# Synthesis and Application of a New Phosphate Ester Based on Nonionic Amphiphilic Polyurethane as Leather Fatliquoring Agent

by

Hanping Li,[A,B] Yong Jin,[A,B*] Baozhu Fan,[C,D] Rui Qi[C,D] and Xinfeng Cheng[C,D†]

[A]*Key Laboratory of Leather Chemistry and Engineering, Ministry of Education,*
Sichuan University, Chengdu 610065, China

[B]*National Engineering Laboratory for Clean Technology of Leather Manufacture,*
Sichuan University, Chengdu 610065, China

[C]*Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Center of Polymer Science and Technology,*
Chengdu 610041, China

[D]*University of Chinese Academy of Sciences,*
Beijing 100049, China

## Abstract

A new polyurethane phosphate ester (PUP-2) was successfully synthesized based on a nonionic amphiphilic polyurethane (PU-2). The structures and properties of PU-2 and PUP-2 were characterized by FTIR and surface tensiometer. The fatliquoring experiments were carried out in three different groups (treated with PUP-2 alone, with the complex of hexadecyl phosphate ester (SLP) and PUP-2, or with the complex of SLP, PUP-2 and other commercialized fatliquoring agents, respectively). The physical and organoleptic properties of the resultant leathers were investigated and SEM was carried out in the study of fiber splitting. The leathers treated in the three different fatliquoring experiments all did not have fatty spew defect. Furthermore, the resultant leathers treated with PUP-2 alone or with the complex of SLP and PUP-2 had the advantage of resistance to yellowing. This new phosphate ester meets the requirements for the leathers with a good performance in resistance to yellowing and avoiding fatty spew defect.

## Introduction

Currently a wide variety of fatliquoring agents are being used in leather manufacturing.[1-3] Phosphorylated fatliquoring agents are widely used due to the advantages of low toxicity, low stimulation and good biodegradability.[4, 5] Most of the phosphate esters used at present are natural phosphate esters or synthetic phosphate esters which are usually synthesized based on modified natural oils or high-carbon alcohols.[6, 7] However, the natural phospholipids have some disadvantages such as easy to mildew, dull color and low emulsion stability.[8,9] In addition, the synthetic phosphate esters based on modified natural oils can be oxidized due to the carbon-carbon double bonds of natural oils,[10] thus resulting in the poor performance of leathers and limiting their applications. What's more, although the high-carbon alcohol phosphate esters can improve the oil feeling, waxy feeling and waterproofness of leathers, they usually result in fatty spew formation on the leather surface when the temperature is low, which can be attributed to their low emulsification, poor permeability and high freezing point. Thus, it was really necessary for the leather industry to develop a new phosphate ester with higher emulsification, richer permeability, lower freezing point and no carbon-carbon double bonds to be substituted for the traditional ones.

In this paper, a new polyurethane phosphate ester (PUP-2) was prepared, which consists of the soft molecular chains. And carbon-carbon double bonds are not involved here, too. Moreover, the nonionic amphiphilic structural features can improve the permeability and stability of the resultant fatliquoring emulsions. The above advantages of the polyurethane phosphate ester are in accord with the growing demand for the leathers with the good properties of resistance to yellowing and avoiding fatty spew defect.

*Corresponding author e-mail: jinyong@scu.edu.cn
Manuscript received March 25, 2016, accepted for publication June 14, 2016.

