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Phenolic monomers in aromatic syntans and their influence on leather:

(Pending) Restricted compounds

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Prologue

Aromatic syntans are widely used in the (re)tanning of leathers. Phenolic monomers such as phenol, phenolsulfonic acid, bisphenol S and bisphenol F are common compounds in aromatic syntans. These compounds are unreacted molecules that are either starting materials or intermediate molecules formed during the manufacturing process. Due to the toxic nature of these compounds, both the regulatory authorities and the leather industry are displaying an increasing interest in these residual phenolic monomers. There are various regulatory proposals in discussion on the amount of phenolic monomers (e.g., a restriction proposal on bisphenols is pending at ECHA.) When approved, it will lead to a combined content restriction of bisphenols in leather articles of 200mg/kg (or 0.02% or 200 ppm). Similarly, bisphenol S is proposed for listing on California Proposition 65. In this context, the authors attempted to study on different phenolic monomers present in aromatic syntans and their effects on leathers.

The effect of monomers on the haptics, light fastness, heat yellowing, and residual floats was studied. The study has discovered the small increase at tightness and hardness in leathers with the increase of monomers phenolsulfonic acid and bisphenol S at low quantities ~2 wt%, while at >10 wt% monomers in aromatic syntans the leathers have become emptier. Further, the research has revealed that monomers have the following order of influence on the light fastness: Phenol>bisphenol S =bisphenol F>phenolsulfonic acid. E.g., Leathers retanned with an aromatic syntan that was containing a free phenol concentration of <50 ppm has a Gray Scale (GS) value of 4.0 which is reduced to a GS 2.0 when a syntan containing >4,000 ppm of free phenol was applied. The study also showed that there was no significant effect of phenolic monomers on the heat yellowing of the leathers. Bisphenol S and F showed an uptake of above 90% while phenol and phenolsulfonic acid have showed values <40%, where the remainder was flushed into the waste waters.

The research study consist of 3 different parts:

(i) Amount of monomers: This part discusses the amount of phenolic monomers in different aromatic syntans across the market.

(ii) Model study: A research study has been conducted to determine the effect of each specific monomer in a specific syntan on the leather. In this study, several model syntan samples were prepared by addition of different loadings of each monomer, in order to determine the effect of each monomer separately.

(iii) Effects of monomers: In this part an attempt has been made to correlate the combined effects in different syntans across the market to the amount of monomers present in them.

Keywords:
(re)tanning, aromatic syntan, waste waters, phenolic monomers, bisphenol S, bisphenol F, phenol, phenolsulfonic acid and restricted compounds.

1. Introduction

Aromatic syntans play an important role in the retanning step or wet end process of leather making. Syntans modify the haptic properties of the leather and give the required softness and fullness to the leathers during the retanning. Syntans are widely used for all types of tanned leathers, namely Chrome (Wet Blue, WB), Glutaraldehyde (Wet White, WW) and vegetable tanned leathers to give the additional strength [Ammenn. J et al. 2015, Murali. S et al. 2019, and Song. J et al. 2018]. The amount of syntan used varies upon the process (retanning or sole tanning), condition of hide/skin, and type of article that will be produced. Aromatic syntans, being synthetic in nature, are well suited for all color shades and result in leathers with a better lightfastness, compared to leathers retanned with vegetable tannins.

In general aromatic syntans are condensates of phenolsulfonic acid and/or phenol and/or dihydroxydiphenylsulfone (DHDPS or bisphenol S) with formaldehyde where urea is optionally used. Depending upon the efficiency of the condensation process, a certain amount of phenolic monomers are left unreacted in the production process. These unreacted phenolic monomers such as phenol, phenolsulfonic acid and bisphenol S/F that are present in the syntans, will be transferred to the leather during the (re)-tanning processes. The presence of unreacted monomers are a problem with respect to the following three main aspects. They are:

(i) Hazard classification of the each monomer and product regulatory aspects
(ii) Efficiency during the (re)-tanning of the leather (monomers either ending up in effluent or causing an undesired effect on the leather) and,
(iii) Effect on the leather haptics and leather properties.

The current article has tried to investigate the important aspects around the amount of phenolic monomers. Namely:

1. What is the amount of monomers in the aromatic syntans across the leather industry?
2. What is the effect of monomers on the leather haptics and leather properties?
3. What are the current regulations stating on these monomers and the impact on the leather industry

Identification and determination of the phenolic monomers in the syntans is the first step for future optimizations, and to produce cleaner products which have less impact on heath safety and environment (HSE) aspects.

