetic Fat liquor 5% Run for 45' +Formic acid 1% 3*10'+30' | Water 100% **+Retanning agent 1*** 16% Run for 60' +Dye 1% Run for 30' +Synthetic Fat liquor 5% Run for 45' +Formic acid 1% 3*10'+30' |

Pile over night. Next day, strike out, set, air off, stake and toggle to dry. After drying, the leathers were buffed.

***Experiments were carried out with the following chemicals individually.**
Retanning Agent 1-----SMFC1
Retanning Agent 2-----SMFC2
Retanning Agent 3-----SMFC3
Retanning Agent 4-----Basyntan FB 6—Melamine based resin (BASF)

The UV spectrophotometer was used to find out the weight percentage of melamine in the solution. 0.05g of SMFC was taken in 200 ml flat-bottomed flask with stopper and then 5 ml of ethanol was added in the flask followed by 50ml of 0.1N HCl. The final mixture was refluxed for 1hr. This refluxed mixture was cooled and then diluted to 0.1N with HCl. The optical density of the solution was found out using CARY 50 bio UV-Visible spectrophotometer. The path length of the analysis was fixed to 1 cm. From the optical density, weight percentage of the given solution was found out using the formula:

$$\text{Weight percentage of melamine} = \frac{(A_{237} - 3A_{255})\ fv}{A_{237} \times bW} \qquad (1)$$

Where,

$A_{237}$ & $A_{255}$ = observed absorbance of subscript wavelength (nm)

f = dilution factor (here 10)

v = ml of solution containing total hydrolysate

a = absorptivity of melamine 79.0 at 237 mμ

W = g sample weighed

The Viscosities of polymers were determined using a Brookfield Viscometer according to ASTM (D 1638-74). The pH of the water-based SMFC was determined by using Elico pH meter LI 127. The measurements were made after standardizing the pH meter by using a series of standard solutions. For determining the solid content, a calculated quantity of the solution was taken and kept in a oven and dried slowly at 150°C for 7hrs. Then the sample was kept in a desiccator, cooled and weighed. The sample was again kept in the oven, taken out, cooled and reweighed. This procedure was repeated until there was no loss in weight. The difference in the initial weight and final weight was calculated. Percentage of total solid content was calculated as per the BIS standard test methods.

**Determination of free formaldehyde**

5 ml of the solution was pipetted out into a 1000 ml volumetric flask, which contained approximately 100 ml of demineralised water and was subsequently filled with demineralised water up to the mark. This solution was the formaldehyde stock solution. From this solution, 10 ml was pipette out into a 250 ml Erlenmeyer flask, mixed with 50 ml of iodine solution and sodium hydroxide was added until it turned yellow. It was allowed to settle for 15 min ±1 at 18–26°C and then 50ml of sulphuric acid was added while swirling. After addition of 2ml of starch solution, the excess iodine was titrated against sodiumthiosulphate until the colour change takes place. The free formaldehyde content was determined in all the experiments. A blank solution was titrated in the same manner.

$$C_{FA} = \frac{(V_0 - V_1).\ C_{1.}\ M_{FA}}{2} \qquad (2)$$

Where,

$C_{FA}$ = concentration of the formaldehyde stock-solution, in mg/10 ml

$V_0$ = titre of the thiosulphate solution for the blank solution, in ml

$V_1$ = titre of the thiosulphate solution for the sample solution, in ml

$M_{FA}$ = molecular weight of formaldehyde, 30.08 g/mol

$C_1$ = concentration of the thiosulphate solution, M

**% Exhaustion of dye in leather processing**

A known quantity of dye, at different concentration levels, was prepared by dissolving it in water. For each concentration of dye, the respective Optical Density (OD) measurements were noted in UV spectrophotometer and λ max was found out. The OD of spent dye liquor was measured at a particular wavelength (λ=577.5) and from this the % exhaustion of dye was estimated.