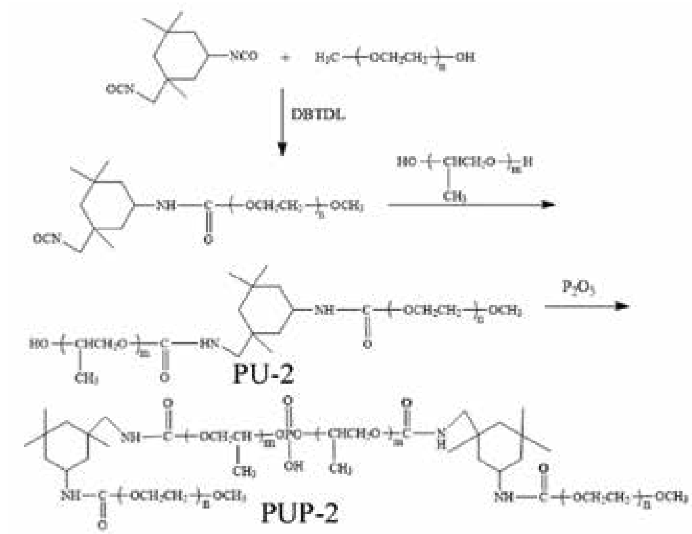
## Experimental

**Materials**
Isophorone diisocyanate (IPDI), polyethylene glycol monomethyl ether (MPEG, Mn=750 g/mol) and polyoxypropylene ether (PPG, Mn=2000 g/mol), AR grade, were purchased from Shanghai Chemical Reagents Corporation, China. Dibutyltin dilaurate (DBTDL), phosphorus pentoxide ($P_2O_5$) and hexadecanol, AR grade, were purchased from Ke Long Chemical Corporation, China. SWA, FG-B, FL-71, NL-20, HN01, A18, JM, JMK, OF, FS-90, melamine, dicyandiamide, dispersing tannin, chestnut and protein filler, purchased from Dowell Technology Co., Ltd., were used as industrial grade. Wattle extract, industrial grade, was purchased from UNITY Corporation, Argentina. PF aldehyde, industrial grade, was purchased from Zschimmer & Schwarz Chemicals. Basic chromium sulphate, industrial grade, was purchased from Ming Feng Chemical Corporation, China. Wet blue bovine hides were purchased from Da Fan Jiu Leather Corporation, China. Other chemicals were of analytical grade and used as received. All of them were used without further purification.

**Synthesis of Hexadecyl Phosphate Ester (SLP), PU-2 and PUP-2**
A certain amount of hexadecanol was plunged into a 100 ml three-necked flask equipped with a stirrer and a thermometer at 50°C. Under the high-speed stirring, a quantitative amount of $P_2O_5$ with a mole ratio of ROH: $P_2O_5$=3: 1 which was divided into four same parts was added with an internal of 10 min. After all of $P_2O_5$ was added and dispersed completely, the system was heated up to 85°C and maintained for 5 h. Then, a small amount of water with a mole ratio of $P_2O_{5:}$ $H_2O$=1: 1 was added at 30°C. After 1.5 h, the product of SLP was obtained.

The calculated amount of MPEG and DBTDL (a mole ratio of MPEG: DBTDI=1: 0.002) were placed in a four-necked flask equipped with a thermometer and a mechanical stirrer. While stirring heated to 60°C, the calculated amount of IPDI with a mole ratio of MPEG: IPDI=1: 1 was added dropwise into the flask. The reaction was carried out at 60°C for 4 h. PPG-2000 with a mole ratio of MPEG: PPG-2000=1: 1 was then added and allowed to react for another 2 h at 80°C. The nonionic amphiphilic diblock polyurethane (PU-2) was obtained.

A certain amount of PU-2 was plunged into a 100 ml three-necked flask equipped with a stirrer and a thermometer at 50°C. A quantitative amount of $P_2O_5$ with a mole ratio of PU-2: $P_2O_5$=1: 2 which was divided into four same parts was added with an internal of 10 min. After all of the $P_2O_5$ was added and dispersed completely, the system was heated up to 85°C and maintained for 5 h. After the reaction, mixture was cooled to 30°C, a calculated amount of water was added with a certain mole ratio ($H_2O$: $P_2O_5$ =2: 1) by stirring. After 1.5 h, the polyurethane phosphate ester (PUP-2) was prepared. The preparation of PU-2 and PUP-2 is shown schematically in Scheme 1.



Scheme 1. Synthesis of PU-2 and PUP-2.

**Application on Leathers**
The wet blue bovine hid was cut into two pieces (200mm x 150mm), which had the symmetry along the spine to make sure the same fiber woven status. One was treated with fatliquoring agents and the other one was not as a comparison. The retanning and fatliquoring process of leathers is shown in Table I, and the three ways of fatliquoring were carried out as follows:

*Experiment 1-* Treated with PUP-2 alone, its weight was 2%, 4%, 8% or 12% of wet blue bovine hide's weight respectively.

*Experiment 2-* Treated with the complex of SLP and PUP-2, and the total weight of them was 8% of wet blue bovine hide's weight. There were four weight ratios between SLP and PUP-2, SLP: PUP-2=1:9, SLP: PUP-2=2:8, SLP: PUP-2=3:7 or SLP: PUP-2=4:6, respectively.