2. Materials and methods

2.1 Chemical analyses

2.1.1. HPLC (High performance Liquid Chromatography) analyses to determine the phenol and phenolsulfonic acid in retanning agents

Methanol of HPLC grade was purchased from Chem-Lab; while phenol, phenolsulfonic acid and tetrabutylammonium bisulfate (analytical grade) were purchased from Merck. Depending on the expected concentration of analytes, 0,5-5 gram of sample was dissolved in 20 ml Milli Q water using a magnetic stirrer. This solution was quantitatively transferred to a 50 ml volumetric flask and filled. An aliquot of this solution was filtered through a 0.45 µm filter (Millipore Phenex RC) and transferred to a 2 ml HPLC vial. The HPLC analyses was performed at a Shimadzu LC-20AD Prominence equipped with a UV–vis photodiode array detector (SPD-M20A), an on-line Degasser filter (DGU-20A5), and a 20-µL sample loop. A Phenomenex Gemini NX C18 (4,6 mm x 250 mm x 5 µm) was used. 10 µl of the sample solutions were injected into the system, using a flowrate of 1,0 ml/min at a column temperature of 40°C, using an isocratic eluent composition of 15% methanol and 85% 0.03M TBAS in Milli Q water for 30 minutes. Quantification of the phenol and phenolsulfonic acid peaks were performed by using external calibration of the peaks at 13,5 (phenolsulfonic acid) and 23,0 (phenol) minutes.

2.1.2. Determination of bisphenol F and S in retanning agents and leathers

Syntan samples and leather samples are outsourced for the analyses of bisphenol F/S at FILK Freiberg institute, CTC Lyon and Ars Tinctoria SRL Santa Croce. The used methods for the analyses are in-house developed methods at the respective institutes.

2.2 Leather properties analyses

Leather properties recipes: The recipes to determine the leather properties (heat yellowing and lightfastness) are different compared to typical wet end recipes, which are also carried out as per Smit & Zoon internal testing methods. These single recipes are executed without dye and fat liquor, but with syntan and are designed to exclusively determine the effect of the syntan

2.2.1 Determination of the heat yellowing of the leathers

Conditioning (heating) of leather pieces (6,0 x 7,0 cm) in a ventilated oven for various time periods such as 24, 48, 72, 144 h and at 100 and 110 °C temperatures. Color determination according to ISO 105-A05:1996, performed using a Xrite SP60 portable spectrophotometer.

2.2.2 Determination of the lightfastness of the leathers

Radiation of leather pieces (6,0 x 7,0 cm) using an Atlas Suntest CPS+ at 50°C for 72 hours. Color determination according to ISO 105-A05:1996 was performed using a Xrite SP60 portable spectrophotometer.

2.3 Haptic properties

Recipes: All the leather tests are carried out as per internal Smit & Zoon wet end recipes. Leather applications for haptic performances are typically used standard recipes where dye, fat liquor and other auxiliary leather chemicals are used along with syntan powder or liquid.

Leather assessments: Each haptic property like softness, fullness, grain tightness etc. is assessed on a 1 to 7 scale. Experimental leathers are within this procedure always assessed with a comparative leather as a reference. Leathers assessments are performed by a minimum of 4 technicians and the ratings are averaged to present the final assessment of the leathers for each haptic property separately.

2.4. Analyses of Waste waters/Uptake

Waste waters are analyzed for phenol and phenolsulfonic acid by HPLC as described in the chemical analyses section 2.1. Waste water analyses are used to indirectly estimate the uptake of phenol and phenolsulfonic acid on to the leathers. Alternatively, the uptake of bisphenol S and F is measured by direct analysis of the leathers, where the bisphenol S and F were first extracted from the leathers, before being analyzed by HPLC.

3. Results

3.1. Amount of phenolic monomers in different aromatic syntans

Several aromatic syntans from across the market are analyzed to determine the small amounts of phenolic monomers. HPLC was used to determine the amount of free monomers, more details can be found in the materials and methods section. Table 1 presents the amounts of phenolic monomers in sulfone based syntans (sulfone condensates, SC) series. The amount of monomers in liquid syntans are corrected to their solid content in order to make a comparison with the powdered syntans.

All sulfone based syntans have bisphenol S amounts above 1 wt% (10,000 ppm), and sometimes as high as 6 wt%. When it comes to free phenol, most sulfone syntans have a concentration lower than 100 ppm (see Table 1). Similarly, bisphenol F concentrations in sulfone syntans are usually also very low, with typical values around 100 ppm for the most sulfone based syntans, barring few exceptions where the amount ranges up to 600 ppm. The amount of phenolsulfonic acid varies from one syntan to another. Two sulfone syntans with a relatively high bisphenol S monomer concentration, contain very low phenolsulfonic acid amounts (<0,1 wt%), while most others have around 1 to 2 wt% phenolsulfonic acid with the two exceptions and which have around 4 and 13 wt%. Relative high amounts of bisphenol S can be attributed to the process chemistry of sulfone syntans.

Table 2 presents the amount of phenolic monomers in phenol condensates (non-sulfone condensates) which are typically phenolsulfonic acid and/or phenol condensates. Due to their difference in chemistry compared to sulfone based syntans, phenol condensates have very low bisphenol S amounts, which are in the range of 100-200 ppm. Alternatively the phenol condensates contain free phenol concentrations in the range of <20 to 8,000 ppm and bisphenol F amounts ranging from 100 to 12,000 ppm. Remarkably, phenol condensates exist with both very low bisphenol F and phenol concentrations. The amount of phenol and bisphenol F monomers in phenol condensates seem to have a proportional relationship. When the phenol monomer concentration is relatively low, automatically bisphenol F concentration is also low (Figure 1).