**Color Measurement Studies**

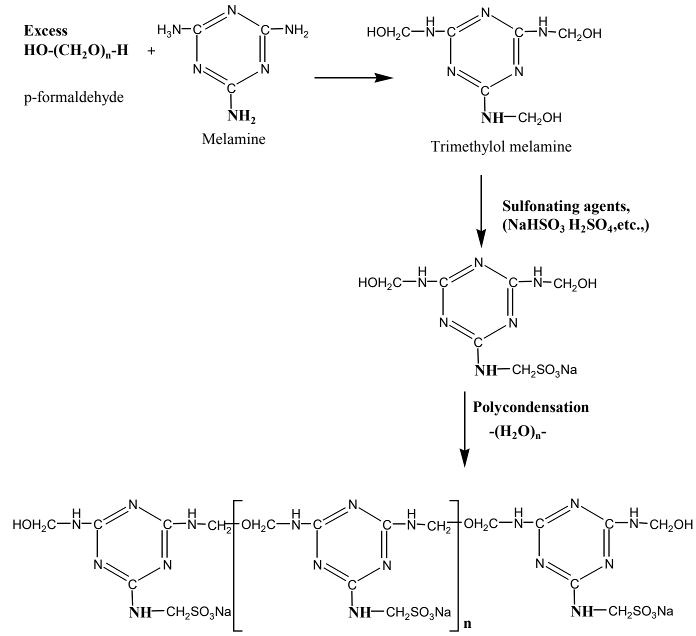
For dye uptake studies, it is important to study the color values of crust leathers. All color measurements were carried out using Gretag Macbeth Spectrolino Spectrophotometer with the measurement geometry of 45°/0° and L, a, b, c, H and ΔE values were calculated using standard procedure.

**Organoleptic properties of leather**

Experimental and control wet blue and crust leathers were assessed for color, softness, grain tightness and general appearance, by hand and visual examination, by experienced tanners. The leathers were rated on a scale of 0-10 points for each functional property by four experienced tanners, and the average value was taken. Higher points on the scale indicated enhanced functional property.

## RESULTS AND DISCUSSION

A novel, water-based, sulfonated melamine formaldehyde ionic condensate has been prepared using mealmine and polymeric formaldehyde followed by addition of sulfonating agent. These ionic condensates have been characterized by the FTIR (Figure 1) and corresponding peak values are listed in Table 2. Further, calcium oxide has been added to the oligomeric solution to neutralize free sulfate ions which enables the product to be used as a retanning agent in leather processing. The product shows free formaldehyde content of 60 ppm which is quite suitable for application in leather processing. Usually, the conventional product has higher formaldehyde content, ranging from 0.5–2%.19 This is an issue of much concern to the tanner considering the growing awareness of the health hazard attributed to the free formaldehyde content in the melamine formaldehyde products, which is turn, restrict their use in leather.




Scheme 1: Preparation of SMFCS

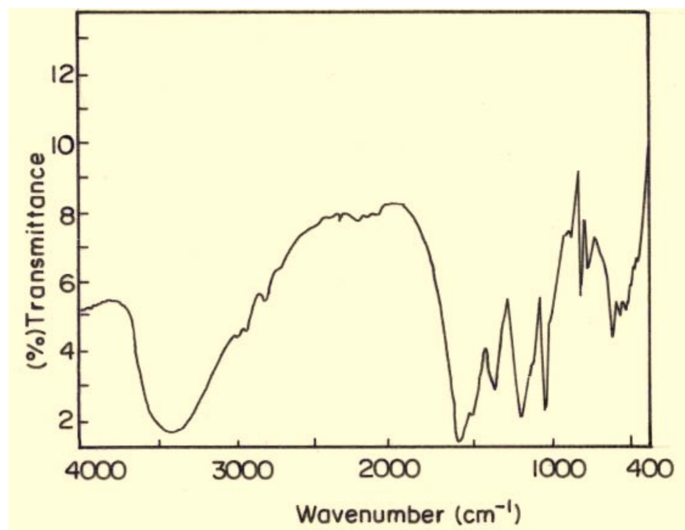



Figure 1. FTIR of SMFC3.