*Experiment 3-* Treated with the complex of SLP, PUP-2 and other commercialized fatliquoring agents. The weight of SLP and PUP-2 was 2% of wet blue bovine hide's weight, and the commercialized fatliquoring agents accounted for the remaining 6% (2.5%JM, 1.5%JMK,1.5%FS-90 and 0.5%OF, respectively).

**Description of the Experimental Tests**
***FTIR Characterization***
The FTIR spectrum was recorded with a Thermo Fisher Nicolet 6700 spectrophotometer in KBr pellets. The range of 400-4000 $cm^{-1}$ was scanned and the result was recorded.

***Surface Tension Measurement***

The surface tension was determined by a BZY-1 automatic tensiometer, which was configured with a platinum plate and a sample cell. The platinum plate was rinsed with ethanol and deionized water several times and then flamed with an alcohol lamp to get rid of the contaminants before and after every test. After calibrating the tensiometer, a quantitative of the product solution, which was stabilized for at least 24h, was measured three times at 25°C, and the final surface tension value of the product was determined by an average of the three values.

***Physical and Organoleptic Properties Test***

The final leathers were sampled and conditioned according to the standard method. [11] With a tensile machine AI-7000S (GOTECH TESTING MACHINES INC, Taiwan), the physical properties, such as tensile strength, tear strength and elongation were tested with the standard methods. [12, 13]

The softness, grain tightness and lubricating sense of the treated resultant leathers were assessed as the organoleptic properties with hand and visual examinations by three different qualified leather technologists and reported as an average value. They were visually examined and measurements were given on a scale of 0-10 points for each functional property, where higher points indicate better properties exhibited.

***Fatty Spew Test***

The leathers which were treated with PUP-2 alone (8%, *w/w*), the complex of SLP and PUP-2 (SLP: PUP-2=3: 7, 8%, *w/w*), or the complex of SLP, PUP-2 (SLP: PUP-2=3: 7, 2%, *w/w*) and other commercialized fatliquoring agents (6%, *w/w*) were respectively placed at a temperature of -37°C for a week.

***Resistance to Yellowing***

Testing: The resistance to yellowing of leathers was tested with a Q-LAB QUV resistant to climate testing equipment (GOTECH TESTING MACHINES INC, Taiwan). The test was conducted according to ISO 105-B02 standard method 2: 50°C, 65%RH, Xenon arc test lamp, 7 IR filter and 42 W/$m^2$. [14]

**Table I**

**Retanning and fatliquoring process.**

| Process | Amount | Product | Time | Temperature | pH |
|---|---|---|---|---|---|
| **Wash** | 200% | Water | 40 min | 40°C | |
| | 0.05-0.2% | Formic acid | | | |
| | 0.20% | SWA | | | |
| | 0.10% | FG-B | | | Check pH (4.0) |
| **Drain & Wash** | | | | | |
| **Retanning** | 100% | Water | | | |
| | 0.50% | FL-71 | 10 min | | |
| | 2% | NL-20 | 30 min | | Check pH (4.5) |
| | 2% | Wattle extract | 40 min | | |
| | 0.2-0.4% | Formic acid | 20 min | | Check pH (3.8) |
| | 3% | Chrome | 30min | | |
| | 4% | ANO1 | | | |
| | 2% | PF aldehyde | 60 min | | |
| | 0.50% | Sodium formate | 20 min | | |
| | 0.35-0.6% | Sodium bicarbonate | 30 min | | Check pH (4.1) |

Table I continued on following page.

Table I continued.

| | | | | | |
|---|---|---|---|---|---|
| **Drain & Wash & Pile over night** | | | | | |
| **Filling** | 150% | Water | | 40°C | |
| | 2% | NL-20 | 20 min | | |
| | 1% | Sodium formate | | | |
| | 0.50% | Sodium bicarbonate | 60 min | | Check pH (5.2) |
| | 80% | Water | | | |
| | 3% | A18 | 20 min | | |
| | 1.50% | Melamine | 40 min | | |
| | 1.50% | Dicyandiamide | | | |
| | 0.50% | Dispersing tannin | | | |
| | 1.50% | Wattle extract | 60 min | 40°C | |
| | 1.50% | Chestnut | | | |
| | 1% | JM | 30 min | | |
| | 1% | JMK | | | |
| | 100% | Water | | 65°C | |
| | 0.40% | Formic acid | 20 min | 45°C | |
| | 0.1-0.4% | Formic acid | 40 min | | Check pH (4.1) |
| **Drain & Wash** | | | | | |
| **Fatliquoring** | 100% | Water | | 55°C | |
| | 2% | Protein filler | 20 min | | |
| | x% | Fatliquor agent | 40 min | | |
| | 0.25% | Formic acid | 30 min | | |
| | 0.25% | Formic acid | 30 min | | Check pH (3.8-4.0) |
| **Drain & Wash** | | | | | |
| **Hook to dry, Stake** | | | | | |

