

Research on aromatic syntans without restricted bisphenols

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Abstract

Bisphenol A and its substitutes, such as bisphenol S, are widely used to produce polycarbonate, epoxy resin and other chemical materials. In leather industry, bisphenol S and bisphenol F can be easily found in aryl synthetic tannins derived from phenols. ECHA and the Member States have assessed a group of 148 bisphenols (BPs) and recommended that more than 30 BPs need to be restricted due to their potential hormonal or reprotoxic effects. In this paper, the current situation of BPs content especially the bisphenol F and bisphenol S in aryl synthetic tannins and in the leather was studied by using HPLC and the formation mechanism of bisphenol F and bisphenol S had also been discussed. At the same time, suitable hydrophilic aromatic sulfonic acids and hydrophobic aromatic monomers were chosen to condense with formaldehyde under optimized conditions to form a series of aryl synthetic tannins without the 148 BPs announced by ECHA. The new synthetic tanning agents have good performances in leather application and the resultant leathers have good physical properties.

Keywords: aromatic syntans, restricted bisphenols



1. Introduction

Bisphenol A and its substitutes, such as bisphenol S, are widely used to produce polycarbonate, epoxy resin and other chemical materials, from which lots of consumer goods include water bottles, canned packaging and thermal paper are made. In leather industry, bisphenol S and bisphenol F can be easily found in aryl synthetic tannins derived from phenols. By far, more and more studies have shown that the structures of some BPs are similar to main estrogen estradiol, such BPs have affinities to estrogen receptors and induce endocrine and reproductive toxicity to animals and humans (Song2018; Grignard2012; Pelch2019). ECHA and the Member States have assessed a group of 148 BPs and recommended that more than 30 BPs need to be restricted due to their potential hormonal or reprotoxic effects. Furthermore, some BPs have already been listed in EU REACH directive of substances of very high concern (SVHC) list, manufacturing restricted substances list (MRSL) of zero discharge of hazardous chemicals (ZDHC) organization, OEKO-TEX leather standard and so on.

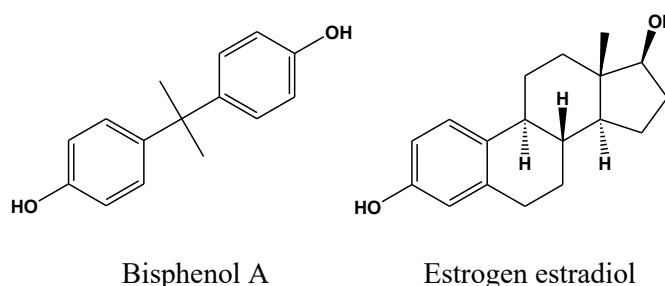


Fig. 1 Chemical structure of bisphenol A and estrogen estradiol

The current situation of BPs content especially the bisphenol F and bisphenol S in synthetic tannins and in the leather was studied by using HPLC and the formation mechanism of bisphenol S and bisphenol F had also been discussed.

At the same time, suitable hydrophilic aromatic sulfonic acids and hydrophobic aromatic monomers were chosen to condense with formaldehyde under optimized conditions to form a series of aryl synthetic tannins without the 148 BPs announced by ECHA. The new synthetic tanning agents have good performances in leather application and the resultant leathers have good physical properties.

2. Material and Methods

2.1 Materials

4,4'-Sulfonyldiphenol (98 wt. %) and 4,4'-Dihydroxydiphenylmethane (98 wt. %) were purchased from Macklin; Naphthalene (99 wt. %), concentrated sulfuric acid (98 wt.%), formaldehyde solution (37 wt. %), ammonia solution (22 wt. %) were of commercial grade and provided by Sichuan Decision New Material Technology Co. Ltd.; Syntan B and syntan S were of commercial grade provided by Sichuan Decision New Material technology Co., Ltd.; Shaved wet blue of cow hide was purchased from Zhoukou Senyuan Leather Industry Co., Ltd.; Pickled sheep skin was purchased from Jiaozuo Yibang Fur Sales Co. Ltd.; All other chemicals used for leather processing were of commercial grade, while those used for analyses were of chromatographic grade.