3.2. Uptake of monomers in the leathers

Bisphenols S and F: Selected leathers made by leather properties recipes are tested for the amount of monomers. An extraction method followed by HPLC measurement was used to determine the monomers in the leathers and leathers produced with SC-4L and PC-2L are tested for the presence of monomers. The uptake of bisphenol S/F are both determined to be above 90%, when compared to the corresponding maximum amount based on the total of bisphenol S/F in the syntans. These results show a very high uptake for these monomers.

Phenol and phenolsulfonic acid: wastewaters from the full recipes of syntans with spiked phenols are analyzed for free phenols. Uptake of phenols into the leathers is indirectly calculated based on the measurement of free phenol in the waste waters. The results show that the uptake of phenol was approximately 30 to 40 wt% of the corresponding maximum amount of free phenol present in the syntan. Like phenol, the uptake of phenolsulfonic acid was calculated from the phenolsulfonic acid that was found in the waste waters.

Accordingly phenolsulfonic acid's uptake was calculated as 20-30% to the corresponding phenolsulfonic acid present in the syntan.

3.3. Effect of monomers on the haptics of the leather

Syntan SC-4 L was spiked with different amounts of phenol to check the effect of the syntans on the leather. The resultant syntan blends are tested on WW leathers. The application of the newly produced syntan (SC-4+ with 10,000 ppm phenol) produced somewhat softer, somewhat fuller and somewhat lighter (in color) leathers compared to SC-4 (<20 ppm free phenol). Small amounts of spiked free phenol <1,000 ppm in SC-4 have shown minimal changes in leathers compared to the reference. Results indicate that free phenol is helping in the retanning process of the leather.

Syntan SC-12 was spiked with different amounts of bisphenol S monomer. The resultant modified syntans SC-12+ with 3,6 wt% bisphenol S and SC-12 with 6,7 wt% bisphenol S are tested as retanning agents against SC-12 with 2,4 wt% bisphenol S on WW leathers. 3,6 wt% and 6,7 wt% bisphenol S containing SC-12 have produced somewhat lighter (color intensity), somewhat harder, somewhat tighter and somewhat fuller leathers.

PC-6 was used to test the effect of the influence of free phenolsulfonic acid on the leather. PC-6 (with 2,2 wt% phenolsulfonic acid) was spiked with different amounts of phenolsulfonic acid to make 4,0 wt%, 5,2 wt% and 8,9 wt% phenolsulfonic acid containing syntan blends. With the increase in the amount of phenolsulfonic acid in the PC-6, we see the increasing effects at hardness, emptier handle, tighter grain, and uneven milling (chicken wires) on the leathers. The monomers bisphenol S and phenolsulfonic acid are assumed to not fully penetrate, but to bond to the surface of the leathers and thereby causing additional hardness. When the monomer concentration of both bisphenol S and phenolsulfonic acid was even more increased, the produced leathers also started showing a decrease in fullness. This behavior is assumed not to be caused by the presence of the monomers, but indirectly by the decrease of the concentration of the polymeric species, which are the main active species for the retanning.

3.4. Influence of monomers on the lightfastness and HF of the leathers

3.4.1. Influence of bisphenol S monomer in syntans:

Figure 2 displays the lightfastness (GS values) of WW leathers prepared by sulfone based syntans containing various amounts of bisphenol S. Results revealed that there is an inversible proportional relationship to the amount of bisphenol S in the syntan to the lightfastness. To confirm this effect, different amounts of bisphenol S monomer was spiked to a specific syntan (SC-12) and the resultant syntan blends are tested for their lightfastness. Contradictory to our expectation, lightfastness of the sulfone syntan blends with varying amounts of spiked bisphenol S, have resulted to produce minimal changes to the lightfastness of the leathers (see the Figure 4).

Varying bisphenol S amounts in the syntans, have not shown any trends on towards the heat yellowing resistance (no figure is presented). Based on this can be concluded that free bisphenol S has minimal influence on the heat yellowing in the leathers.

3.4.2. Influence of phenol in syntans

Figure 3 shows the lightfastness (GS values) of WB leathers prepared by various phenol condensates containing different amounts of free phenol. Results have showed an inversible proportional relation of the free phenol concentration in the syntan to the lightfastness of the treated leathers. To confirm this effect, different amounts of phenol monomer was spiked to PC-3 L and the resulting PC-3 L+ treated leathers were tested for lightfastness. Like in the case of bisphenol S, here too, different amounts of spiked phenol containing syntans have shown minimal changes in the lightfastness of the leathers (Figure 5).

3.4.3. Influence of Phenolsulfonic acid in syntans

Figure 6 presents the effect of the spiked phenolsulfonic acid in the PC-6. Results indicate that free phenolsulfonic acid also has a minimal effect on the lightfastness of the leathers.