Evaluation: An X-RiteColor Premier 8200 spherical spectrophotometer (X-Rite, USA) was used to measure the coloring of leather samples. Spectral reflectance values were measured between 400-700 nm range with 20nm intervals, and 16 readings were obtained for each sample. The reflectance readings were converted to CIE L*a*b* values with related formulas, and color differences were calculated by CIELAB 1967 color difference formula listed in Eq.1.[15]

$$\Delta E = [(L-L_0)^2 + (a-a_0)^2 + (b-b_0)^2]^{1/2} \quad (1)$$

The CIELAB 1976 color difference formula calculates the linear distance between the coordinates of the sample and target color, and this difference is shown by ΔE.

***Scanning Electron Microscopic Analysis (SEM)***

A JSM-5900LV scanning electron microscope (Shimadzu, Japan) was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 20kV at the same magnification level.

## Results and Discussion

**Characterization of Synthetic Chemicals**

***FTIR of SLP, PU-2 and PUP-2***

As shown in Figure 1, the common structures of PU-2 and PUP-2 were evidenced by the common peaks at 3444-3480 $cm^{-1}$, 2867-2869 $cm^{-1}$, 1720-1639 $cm^{-1}$ and 1108-1105 $cm^{-1}$ related to different common groups (N-H, C-H, C=O, and C-O-C, respectively). The characteristic peaks of phosphate ester at 1151-1295 $cm^{-1}$ and 1015-1028 $cm^{-1}$ ascribed to P=O and P-O-C were observed for PUP-2 and SLP. The results indicated that SLP, PU-2 and PUP-2 were all synthesized successfully.

***Surface Tension of PUP-2 and PU-2***

From the results of surface tension shown in Figure 2, it was very clear that the surface tension was lower in PUP-2 solution than in PU-2 solution at every same concentration. Meanwhile, the CMC of the PUP-2 was much lower than that of PU-2 according to the CMC data ($4.12 \times 10^{-6}$ mol/L for PUP-2 and $1.01\times10^{-5}$ mol/L for PU-2). The results indicated that PUP-2 was more effective in reducing surface tension, which suggested that PUP-2 might play a good role in fatliquoring process. A possible explanation was that hydrophobic groups in PUP-2 were closer between each other because of the phosphorylation.[16]

**Characterization of Resultant Leathers**

***Physical and Organoleptic Properties of Leathers***

The resultant leathers were treated with different amounts of PUP-2 alone (Experiment 1), with the complex of SLP and PUP-2 in different weight ratios (Experiment 2), or with the complex of SLP, PUP-2 and other commercialized fatliquoring agents (Experiment 3), and their physical and organoleptic properties were tested. As seen from Figure 3, Figure 4 and Table II, the leathers treated with three different kinds of PUP-2 based fatliquoring agents showed a clearly improvement in physical (tensile strength, elongation and tear strength) and organoleptic properties (softness, lubricating sense and grain tightness) compared with non-fatliqured leathers, especially when PUP-2 alone (8%, *w/w*) or the complex of SLP and PUP-2 (SLP: PUP-2=3:7, 8%, *w/w*) was applied.

***SEM Analysis***

SEM studies of the grain pattern of leathers are given in Figure 5, at a magnification of ×1000. As compared with the A, the fiber splitting of B, C, and D were comparatively better in SEM. The fatliquoring agents based on PUP-2 penetrated deeply resulting in better fiber splitting and softness due to its nonionic amphiphilic structure and soft molecular chains.