2.2 Methods

2.2.1 Quantitative analysis of BPF and BPS

The content of BPF or BPS in syntans and in the resultant leathers was determined by using HPLC (Essentia LC-60, Shimadzu, Kyoto, Japan) coupled with Shim-pack GIST C18-AQ column (5 μ m, 4.6 \times 250mm) according to the standard SN/T 4424-2022.

2.2.2 Synthesis of syntan M without restricted BPs

Naphthalene sulfonic acid was synthesized by the reaction of naphthalene with concentrated sulfuric acid first, then condensed with formaldehyde and R group substituted phenols in water solution of a suitable concentration at the temperatures between 95 $^{\circ}$ C to 100 $^{\circ}$ C for 8h. The above reaction liquid was neutralized by ammonia solution to pH 3.0 to pH 5.0 at last.

2.2.3 Synthesis of syntan N without BPs

R group substituted aryl sulfonic acid was obtained by the reaction of the R group substituted aryl compound with concentrated sulfuric acid, then condensed with formaldehyde and R group substituted benzoic acid in water solution of a suitable concentration at temperatures between 95 $^{\circ}$ C to 100 $^{\circ}$ C. The above reaction liquid was neutralized by ammonia solution to pH 5.0 to pH 7.0 at last.

2.2.4 Molecular weight determination of syntan

The molecular weight of syntan M, N, and B was determined by a GPC (coupled with a HPLC (Essentia LC-20, Shimadzu, Kyoto, Japan) which was with a differential refractive index detector (RID-20 Shimadzu, Kyoto, Japan), and a TSK gel GMPWXL column (Tosoh, Japan)) using 0.1 mol/L NaNO₃ aqueous solution as mobile phase (flow rate 0.6 mL/min) at temperature 35 $^{\circ}$ C.

2.2.5 Tanning experiment

Four pieces of pickled sheep skins were tanned by syntans as shown in Table 1.

Table 1 Tanning processes

| Process | chemicals | Dosage ^a (%) | Temperature($^{\circ}$ C) | Time(min) | remark |
|------------|----------------------|-------------------------|----------------------------|---------------|-----------------|
| Depickling | Water | 80 | Room temperature | | |
| | Sodium chloride | 10 | | 10 | |
| | Pickled sheep skin | | | 10 | |
| | Sodium bicarbonate | 2 | | 30 \times 2 | |
| | Degreasing agent | 3 | | 90 | pH 6.5, rinsing |
| Tanning | Water | 100 | 35 | 10 | |
| | Syntans ^b | 25 | | 180 | |
| | Fomic acid | 1-2 | | 180 | pH 3.5 |

^a The percentage of chemicals was based on the weight of limed pelt

^b Syntans referred to syntan B, syntan M, and syntan N



Shrinkage temperature of the tanned wet white was determined by using a digital leather shrinkage temperature tester (MSW-YD4, College of Electric and Information Engineering, Shaanxi University of Science and Technology, China).

2.2.6 Retanning and fatliquoring experiment

Six pieces of shaved wet blue (21cm×30cm for each piece) were rewetted, chrome retanned and neutralized to pH 5.0 according to conventional processes. These leather samples were then retanned and fatliquored as shown in Table 2.

Table 2 Retanning and fatliquoring processes

| Process | chemicals | Dosage ^a (%) | Temperature(°C) | Time(min) | remark |
|--------------------------------------------------------------------------------------------------|----------------------|-------------------------|-----------------|-----------|-------------------------------|
| Retanning | Water | 100 | 35 | | |
| | Syntans ^b | 20 | | 60 | |
| Fatliquoring | Water | 100 | 50 | | |
| | Synthetic fatliquor | 10 | | 60 | |
| | Formic acid | 2 | | 20×2 | pH 3.8, collect effluent |
| Washing | Water | 200 | | 10 | |
| Vacuum drying at 50°C for 3min, hang-drying and staking, conditioning at 20°C and 65% RH for 48h | | | | | Collect crust leather samples |

^a The percentage of chemicals was based on the weight of shaved wet blue

^b Syntans referred to syntan B, syntan M, and syntan N

2.2.7 Determination of uptake rate of syntan in leather

Aromatic syntans exhibit significant UV absorption in aqueous solution, and the linear correlation between UV absorbance values and syntan concentrations is very good. The initial and final UV absorbance values of the retanning bath were tested and recorded as Abs ini and Abs res, and the uptake rate of syntans in leather was calculated by formula (1).

$$\text{Uptake rate (\%)} = \frac{\text{Abs ini} - \text{Abs res}}{\text{Abs ini}} \times 100 \quad (1)$$

2.2.8 Determination of leather softness

The softness of the staked crust leather was determined by a leather softness tester (DZ-326, Following Large and Medium-sized Instrument Co., Ltd., China) according to the standard IUP 36.