4. Discussion

4.1. Efficiency during the (Re)- tanning on the leather:

Many aromatic syntans have total monomer concentrations in the range of 2-5 wt%, while very few are in the range of 10 wt% or above. Based on the current studies, as well from earlier studies, it is clear that polymers are the ones that have more (re)tanning effect [Ammenn. J 2009] compared to the monomers. Monomers are effecting leather haptics and waste waters negatively. Leather chemical producers need to constantly work towards optimization of their processes and to minimize the amount of leftover monomers and the resultant products have less wastage and show in turn more efficiency on the leathers.

4.2. Impact of phenolic monomers (in the aromatic syntans) in leather chemicals:

From the four phenolic monomers researched, phenolsulfonic acid shows to be the least problematic with regard to possible health issues and classification. According to the European Chemicals Agency (ECHA) database, phenolsulfonic acid is labelled as corrosive, and the acute toxicity of the chemical is quite low (LD50 = 1410 mg/kg).

According to the Hazard classification & labeling by ECHA, phenol shows high acute toxicity (LD50 = 340 mg/kg) and suspected to be mutagenic, which is of high concern when high concentrations are present in retanning agents. Phenol is widely researched for its adverse effect on health [Gami. A. A et al., 2014; Yonghong. X et al. 2006]. There are no limits on the amount of phenol for retanning agents now. However, phenol is in the ZDHC MRSL 2.0 candidate list for textiles, which will in the future result in a maximum allowed concentration of this substance in the produced chemicals. A similar future restriction level can be expected for leather chemicals. Several consumer brands have been asking on the amount of phenols in the retanning agents and leathers.

Bisphenol S has no ECHA hazard classification & labeling now. Bisphenol S shows very low acute toxicity (LD50 = 2830 mg/kg) and suspected to be toxic to the reproduction system and under assessment as endocrine disrupting. This is also evident from several recent research studies [Fouyet. S et al. 2021]. Research studies have demonstrated that bisphenol S shows very similar toxicity behaviour as bisphenol A, therefore a strong argument may be made to regulate bisphenol S in exactly the same manner as BPA. There is a regulation proposal in front of ECHA for all the bisphenols, which also includes bisphenol F.

Currently there is little impact on the industry in relationship to bisphenol S. However there is an intention for a harmonized classification and labelling of bisphenol S as reprotoxic 1B by European Union. This would mean that all products containing >0,3% bisphenol S will be classified and labelled accordingly. This classification would also qualify bisphenol S as substances of very high concern (SVHC). Once the restriction is published, a transition period will be included in the legal text. Once the proposed restriction comes into force, (leather) articles containing >0.02% of any bisphenol are prohibited in the EU. This limit will be for individual bisphenols and there is no indication that there will be a summation limit for all bisphenols combined. In a future timeline of 5 to 7 years, these restriction can come into place. Currently, consumer brands are already asking for a reduction of bisphenol S concentrations in leathers.

4.3. What are the compounds in the syntans that are effecting the lightfastness?

Lightfastness of the leathers prepared using syntans, is also an important subject. Many different compounds in syntans can have influence on the lightfastness of the leathers. Among all, some compounds can have bigger influence than others. Based on the initial results of this research, it is believed that the free phenol and bisphenol S in the syntans have inversely proportional relationship to the lightfastness of the syntans. However it is evident from the later studies that neither phenol nor bisphenol S have direct effect on the lightfastness of the syntans. Bisphenol S and phenol are believed to be marking compounds for the inversely proportional effect on the lightfastness of the leathers. Real compounds that are effecting lightfastness are currently hypothesized as intermediates during condensation(2 or 4-hyroxymethyl phenol and 2-hydroxymethyl bisphenol S), which are formed during the condensation reaction; The concentration of these compounds in syntans, is expected to be in the same range compared to phenol and bisphenol S. Hence the concentration of phenol and bisphenol S could have shown inversely proportional to the lightfastness. A previous work on the lightfastness of the syntans has demonstrated the positive effect of the urea in the condensation along with phenol and formaldehyde; where phenol, urea and formaldehyde condensed products show to provide a better lightfastness in the leathers compared to phenol and formaldehyde leathers [Venkataboopathy. K et al. 2001]. These results further confirm the current hypothesis on the effect of compounds contributing to the poor lightfastness.

4.4. Challenges to sulfone based syntans:

Sulfone based syntans contain relatively high amount of bisphenol S in the syntans. This is correlated to the relatively low reactivity of bisphenol S in comparison to other phenolic monomers, such as phenol. Additionally, bisphenol S has shown to have a very high uptake on the leather and both factors combined make it quite challenging to produce sulfone based syntans that, after application in the leather production recipe, result in leathers with a bisphenol S concentration of less than 200 ppm. Chemical producers of sulfone based syntans have to either minimize the amount of bisphenol S by optimization of the current process or develop a new process to produce similar products without free bisphenol S. There is already research in this direction to minimize the bisphenol S [Zhang. S et al. 2021]

4.4. Future of phenol condensates:

When comes to the phenol condensates, phenol shows to be relatively reactive. By utilizing this advantage, the producers of phenol condensates have a good possibility to optimize the production processes towards an extremely low concentration of free phenol in the syntans. Phenol has a moderate uptake into the leather, but this also means that a big proportion of the free phenol present in the syntans will end up in the waste waters. When it is possible to reduce the phenol concentrations in syntans sufficiently, there is a strong reason to prefer phenol condensates over sulfone condensates.

