Typical Defects of Natural Phospholipid Fatliquors in Leather Industry and Their Solutions

by

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Abstract

Leather made with soybean phospholipid fatliquors is prone to problems such as yellowing, elevated hexavalent chromium content, and undesirable odor. In this study, the aforementioned typical defects of soybean phospholipid fatliquors were investigated in respect to the main components, the antioxidants and the unsaturation degree of the natural soybean phospholipid. The results showed that the oxidation of soybean phospholipid is the primary source for its yellowing, elevated hexavalent chromium content, and undesirable odor. The volatile aldehydes produced by lipid oxidative rancidity are the main components of the undesirable odor. The purification of natural soybean phospholipid through removing the non-phospholipid components cannot solve the problems caused by oxidation of phospholipid. Furthermore, as a typical natural antioxidant existing in natural soybean phospholipid, tocopherols can restrain the oxidation of phospholipid to a certain degree, however, the dissolving out and destruction of tocopherols at high temperature in the phospholipid purification process can lead to more obviously oxidation of phospholipids. Additionally, the oxidation defects of phospholipid cannot be completely resolved by adding extra tocopherols, even at high dosages. The research finds that the defects of soybean phospholipid fatliquors can be thoroughly solved by increasing the saturation degree of lipid through addition reaction, the suggested iodine value of phospholipid products is lower than 20 g I_2/100 g.

Introduction

Phospholipids are phosphorus-containing fats isolated from plant or animal, such as oilseeds, grain germ, egg yolks and fish. The main source of phospholipids in plants is soybeans,[1] which is large in yield, rich in phospholipid content, and available at larger scale due to lower cost compared to synthetic phospholipids.[2] Today, "Phospholipid" has become the trade name for the mixture of phosphatides typically used in a vast range of foods, feed, pharmaceutical and technical applications.[3-4]

Fatliquoring is an important unit in leather making processes; it can endow leather with good softness by lubricating its fibers.[5] Phospholipids are surface active amphiphilic molecules, which comprise a polar head group and a lipophilic tail that can be used as the primary basis for a fatliquor. The compound fatliquor with soybean phospholipids as primary basis can give leather excellent softness, fullness, wetting properties and so on. Moreover, soybean phospholipids have low production cost and good biodegradability.[6] To this end, soybean phospholipid is often used as a raw material in the production of soft leather, such as sofa, garment and gloves. However, there are still facing some problems during the application of phospholipids in leather making industry. For example, soybean phospholipid fatliquored leather is prone to yellowing, elevated hexavalent chromium content, and conferring offensive odors after a period of time use and storage. However, the primary causes for these problems are still lack of systematic research until now, which restricted the further development of phospholipid fatliquor applications.

Concentrated soybean phospholipid is a by-product of soybean oil refining industry, which is mainly composed of phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidyl acid (PA) and phosphatidylinositol (PI), as well as glycolipids, triglycerides, free fatty acids (FFAs) and sterols.[7-8] Additionally, it also contains some amounts of protein, tocopherol, carbohydrates, waxes, pigments, and so on.[9-10] The phospholipid components in concentrated soybean phospholipids can be extracted by organic solvents, of which acetone is the most commonly used. Acetone insoluble substance (AI) is generally considered as phospholipid component, and acetone soluble substance (AS) is non-phospholipid component, which is mainly including pigments, carbohydrates, free fatty acids, soybean oil and tocopherol.[11]

Phospholipids provide nutritional value owing to the high poly-unsaturated fatty acid composition, including oleic, linoleic, linolenic and arachidonic fatty acids.[12] A high degree of unsaturation can cause phospholipids to be prone to oxidative rancidity,[13] which affects the application effect of phospholipid fatliquor and may be the main reason for the defects of phospholipid fatliquor. It is important to note that other components, such as the acetone insoluble substances, pigments, glycolipids, FFAs and antioxidants, may also lead to the abovementioned phenomenon.

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FFAs are products of hydrolysis and degradation of triglycerides in concentrated soybean phospholipids, and their concentration is considered an important quality indicator of oil products. FFAs can reduce the surface tension of soybean oil, increase the diffusion rate of oxygen into the oil, thereby increasing the oxidation rate of oil.[14] In oil-water emulsions, FFAs can concentrate on the surface of the emulsion droplets and attract transition metals that promote the oxidation of oil. In addition, some experimental studies have shown that FFAs can promote the oxidation of oil as well.[15-17]

Tocopherol (VE) is a typical natural antioxidant to improve the oxidative stability of oil[18] and protect other oxidized substances from being destroyed. VE can be added to the oils as an antioxidant, which not only prevents the oxidation reaction, but also improves the nutritional value, and reduces the risk of cancer, cardiovascular disease and inflammation in human body.[19-20] In recent years, with the safety of synthetic antioxidants being generally questioned, vitamin E, a natural fat-soluble antioxidant, has attracted the edible oil industry's attention.[21-22]