***Fatty Spew Test***

Fatty spew formation was not observed on the surface of three kinds of leathers which were treated with PUP-2 alone, the complex of SLP and PUP-2, or the complex of SLP, PUP-2 and other commercialized fatliquoring agents. It can be attributed to the soft C-O-C bonds of PUP-2 with a low freezing point and the nonionic amphiphilic structure resulting in better dispersion and deeper penetration of fatliquoring agents as reported by Nashy.[17]

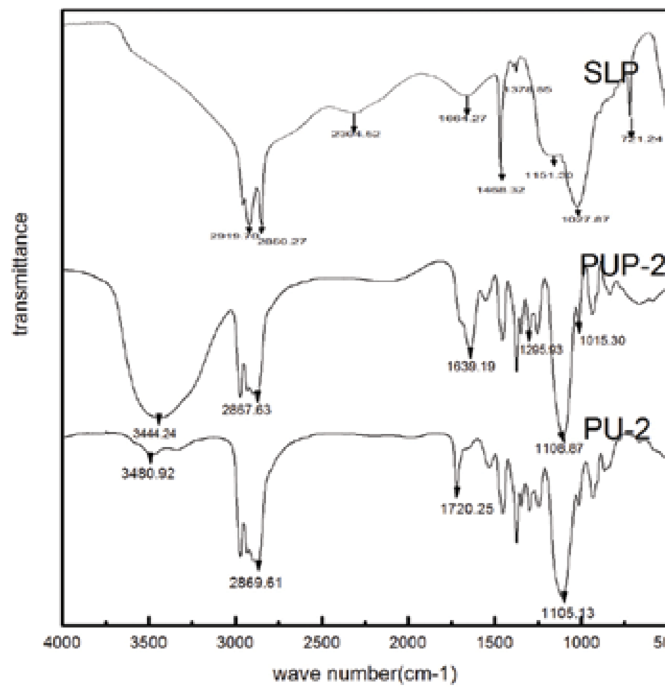



Figure 1. FT-IR spectra of SLP, PU-2 and PUP-2.

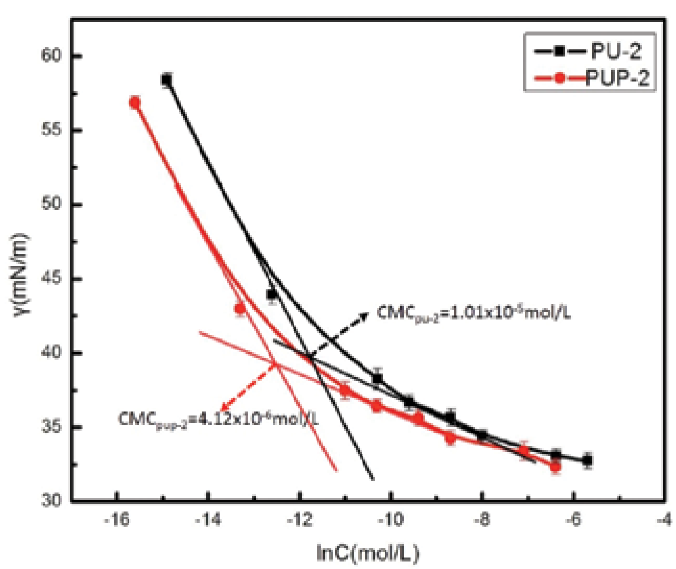



Figure 2. Surface tension at different concentrations of PU-2 and PUP-2.

***Resistance to Yellowing***

Reflectance measurements were carried out for all combination leathers. The 'L', 'a' and 'b' values used as the parameters to assess color are given in Table III. 'L' represents whiteness, which on a scale of 0-100; and 100 means pure white. 'a' represents red and green axis, where 'a' >0 means red and 'a' <0 means green. 'b' represents yellow and blue axis, where 'b' >0 means yellow and 'b' <0 means blue. 'ΔE' shown in Table III means the color difference between the sample and the target color. Table III shows the 'L', 'a', 'b' values of leather samples at 0, 6, 12 and 24 hours and the CIE Lab color difference values between 0-6 hours, 0-12 hours and 0-24 hours. When the values were considered, it was found that the changes of 'L' and 'a' values from I, II and III were a little tendency to decrease, which meant

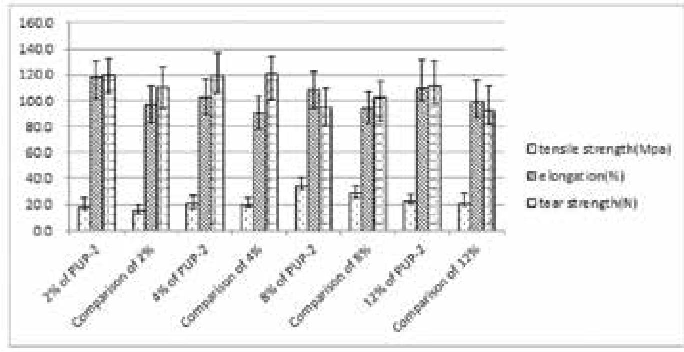



Figure 3. Physical properties of leathers treated with different amounts of PUP-2. (The Y axis is a normalized scale for all three measured values.)