5. Conclusions

Sulfone based syntans across the market have relatively high amounts of bisphenol S (1 to 6 wt%), while they contain only small amounts of phenol (<100 ppm).

Phenol condensates (non-sulfone based syntans) have free phenol concentrations in a wide range (<20 to 8000 ppm) and bisphenol F in proportional amounts.

Amounts of bisphenol S and phenol in the syntans are appeared as inversely proportional to the lightfastness of the leathers. However model syntans have suggested these are only markers while the real responsible compounds for the poor lightfastness are different and which are hypothesized as intermediates during condensation(like 2- or 4-hyroxymethyl phenol and 2-hydroxymethyl bisphenol).

Leathers have shown to become harder and tighter, with the increase of the amount of phenolsulfonic acid and bisphenol S in the syntans. In the syntans where monomer concentrations are increased to above 5 wt%, the produced leathers have shown to become emptier. Conversely, with the increase of phenol in the syntans, leathers show to become softer and fuller.

Results have demonstrated that phenol condensates with lower concentrations of free phenol, are able to create leathers with higher lightfastness properties in comparison to sulfone based syntans.
Bisphenol S and bisphenol F both have an excellent uptake into the leather, which is determined to be above 90% corresponding to the maximum available amount of monomers in the syntans. Phenol shows a moderate uptake into the leather, which is of around 30-40 wt%.

Based on the toxicity studies, a restriction proposal on all bisphenols is under assessment at ECHA. There is a strong indication that bisphenol S and F, will also get the similar indication as bisphenol A, that is labeled as both reprotoxic and endocrine disrupting.

The focus of the syntan market could be shifted from sulfone condensates towards phenol condensates when manufacturers of the phenol condensates are able to optimize their production processes to create low phenol containing syntans.

6. The acknowledgements

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Appendices

Table 1: Amount of phenolic monomers (in ppm) in different sulfone based syntans across the Leather industry*

Type of Syntan	Phenol, in ppm	Phenolsulfonic acid, in wt%	Bisphenol F, in ppm	Bisphenol S, in wt%
SC-0	<20	1,5	300	0 (<75 ppm)
SC-1	<100	0,5	600	2,6
SC-2 L	<100	13,6	ND	4,3
SC-3	100	1,9	ND	2,6
SC-4 L	<20	3,3	<75	2,2
SC-5	2000	2,6	ND	1,9
SC-6 L	<20	0,1	<75	6,1
SC-7	<100	2,2	<75	1,5
SC-8 L	220	1,4	ND	2,4
SC-9	90	0,9	ND	1,6
SC-10 L	50	4,4	<20	1,5
SC-11 L	<20	0,1	ND	6,4
SC-12	<50	2,1	<75	2,4

*HPLC method was sued to determine the monomers in the syntans

*The monomers weights in the liquids are corrected to dry weight

ND= not determined

Table 2: Amount of phenolic monomers (in ppm) in different phenol based syntans across the Leather industry*

Type of Syntan	Phenol, in ppm	Phenolsulfonic acid, in wt%	Bisphenol F, in ppm	Bisphenol S, in wt%
PC-1	1500	8,6	2000	<75
PC-2 L	100	2,5	1500	<75
PC-3 L	<20	1,5	300	<75
PC-4	5000	4,7	12000	<75
PC-5	3000	ND	10000	100
PC-6 L	500	3,0	1100	<50
PC-7	<20	0,0	2000	ND
PC-8	<20	0,03	1800	ND
PC-9	200	0	590	0
PC-10	4500	3	10000	0
PC-11	7600	1,4	10500	0