The elevated hexavalent chromium content and undesirable odor of phospholipid fatliquored leathers are serious problems. The qualitative and quantitative detection of leather volatile compounds is very important to study the causes of the above problems. Headspace Solid phase Micro extraction (HS-SPEM) technology is a new technology for collecting volatile substances.[23-24] HS-SPME consumes less sample volume than that of Solid phase extraction (SPE). Additionally, HS-SPME integrates extraction, enrichment and sampling, and it can minimize the loss of analyte components to ensure the accuracy of the testing results.[25] Therefore, the main volatile substances in the fatliquored leather might be able to be determined and analyzed by headspace solid phase microextraction-gas chromatography-mass spectrometry (HS-SPEM-GC-MS) method.

In order to solve the typical defects of soybean phospholipids fatliquors, the effects of the main components (AS and AI), FFAs, tocopherols and oil saturation degree on the odor, hexavalent chromium content and yellowing resistance ability of phospholipid fatliquored leather were investigated in this study. Methods for solving these defects were explored, which can provide some direction for the development of high-quality phospholipid fatliquors.

Materials and Methods

Main instruments

Pump heat circulation stainless steel drum GLSD-40 (Wuxi Ronghao Leather Machinery Manufacturing Co., Ltd.), SHZ-B constant temperature water bath oscillator (INASE Scientific Instrument Co., Ltd.), Color i5 desktop colorimeter (X-rite Co., Ltd), GX-503-A yellowing resistance tester (High-speed Railway Testing Instrument Co., Ltd.), GT-303 Softness Tester (Gotech Testing Machines Co., Ltd.), Agilent 1260 High Performance Liquid Chromatograph (Agilent Technology Co., Ltd.), Trace Q9000 GC-MS (ThermoFisher Scientific Co., Ltd.).

Experimental materials

(α) tocopherol (HPLC) was purchased from Aladdin Biochemical Technology Co., Ltd.; UB60 Concentrated soybean phospholipid and soybean oil are industrial grade and provided by Guangzhou Hisoya Biological Science & Technology Co., Ltd.; Cattle wet blue leather was provided by Zhejiang Tongtianxing Group Joint-Stock Co., Ltd. All the other chemicals used for the analysis were of analytical grade and other chemicals used for leather processing were of commercial grade.

Purification of concentrated soybean phospholipid

50 g of concentrated soybean phospholipids (UB60) and 100 mL of acetone were added to a 250 mL round-bottom flask and stirred at 50°C for 30 minutes. Samples were placed in an ice-water bath for 5 minutes to reduce the solubility of phospholipids in acetone, then, suction filtered. Sediments were placed in a vacuum drying oven at 40°C to volatilize the acetone until constant weight. Repeat the above acetone washing operation to obtain phospholipids with different washing times.

AS was obtained by distilling the collected filtrate to remove acetone. Filtrates with different times of acetone washing were mixed. Acetone contained in the mixture was removed by distillation at 80°C and rotary evaporation at 40°C, respectively. The products were labeled as AS-80 and AS-40.

Preparation of modified phospholipids

15 g of concentrated soybean phospholipid was added to a 250 mL round-bottom flask, 15 mL of dichloromethane (or petroleum ether) was added. Samples were placed in a constant temperature water bath with an electronic stirrer, 150 r/min. Then, a certain amount of bromine was slowly added and reacted for 2 h. After the reaction, the solvent was recovered by distillation to obtain the finished product.

Determination of AI and AS content and phospholipid characteristic indexes

Content determination of AI and AS

2 ± 0.001 g of phospholipids and 30 mL of acetone were added to a beaker and stirred with a glass rod in a water bath at 50°C for 2 minutes. Samples were placed in an ice-water bath for 5 minutes to reduce the solubility of phospholipids in acetone at low temperature, then, suction filtered. The above operations were repeated 5 times. The obtained phospholipid and filtrate were dried in vacuum at 40°C to constant weight.[26] The contents of AS and AI were calculated according to their respective proportions (*W/W*) in phospholipids.

Determination of acid value

0.2~0.5 g of samples (concentrated phospholipids, AI or AS components) were added to a 300 mL Erlenmeyer flask. 70 mL of ether, 30 mL of neutral ethanol and 0.5 mL of phenolphthalein indicator solution were added and mixed. 0.1 moL/L potassium

hydroxide-neutral ethanol standard solution was used to titrate the sample until the solution turned pale red and did not fade within 30 seconds as the endpoint. The acid value is obtained by dividing the mass of potassium hydroxide consumed by the mass of sample *(mg KOH/g)*.