2.2.9 Determination of leather CIELAB L* value

The CIELAB L* value of leather was determined by using a colorimeter (COLOR I5, X-Rite, America) to show the bleaching effect of syntans on leather according to the standard IUF 474.



2.2.10 Determination of formaldehyde content of leather

The formaldehyde content of leather was determined according to the standard IUC 19-1.

2.2.11 Color fastness and ageing of leather

Color fastness and ageing of leather to artificial light at high temperatures was tested by using a Xenon arc lamp weather resistance test chamber (SN-80A, Htfk, China) according to the standard ISO 105-B06.

Hydrothermal stability of leather was tested by using a constant temperature and humidity box (GT-7005-T, Gotech Testing Machines Inc., China) according to the standard IUF 412.

3. Results and Discussion

3.1 Studies of BPF and BPS in aryl syntans and in the leather

Phenolic syntans are one main kind of aryl syntans, syntan B is an excellent classical phenolic syntan and its possible chemical structure is shown in Fig. 2. Phenolic syntans are usually synthesized by condensation of phenol, formaldehyde and phenol sulfonic acids. During the condensation process, two molecules of phenol and one molecule of formaldehyde condense to form BPF and its isomers, the chemical structures are shown in Fig. 3. Phenol undergoes sulfonation reaction with concentrated sulfuric acid to form phenol sulfonic acids as the hydrophilic condensation monomers, while a small amount of BPS and its isomers are inevitably formed due to the dehydration reaction of phenol sulfonic acids. The chemical structures of BPS and its isomers are shown in Fig. 4.

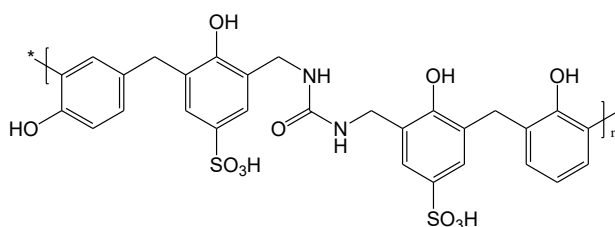


Fig. 2 Chemical structure of phenolic syntan B

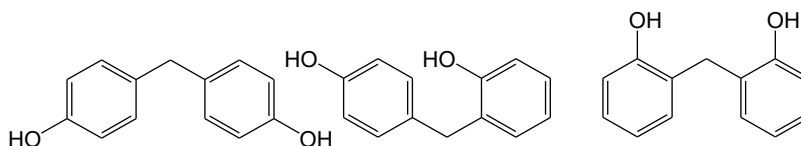


Fig. 3 BPF and its isomers

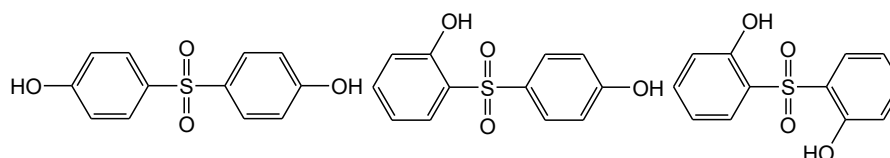


Fig. 4 BPS and its isomers



Sulfone based aryl syntans are another main kind of the aryl syntans, syntan S is a classical sulfone based syntan and its possible chemical structure is shown in Fig. 5. BPS and its isomers are the main raw materials for sulfone based syntans, which are difficult to be completely consumed during condensation reaction and remain in the products.