*HPLC method was sued to determine the monomers in the syntans

*The monomers weights in the liquids are corrected to dry weight

ND= not determined

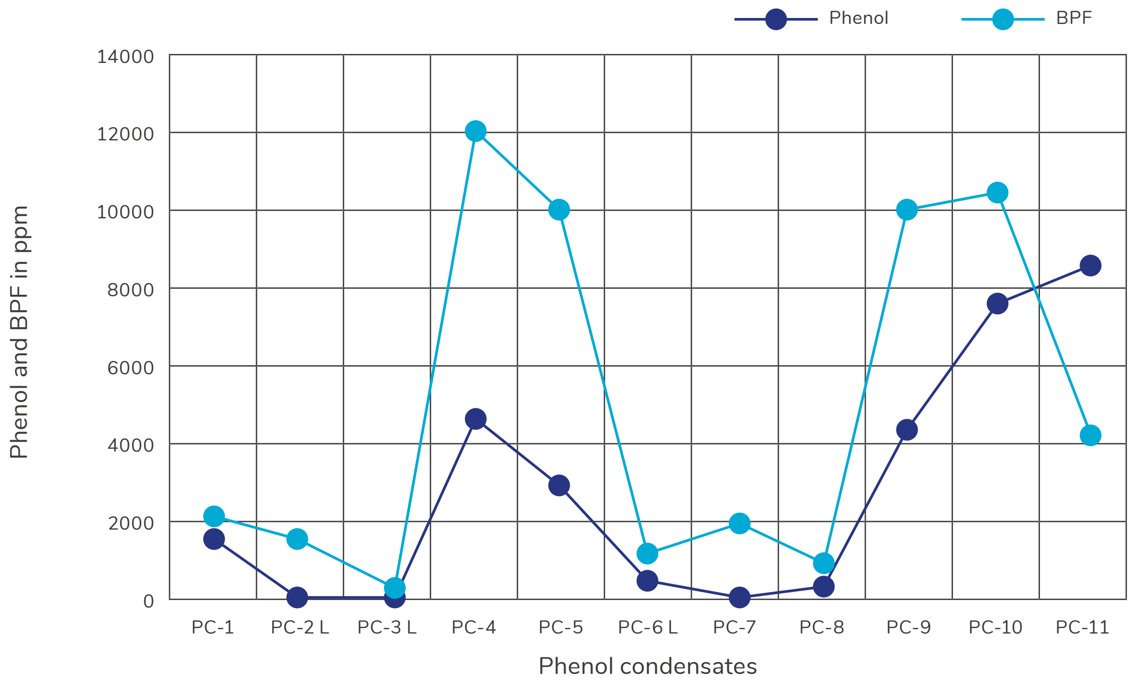

Figure 1: Amounts of phenol and bisphenol F (ppm) in the phenol condensates

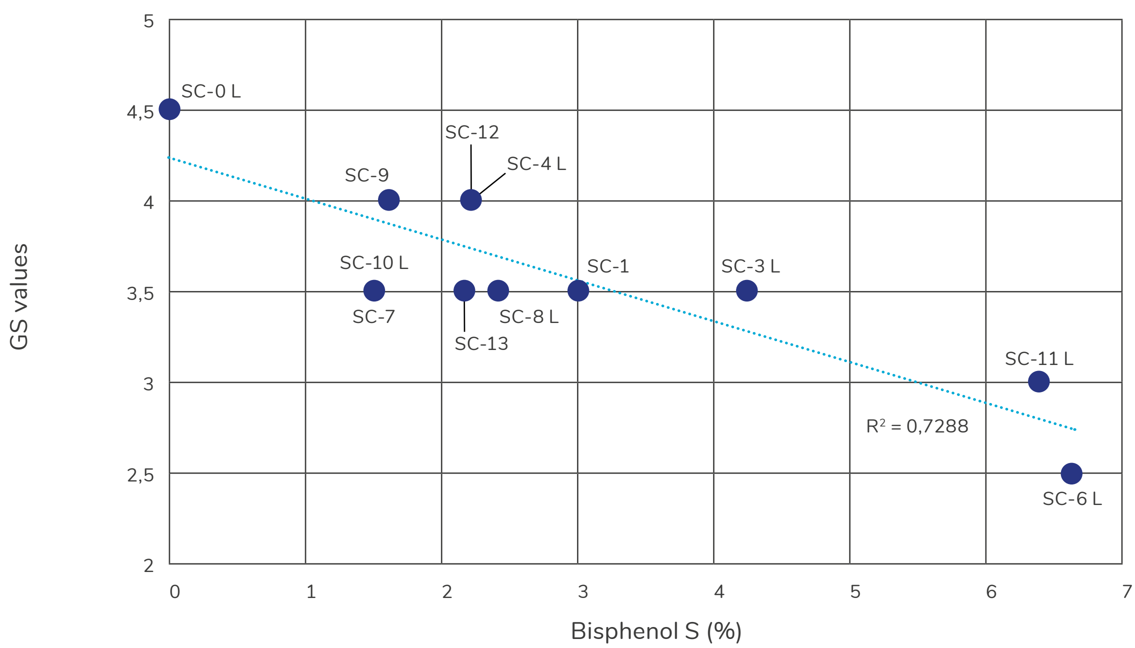

Figure 2: Lightfastness of WW leathers prepared by various sulfone based syntans. Figure presented the amount of free bisphenol S (wt%) versus Grey Scale (GS) values collected at 72 h/BST 50°C (Blank WW leather GS value =3,5)