## Table II
**Organoleptic properties of resultant leathers.**

| Experiment | The amount of fatliquoring agents | Softness | Grain tightness | Lubricating sense |
|---|---|---|---|---|
| **Experiment 1** | 2% of PUP-2 | 7 | 6 | 4 |
| | Comparison of 2% PUP-2 | 6 | 6 | 1 |
| | 4% of PUP-2 | 8 | 8 | 6 |
| | Comparison of 4% PUP-2 | 6 | 6 | 2 |
| | 6% of PUP-2 | 9 | 10 | 8 |
| | Comparison of 6% PUP-2 | 7 | 7 | 2 |
| | 8% of PUP-2 | 8 | 9 | 8 |
| | Comparison of 8% PUP-2 | 7 | 7 | 3 |
| | | | | |
| **Experiment 2** | SLP : PUP-2=1:9 | 6 | 10 | 6 |
| | Comparison of SLP : PUP-2=1:9 | 5 | 9 | 3 |
| | SLP : PUP-2=2:8 | 7 | 9 | 7 |
| | Comparison of SLP : PUP-2=2:8 | 6 | 9 | 3 |
| | SLP : PUP-2=3:7 | 8 | 8 | 8 |
| | Comparison of SLP : PUP-2=3:7 | 6 | 8 | 2 |
| | SLP : PUP-2=4:6 | 8 | 6 | 8 |
| | Comparison of SLP : PUP-2=4:96 | 6 | 8 | 2 |
| | | | | |
| **Experiment 3** | SLP, PUP-2 and commercialized fatliquoring agents | 8 | 9 | 9 |

a little decrease in white and a little increase in green. However, the increase of ‘b’ value from I, II and III was 2-4, which meant an increase in yellow tones when exposed to light. As a result, the increase of ‘ΔE’ value from I, II and III was 3-5. As seen from the Table III, the changes of ‘b’ and ‘ΔE’ mainly happened between 0-6 hours. Compared with II and III, I, which was the non-fatliquored leathers, also had a 2-4 change on ‘b’ and 3-5 on ‘ΔE’, which meant that the change of ‘b’ and ‘ΔE’ of II and III was not attributed to SLP or PUP-2. However, the natural phospholipids, which usually contain the unsaturated acids, are prone to oxidation [18-21] and the oxidation reaction always leads to the performance of yellowing. [22-24] In summary, the leathers treated with PUP-2 alone (8%, *w/w*) or the complex (SLP: PUP-2=3:7, 8%, *w/w*) all showed a good performance in resistance to yellowing. It can be attributed to no unsaturated carbon-carbon double bonds, which were easily oxidized. [25]

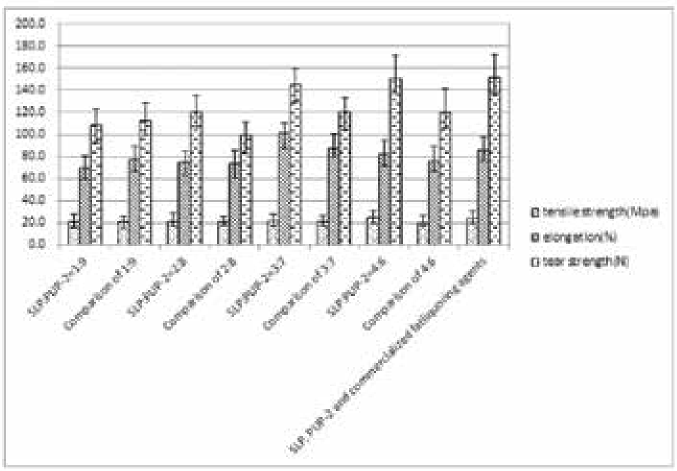



Figure 4. Physical properties of leathers treated with the complex of SLP and PUP-2 in different weight ratios, or with the complex of SLP, PUP-2 (SLP: PUP-2=3:7, 2%, w/w) and other commercialized fatliquoring agents (6%, w/w). (The Y axis is a normalized scale for all three measured values.)