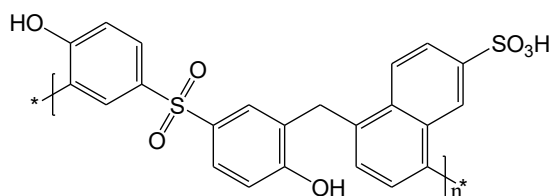


Fig. 5 Chemical structure of sulfone based syntan S

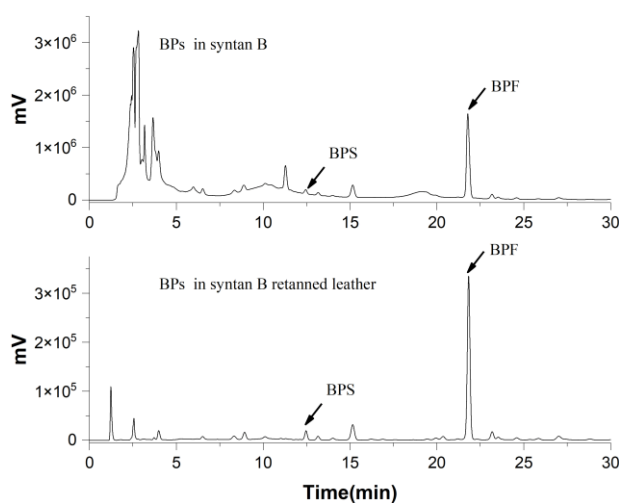


Fig. 6 Liquid chromatogram of syntan B and the extraction liquid of the retanned leather

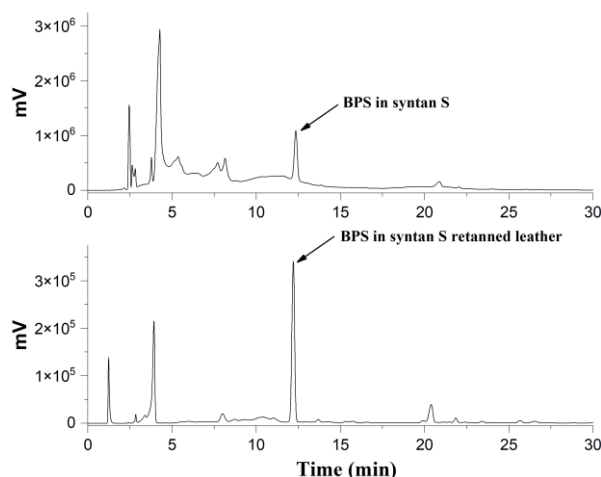


Fig. 7 Liquid chromatogram of syntan S and the extraction liquid of the retanned leather

The content of BPF and BPS both in syntan B and syntan S and in the retanned leathers was determined by liquid chromatography as shown in Fig. 6 and Fig. 7. The BPF content in syntan B was about 10000 mg/Kg but was ND in syntan S, the BPS content in syntan B was only about 200 mg/Kg, but was about 12000 mg/Kg in syntan S. At the same time, as we tested, the content of BPF in the leather retanned



with syntan B (20% based on shaved weight) was about 1000 mg/Kg, the content of BPS in the leather retanned with syntan S (20% based on shaved weight) was about 1200 mg/Kg.

If the molar ratio of formaldehyde to BPF or BPS was raised, the condensation reaction temperature was raised, or the reaction time was prolonged, the amount of BPF or BPS in syntans decreased significantly, but cannot be eliminated.

3.2 Restricted BPs free syntan M

As ECHA and the member states have assessed a group of 148 BPs and recommended that more than 30 BPs need to be restricted, we chose two R group substituted phenols to condense with formaldehyde and naphthalene sulfonic acid to form syntan M which was free from 148 BPs mentioned above. The main components of syntan M were shown in Fig. 8, among which component D contained kinds of BPs without restriction by far.