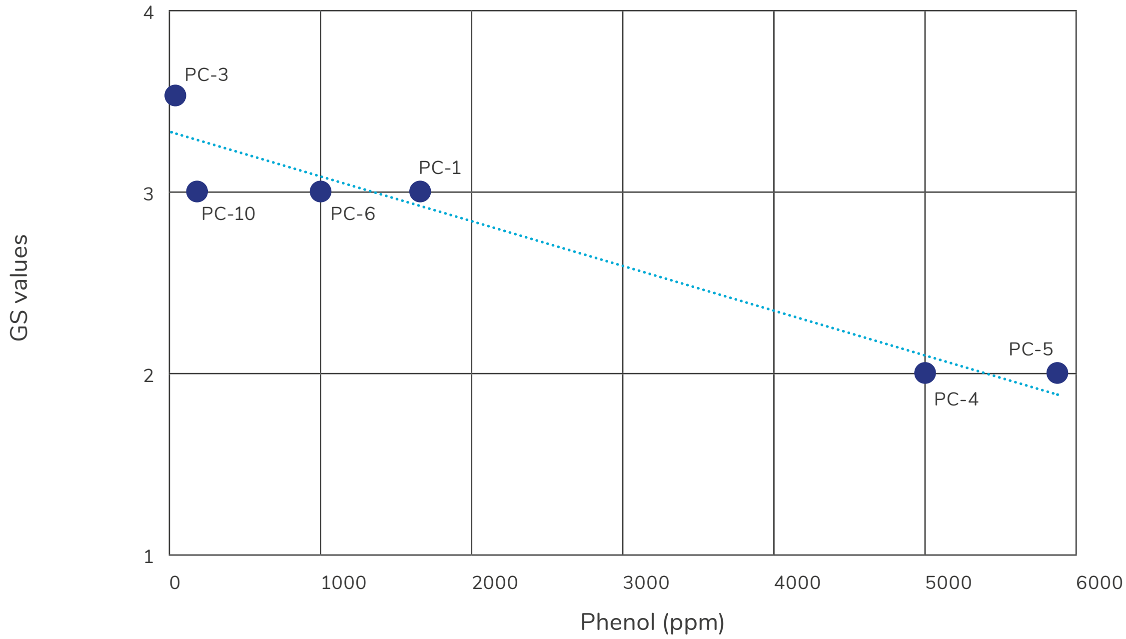

Figure 3: Lightfastness of WB leathers prepared by various phenol condensates. Figure presented the amount of free phenol (in ppm) versus Grey Scale (GS) values collected at 72 h/BST 50 °C (Blank WB leather GS value =4,5)

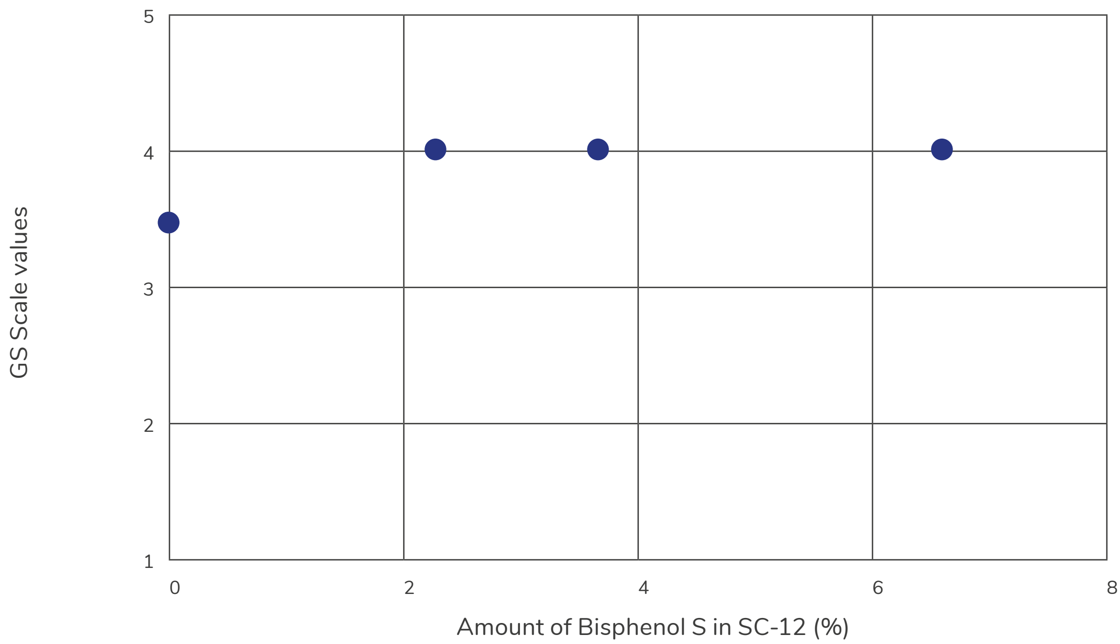

Figure 4: Lightfastness of WW leathers prepared by the syntan blends prepared by SC-12 by spiking different amounts of Bisphenol S. Graph depicted the amount of Bisphenol, wt% versus Grey Scale values collected at 72 h/BST 50 °C (Blank WW leather GS value = 4,0)