Particle size is a very important parameter for chemicals that are used in processing industry. Leather processing requires a range of chemicals useful for filling up voids and imparting fullness to the leather. The melamine formaldehyde ionic condensate resin is widely used as a synthetic tanning agent in leather industry. However, bigger particle size of the product, of more than 10 μm, poses a limitation in its use in retanning i.e., inadequate penetration in the cross section, of the leather. The SMFC 1–3 show a particle size in the range of 100 to 800 nm. This low particle size is the unique property of this product. The pH of the product is 8.5–9.5, which is most suitable for retanning application along with other ionic post-tanning auxiliaries. The viscosities of SMFC 1–3 show a range of 10–30 mPa.s (See Table 3), which is suitable for leather application because of reduced surface tension resulting in better and uniform

## TABLE 2
## FTIR data of SMFCs

| Vibrations | Wave numbers |
|---|---|
| N-H and O-H bonds of amines and alcohols | 3400 cm$^{-1}$ |
| Antisymmetric and symmetric valence vibrations of the methylene group | 2940 and 2850 cm$^{-1}$ |
| Scissoring deformative vibrations of the methylene group | 1490 cm$^{-1}$ |
| Rocking vibrations of the methylene group | 703-780 cm$^{-1}$ |
| Plain deformation vibration C-O-H | 1350 cm$^{-1}$ & 1143-1130 cm$^{-1}$ |
| Secondary amine groups, C-N-C vibrations | 1190-1130 cm$^{-1}$ |
| –$SO_3$Na: valence vibration v-$SO_2$ : deformation vibrations | 1220–1190 cm$^{-1}$(antisymmetric) 1030-1040 cm$^{-1}$(symmetric) 500–600 cm$^{-1}$ |
| 1,3,5-triazine ring, deformative vibrations | 820 to 805 cm$^{-1}$ |

penetration through the nanometer pore size of the collagen matrix. The number average molecular weight of the SMFC is in the range between 34000 and 40000 was determined using polyethylene glycol standard by GPC. The melamine content is determined using the UV spectrophotometer (See Figure 2) and values are given in Table 3.

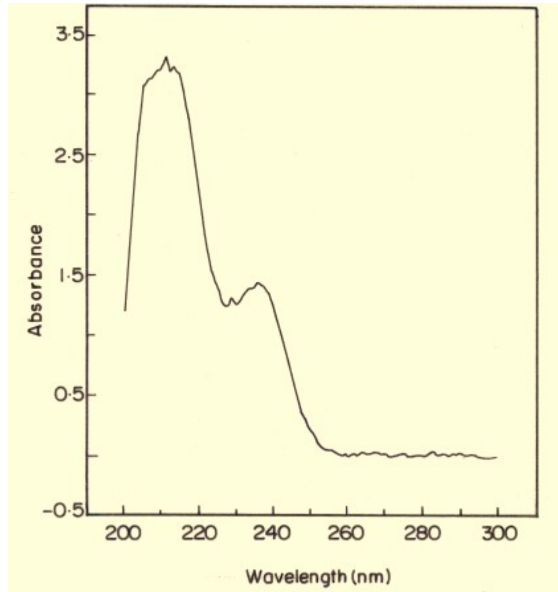


Figure 2. UV absorbance of the SMFC3.

Table 4 shows the use of the condensate product in retanning and dying process with improved dye uptake properties. It is seen from the table that 2-3% of the condensate on the shaved weight of the leather improved the dye uptake properties tremendously. The % uptake of dye is found to be in the range of 98-99%. The control experiment showed 96.5% dye uptake with the same level of retanning agent offered. The improved uptake of the dye may be attributed to the fact that more electrovalent linkages are formed by the condensate with the dye and collagen in the resultant leather. Moreover, the percentage free sulphate in the product is very much reduced by the alkali treatment in the preparation of the condensate, thereby improving the color retention property of the oligomer.

The organoleptic properties of the polymer-treated crust leather are given in Table 5. It is seen from the table that the 2% offer of SMFC on shaved weight gave better fullness and grain tightness to the treated leather as compared to the leather

## TABLE 3
## The solid content, pH, free formaldehyde content, melamine content and viscosity of the prepared samples

| S.No. | Sample Code | Free Formaldehyde Content (%) | pH | Solid Content (%) | Melamine Content (%) | Viscosity (CPs) |
|---|---|---|---|---|---|---|
| 1. | SMFC1 | 0.115 | 8.70 | 42 | 18.5 | 10–20 |
| 2. | SMFC2 | 0.080 | 9.20 | 43 | 24.0 | 10–25 |
| 3. | SMFC3 | 0.006 | 8.60 | 35 | 18.5 | 10–20 |