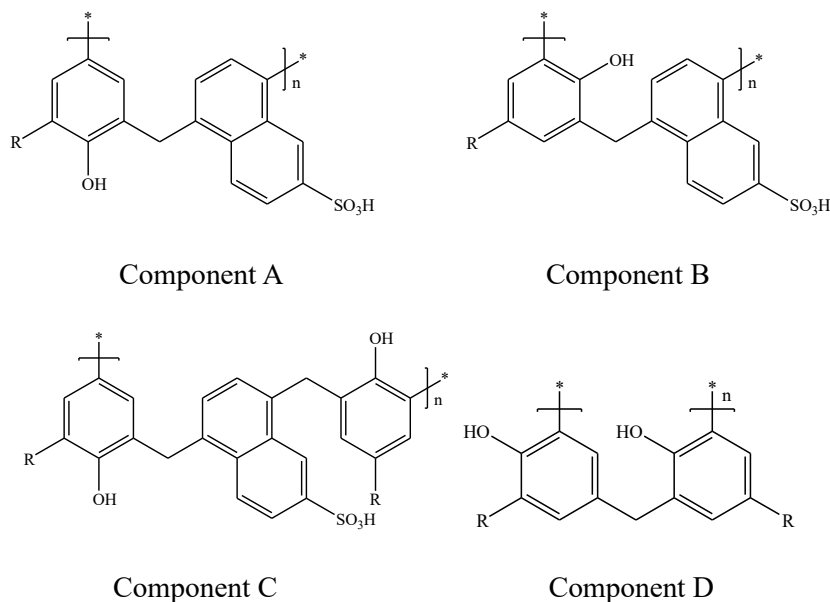


Fig. 8 The main components of syntan M

We first conducted liquid chromatography analysis of BPS and BPF in syntan M, and the result was ND as shown in Fig. 9.

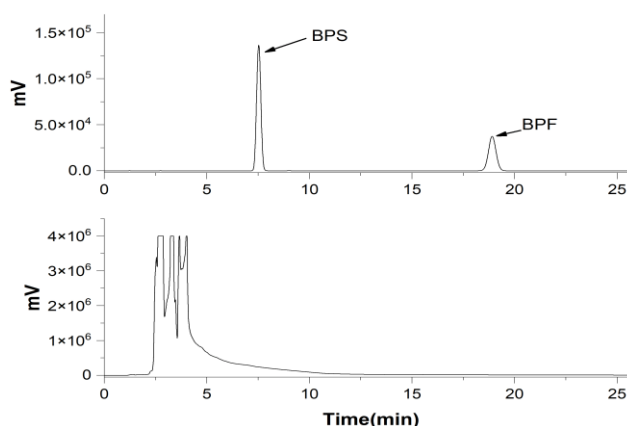


Fig. 9 Analysis of BPS, BPF in syntan M by liquid chromatography



Then molecular weight of phenolic syntan B and syntan M was tested and the results compared with the classical aromatic syntans Huang(2000) were shown in Table 3.

Table 3 Molecular weight distributions of syntan B and syntan M

| Molecular weight range | Classical phenolic syntans /% | Syntan B/% | Syntan M/% |
|------------------------|-------------------------------|------------|------------|
| 200-500 | 33.6 | 26.0 | 17.5 |
| 500-1000 | 41.5 | 45.6 | 22.5 |
| 1000-10000 | 23.7 | 28.4 | 60.0 |
| >10000 | 1.2 | 0 | 0 |

The molecular weight of syntan M was slightly higher than phenolic syntan B, what will be the application performances in leather retanned separately by syntan M and syntan B? Detailed results can partly be found in Table 4. Leather M and leather B were retanned separately by syntan M and syntan B at the dosage of 20 percent based on the weight of shaved wet blue according to conventional process.

Table 4 Application performances of syntan M and syntan B

| Sample | Softness | L* value | Content of Formaldehyde | Resistance to light | Hydrothermal stability | Uptake rate |
|-----------|----------|----------|-------------------------|---------------------|------------------------|-------------|
| Leather M | 6.23 | 83.92 | <5 mg/Kg | Grade 3 | Grade 4-5 | 90% |
| Leather B | 6.00 | 84.86 | <5 mg/Kg | Grade 2-3 | Grade 4-5 | 90% |

The softness and light resistance of leather M were slightly better than leather B, the content of formaldehyde in leather M and B was very low, and the uptake rate in leather of syntan M and syntan B was both about 90%. Some leather technicians evaluated the handle of leather M and leather B, the fullness and tightness were almost the same, the smoothness of leather M was slightly better than leather B.

The shrinkage temperature of wet white tanned with syntan M and syntan B increased by 9°C and 12°C separately, which might indicate the tanning ability of syntan M was slightly weaker than syntan B.

The performances of syntan M and phenolic syntan B were almost the same, because the main monomers of syntan M were phenol derivatives and at the same time the condensation reaction conditions were optimized.

What should we do if the restrictions on BPs become more rigid, and all the BPs are not allowed to be used any longer.



3.3 BPs free syntan N

We also tried to choose R_1 group substituted aryl sulfonic acid and R_2 group substituted benzoic acid to condense with formaldehyde under optimized conditions to give syntan N which was BPs free as shown in Fig. 10.