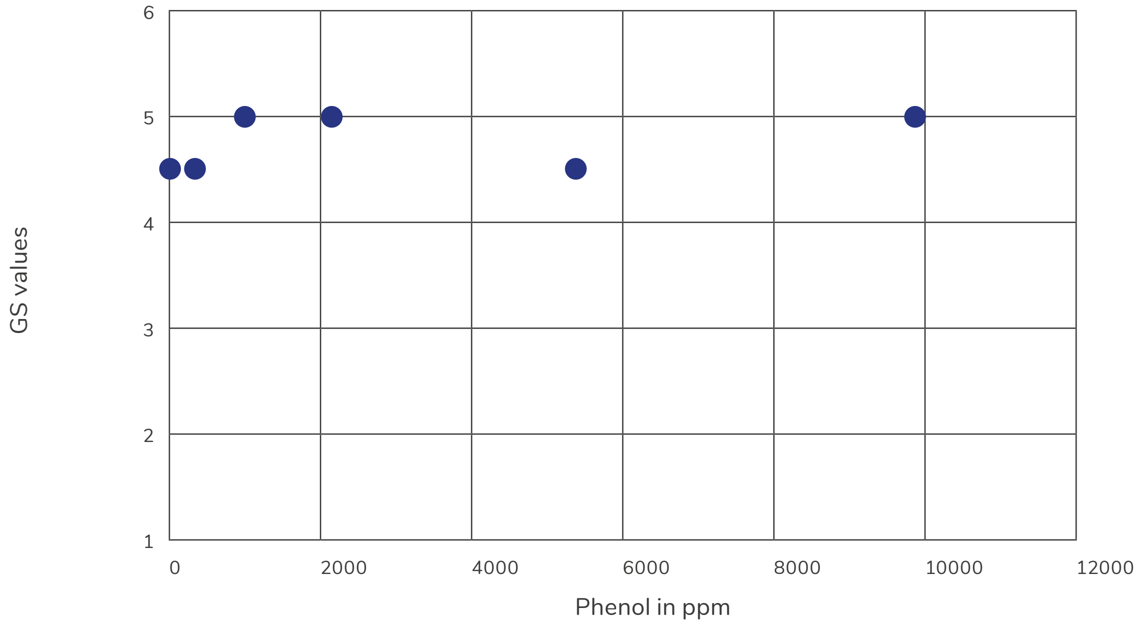

Figure 5: Lightfastness of WW leathers prepared by the syntan blends prepared by PC-3 L (free phenol <20 ppm) by spiking different amounts of free phenol. Graph depicted the amount of free phenol (in ppm) versus Grey Scale values collected at 72 h/BST 50 °C (Blank WB leather GS value =4,5)

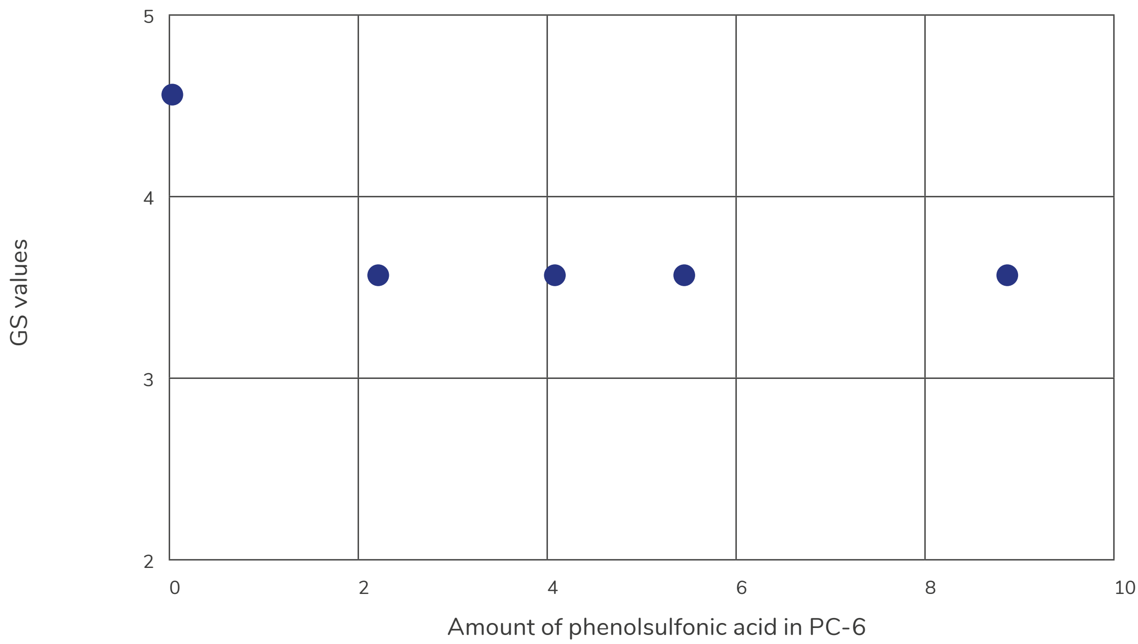

Figure 6: Lightfastness of WB leathers prepared by the syntan blends prepared by PC-6 by spiking different amounts of phenolsulfonic acid. Graph depicted the amount of phenolsulfonic acid, wt% versus Grey Scale values collected at 72 h/BST 50 °C (Blank WB leather GS value = 4,5)

More information

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