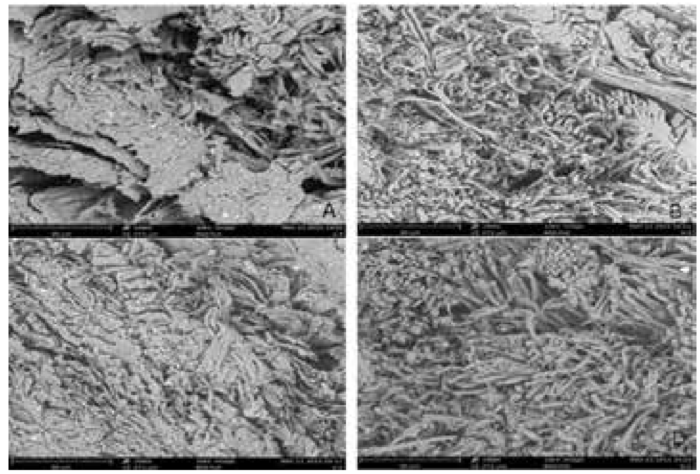


Figure 5. SEM images of the cross section of leathers. (A) Non-fatliqured leathers, 1000× (B) Leathers treated with PUP-2 alone (8%, *w/w*), 1000×. (C) Leathers treated with the complex of SLP and PUP-2 (SLP: PUP-2=3:7, 8%, *w/w*), 1000×. (D) Leathers treated the complex of SLP, PUP-2 (SLP: PUP-2=3:7, 2%, *w/w*) and other commercialized fatliquoring agents (6%, *w/w*), 1000×.

**Table III**

**Yellowing resistance of resultant leathers.**

| Time (h) | I | | | | II | | | | III | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | L | a | b | ΔE | L | a | b | ΔE | L | a | b | ΔE |
| **0** | 77.54 | -0.52 | 9.56 | | 76.94 | -1.62 | 10.31 | | 77.74 | -2.18 | 10.41 | |
| **6** | 76.28 | -0.93 | 12.91 | 3.52 | 76.63 | -1.84 | 13.38 | 3.09 | 77.26 | -2.33 | 13.24 | 2.95 |
| **12** | 75.34 | -1.04 | 13.40 | 4.46 | 76.29 | -2.24 | 13.64 | 3.45 | 76.85 | -2.71 | 13.39 | 3.13 |
| **24** | 75.20 | -1.39 | 13.64 | 4.78 | 76.04 | -2.92 | 13.95 | 3.97 | 76.70 | -3.24 | 13.89 | 3.78 |
| **Δ6** | -1.26 | -0.41 | 3.26 | | -0.31 | -0.22 | 3.07 | | -0.84 | -0.15 | 2.83 | |
| **Δ12** | -2.20 | -0.52 | 3.84 | | -0.65 | -0.62 | 3.33 | | -0.89 | -0.35 | 2.98 | |
| **Δ24** | -2.34 | -0.87 | 4.08 | | -0.90 | -1.30 | 3.64 | | -1.04 | -1.06 | 3.48 | |

I: Non-fatliquored leathers (the comparison of the leather treated with 8% PUP-2).
II: Leathers treated with PUP-2 alone (8%, *w/w*).
III: Leathers treated with the complex of SLP and PUP-2 (SLP: PUP-2=3:7, 8%, *w/w*).

## Conclusions

A new phosphorylated ester (PUP-2) was successfully synthesized, which was effective in reducing surface tension and had a good performance in improving physical and organoleptic properties of resultant leathers. The fatty spew formation was not observed on the surface of three kinds of leathers treated with PUP-2 based fatliquoring agents. Meanwhile, since all basic raw materials of PUP-2 do not contain carbon-carbon double bonds, the leathers treated with PUP-2 alone (8%, *w/w*) or the complex of SLP and PUP-2 (SLP: PUP-2=3:7, 8%, *w/w*) had a good resistance to yellowing. Therefore, PUP-2 completely meets the requirements of resistance to yellowing and avoiding fatty spew defect for leathers.

## Acknowledgements

This work was financially supported by the National High-tech Research and Development Projects (863) (2013AA06A306), National Natural Science Foundation of China (21474065) and Sichuan Province Leaders in Academic and Technical Training Project Funding (2015/100-5).