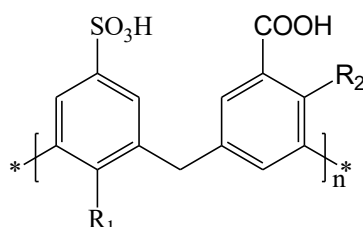


Fig. 10 The main component of syntan N

Then molecular weight of syntan N was tested and the results compared with the classical aromatic syntans Huang(2000) and syntan B were shown in Table 5.

Table 5 Molecular weight distributions of syntan B and syntan N

| Molecular weight range | Classical phenolic syntans /% | Syntan B/% | Syntan N/% |
|------------------------|-------------------------------|------------|------------|
| 200-500 | 33.6 | 26.0 | 20.3 |
| 500-1000 | 41.5 | 45.6 | 25.2 |
| 1000-10000 | 23.7 | 28.4 | 54.5 |
| >10000 | 1.2 | 0 | 0 |

The molecular weight of syntan N was also slightly higher than the classical phenolic syntan B, the application performances in leather retanned separately by syntan N and syntan B were partly summarized in Table 6.

The softness and light resistance of leather N was better than leather B, the content of formaldehyde in leather N and B was very low, and the uptake rate in leather of syntan N and syntan B was both about 90%. As evaluated by leather technicians, fullness and tightness of leather B was slightly better than syntan N, the smoothness of leather N was slightly better than leather B. The fullness and tightness can be improved by changing the molar ratio of R_2 group substituted benzoic acid to R_1 group substituted aryl sulfonic acid.

The shrinkage temperature of the wet white tanned with syntan N and syntan B increased by 6°C and 12°C separately, which might indicate the tanning ability of syntan N was weaker than syntan B possibly due to the hydrogen bonding strength between benzoic acids and collagen fibers was weaker than that between phenols and collagen fibers.



Table 6 Application performances of syntan N and syntan B

| Sample | Softness | L* value | Content of Formaldehyde | Resistance to light | Hydrothermal stability | Uptake rate |
|-----------|----------|----------|-------------------------|---------------------|------------------------|-------------|
| Leather N | 8.0 | 79.92 | <5 mg/Kg | Grade 4-5 | Grade 4-5 | 90% |
| Leather B | 7.4 | 81.29 | <5 mg/Kg | Grade 2-3 | Grade 4-5 | 90% |

4. Conclusion

The content of BPF and BPS in synthetic tannins and in the leather was studied by using HPLC and the formation mechanism of BPS and BPF had also been discussed. Phenolic syntan B mainly contained about 10000 mg/Kg of BPF, while sulphone based syntan S contained 12000 mg/Kg BPS. the leather retanned by syntan B or syntan S at the dosage of 20% based on the weight of shaved wet blue contained approximately 10 wt. % BPF or BPS of syntan B or syntan S. The content of BPF or BPS in aryl syntans can be reduced significantly by optimizing the condensation reaction conditions, but cannot be eliminated.

So, we chose R group substituted phenols to condense with formaldehyde and naphthalene sulfuric acid to form syntan M which was free from 148 BPs mentioned above. Further more, in order to obtain the BPs free syntan, we tried to choose R₁ group substituted aryl sulfonic acid and R₂ group substituted benzoic acid to condense with formaldehyde under suitable conditions to give syntan N which was BPs free. The new aryl synthetic syntan M and syntan N have good performances in leather application and the resultant leathers have good physical properties.

5. References

1. Song, S. L., Ma, S. M., Toxicology, human exposure and health effects of bisphenol S, *Environ. Chem.*, **37(2)**: 200-208, 2018.
2. Grignard E., Lapenna S., Bremer S., Weak estrogenic transcriptional activities of Bisphenol A and Bisphenol S, *Toxicol. In Vitro*, **26**: 727-731, 2012.
3. Pelch K.E., Li Y., Perera L., Thayer K.A., Korach K.S., Characterization of Estrogenic and Androgenic Activities for Bisphenol A-like Chemicals (BPs): In Vitro Estrogen and Androgen Receptors Transcriptional Activation, Gene Regulation, and Binding Profiles. *J. Toxicol. Sci.* **172(1)**: 23-37, 2019.
4. Huang, W., Shi, B., Tanning mechanisms for aromatic syntans, *China Leather*, **29**, 17-19, 2000.