## TABLE 4

### Percentage dye exhaustion in leather processing

| Retanning using SMFC3 | Amount of dye used (%) | % Dye exhaustion |
|---|---|---|
| Sulfonated Melamine-Formaldehyde retanning | 1 | 96.0 |
| Sulfonated Melamine-Formaldehyde retanning | 2 | 98.2 |
| Sulfonated Melamine-Formaldehyde retanning | 3 | 98.8 |
| Commercial retanning agent based on melamine based resin | 3 | 96.5 |

Dye offer to all the above experiments: 1–3%

## TABLE 5

### Organoleptic properties of various leather samples treated with different % of SMFC

| | EXPT. 1 | EXPT. 2 | EXPT. 3 | CONTROL (without SMFC syntan) |
|---|---|---|---|---|
| Softness | 7 | 7 | 8 | 8 |
| Fullness | 8 | 8 | 7 | 6 |
| Dye Uptake | 7 | 8 | 8 | 7 |
| Grain Tightness | 9 | 9 | 8 | 6 |
| General Appearance | 8 | 8 | 8 | 8 |

treated with control or leathers treated with melamine based syntans. Fullness and general appearances are not affected with these SMFC syntans. The reason for enhanced fullness and grain tightness may be due to the fact that the product has smaller particle size (see Figure 2) enabling the product to penetrate uniformly and thoroughly through pores of the collagen matrix.

The SMFC treatment increases the fiber splitting of the collagen. This fiber splitting may influence the uptake of the chemicals. Hence we have studied the color measurements of the crust leather. Table 6 shows the color measurement study of the crust leather process conventionally. It is seen from the table that there is an appreciable change in L, a, b, c, H and ΔE CIE values because the uptake of the dye is better in all the experiments, when compared to the control leather sample. For the physical strength properties of the full chrome upper leather from experiment 4, see Table 3. The experimental leather shows comparable tensile strength; distension and load at grain crack characteristics in comparison to control (see Table 7). It is significant to observe that percentage elongation at break and tear strength in experimental leathers are comparable to control samples. It could be inferred that addition of SMFC in the retanning operation does not alter the strength characteristics of the leather.

## CONCLUSION

Ionic sulfonated melamine formaldehyde condensates have been prepared by condensation polymerization technique. The condensates were identified by their functional groups by FTIR and UV spectra. The peaks at 1120 and 1039 $cm^{-1}$ are attributed to $SO_3H$ groups. The SMFC treated leather exhibited good grain tightness, softness, fullness and dye uptake in the resultant leather. It has been shown that the end product is attributable to a very low (<10 ppm) free formaldehyde present in the product.

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## TABLE 6

### Color measurement study of crust leather

| SAMPLE | L | a | b | c | H | ΔE |
|---|---|---|---|---|---|---|
| Control | 54.2 | 34.7 | 31.2 | 46.6 | 41.9 | |
| Expt 1 | 52.7 | 37.3 | 32.0 | 46.2 | 40.6 | 2.1 |
| Expt 2 | 54.2 | 38.9 | 34.3 | 47.7 | 41.0 | 4.2 |
| Expt 3 | 50.4 | 39.0 | 35.5 | 52.1 | 43.0 | 2.8 |
| Expt 4* | 51.9 | 41.4 | 38.4 | 51.9 | 40.0 | 3.1 |

L, a, b, c, H—colour values, ΔE—Total color difference
(*) Commercial retanning agent based on melamine based resin

## TABLE 7

### Physical strength properties of full chrome upper leather

| Parameters | Chrome tanning experiment by using SMFC syntan (Experiment 3) | Chrome tanning (without SMFC syntan) |
|---|---|---|
| Tensile strength (kg / cm$^2$) | 240 ± 6.0 | 222 ± 5.0 |
| Extension at break (%) | 80 ± 4.0 | 72 ± 3.0 |
| Tear strength (kg / cm thickness) | 60 ± 13 | 56 ± 4.0 |
| Load at grain crack (kg) | 32 ± 1.0 | 30 ± 1.0 |
| Distension at grain crack (mm) | 10 ± 0.4 | 10 ± 0.3 |

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