## References

1. Wang, X. C., Feng, J. Y and An, H. R.; Phosphate modified lanolin fatliquors produced by a sustained-release method. *JSLTC* **88**, 228-230, 2004.
2. Ornes, C.L.; Studies of fatliquoring: II. The influence of type of oil, degree of sulfation, and neutralization level of fatty acids on some physical properties of shoe upper leather. *JALCA* **55**, 372-386, 1960.
3. Ornes, C.L.; Studies of fatliquoring: III. The influence of oil level, neutralization, and vegetable mordanting on some physical properties of side upper leather. *JALCA* **57**, 107-115, 1962.
4. Fan, B. Z., Jin, Y and Qi R.; Research progress on phosphate leather fatliquoring agent based on natural oils and fats. *China Leather* **44**, 37-38, 2015.
5. Kalyanaraman, B., Kameswari, K. S. B., Sudharsan, N. M and Priyadharsini, P.; Biodegradation of lecithin-based fatliquor: optimization of food to microbes ratio and residence time. *JALCA* **103**, 1-10, 2013.
6. S. Kanth., S. Sadulla., J. Rao., B. Madhan., G. Balaji and R. Aravindhan.; Glove leather manufacture from sheepskins: Influence of fatliquors and syntans on the gloving properties. *JALCA* **108**, 182-190, 2008.
7. Zheng, S. J., Cao, X. Y., Li, X. B and Li, Bo.; Research of property of leather based high-carbon alcohol phosphate ester fatliquoring agents with different structure and components. *Journal of Qiqihar University* **22**, 82-84, 2006.
8. Xing, X. B.; A summary and discussion about preparation of fatliquors with phospholipid. *China Leather* **26**, 8-9, 1997.
9. Baskar, G., Vijayalakshmi, K., Parthasarathy, K., Rao, V. V. M., Jayaraman, K. S and Rajadurai, S.; Development of phosphorylated fatliquors and their application in the manufacture. *JALCA* **86**, 159-165, 1991.
10. Ozgunay, H.; Lightfastness properties of leathers tanned with various vegetable tannins. *JALCA* **103**, 345-351, 2008.
11. IUP 2, Sampling. *JSLTC* **84**, 303-309, 2000.
12. IUP 6, Measurement of tensile strength and percentage of elongation. *JSLTC* **84**, 317-321, 2000.
13. IUP 8, Measurement of tear load-double edge load, *JSLTC* **84**, 327-329, 2000.
14. International standard ISO 105-B02:2000/Amd.2.2000 (E), Color fastness to artificial light: Xenon are fading lamp test.
15. CIE (Commission Internationale de L'Eclairage), Official Recommendation on Uniform Color Spaces Color Difference Equations Metric Color Terms, 1976.
16. Miao, Q., Jin, Y and Dong, Y.; Surface behavior and micelle morphology of novel nonionic polyurethane bolaform amphiphilic block copolymers, *Journal of Polimer Research* **06**,911-921, 2010.
17. Nashy, E. S. H. A and Abo-Elwafa, G. A.; Highly Stable Nonionic Fatliquors Based on Ethoxylated Overused Vegetable Oils. *Journal of the American Oil Chemists Society* **88**, 1611-1620, 2011.
18. Song, H. B and Li, Z. J.; Chemical modification of nature phospholipids and characteristics of products. *West Leather* **28**, 27-32, 2006.
19. Liu, D. C and Ma, F. C.; Soybean Phospholipids. INTECH Open Access Publisher, 2011.
20. Hu. S., Li. Z. Q and Cheng H. M.; Review of Phospholipid Fatliquors. *West leather* **5**, 22-24, 2001.
21. Peter, V. H and Armin, W.; The use of natural and synthetic phospholipids as pharmaceutical excipients. *European Journal of Lipid Science & Technology* **116**, 1088–1107, 2014.
22. Puntener, A.; The influence of fatliquors on the lightfastness of dyed leather. *JALCA* **91**, 126-135, 1996.
23. Liu, C. K., Latona, N. P and Lee, J.; Glutaraldehyde-tanned leather treated with tocopherol. *JALCA* **100**, 102-110, 2005.
24. Gao. H., Fang. Y. J and Cheng, H. J.; Synthesis and Application of a New Sulfonated Soybean Phospholipid Faliquoring Agent. *LEATHER SCIENCE AND ENGINEERING* **3**, 49-52, 1999.
25. Shimizu, T., Komatsuzaki, S and Hirabayashi, K.; Synthesis, Structure, and Complexation Behavior of 14-and 28-Membered Partially Unsaturated Thiacrown Ethers. *Heteroatom Chemistry* **22**, 287-293, 2011.