Determination of iodine value

The iodine values of the samples were determined according to the method in the literature.[27]

Determination of (α)tocopherol content by HPLC-DAD

(α) tocopherol content in samples was determined through HPLC-DAD method. Chromatographic conditions: Agilent C18 column (250 mm × 4.6 mm, 5 μm); Diode Array Detector (DAD) detector (wavelength was 294 nm); Column temperature was 30°C and the mobile phase was pure methanol. The flow rate was 1 mL/min and the injection volume was 10 μL.

Fatliquor compounding and fatliquoring process

Fatliquor compounding

Phospholipids, mineral oils, surfactants and water were weighed and mixed according to the mass ratio of 5:1:10:6. the pH value of emulsion (fatliquor is compounded with water in the mass ratio of 1:9) was adjusted to 7-8 by using sodium hydroxide solution (4.0 mol/L).

Fatliquoring process

Cattle wet blue with the thickness of 1.8 mm-2.0 mm was selected and sampled symmetrically along the backbone. Samples were wetted, retanned and neutralized to pH 6.0 ± 0.1 as per the standard leather making process. Samples were fatliquored with different fatliquors at 50°C with 100% of water and 20% of fatliquoring agents for 2 h. Then, the pH was adjusted to 3.6 ~ 3.8 by using formic acid solution (1:20). The crust leathers were naturally dried. The odor, color difference value and hexavalent chromium content were determined.

Physical and chemical properties of the crust leather

Organoleptic investigation of odor

According to the "Geely Automobile leather odor determination method", the specific determination steps are as follows: 100 mm × 200 mm of crust leather samples were put into a sealed bag and placed at room temperature for a certain time after sealing. The mouth of the bag was slightly opened and the assessor's nose is 2-3 cm away from the mouth of the bag to evaluate it.

An evaluation team composed of 4 members conducted a fatliquored leather odor sensory assessment. Using a 9-point system (1=no peculiar smell, 5=moderate peculiar smell, 9=strong peculiar smell) the average was used to arrive at a quantitative assessment for each sample.

Thermal aging of leather and hexavalent chromium determination

100 mm × 200 mm of crust leather samples were placed in an oven at 80°C for 12 h, then cooled at room temperature for 30 min. The contents of hexavalent chromium in the crust leathers were determined according to the reported method.[28]

Color difference values determination

(a). Illumination treatment: 50 mm × 50 mm of crust leather samples were placed in an GX-503-A yellowing resistance tester at 50°C, and irradiated with a 300W power bulb for 24 hours. The color difference values of leather samples before and after illumination were detected by a colorimeter.

(b). Dry heat treatment: 100 mm × 200 mm of crust leather samples were placed in an oven at 120°C for 24 hours, and the color difference values of the leather samples before and after heating were detected by a colorimeter.

HS-SPEM-GC-MS detection of volatile gases

The volatile compounds in leathers were collected and studied by HS-SPEM-GC-MS. The volatile compound mass spectrum data was automatically vetted through the atlas library and the components with low content and low confidence were discarded. Finally, the relative percentage of volatile compounds was determined by gas chromatography peak area percentage method.

2 g of sheared leather samples (approximately 2 mm × 2 mm) were put into a 20 mL headspace bottle that sealed with a rubber stopper of PTFE film and equilibrated at 80°C for 1 h. After equilibration, the extraction needle was used for headspace adsorption for 30 minutes and directly inserted into the GC-MS injection port for desorption at 250°C for 5 min.

Chromatographic conditions: capillary column (30 m × 0.25 mm × 0.25 μm); inlet temperature was 250°C; carrier gas was helium (99.999%), and the flow rate was 1.2 mL/min. Heating program: the initial temperature was 80°C; then, heated up to 230°C at 5 °C/min; Injection mode: Split less injection. Mass spectrum conditions: electron bombardment ion source (EI); electron impact energy (70 EV); Ion source temperature was 230°C. Interface temperature was 250°C and the full mass scan range was m/z 50-500.

Results and Discussion

Main components and characteristic indexes of soybean phospholipids

Concentrated soybean phospholipid is extracted from soybean meal, and its components are complex. According to its solubility in acetone, it can be divided into acetone insoluble substance (AI) and acetone soluble substance (AS). Generally, AI is considered as the main phospholipid component, and AS is non-phospholipid component. In order to explore the effects of these two components on the properties of phospholipid fatliquor, concentrated soybean phospholipid (UB60) was washed with acetone for several times to obtain PL1 phospholipid (1 time washing), PL2 phospholipid (2 times washing), PL3 phospholipid

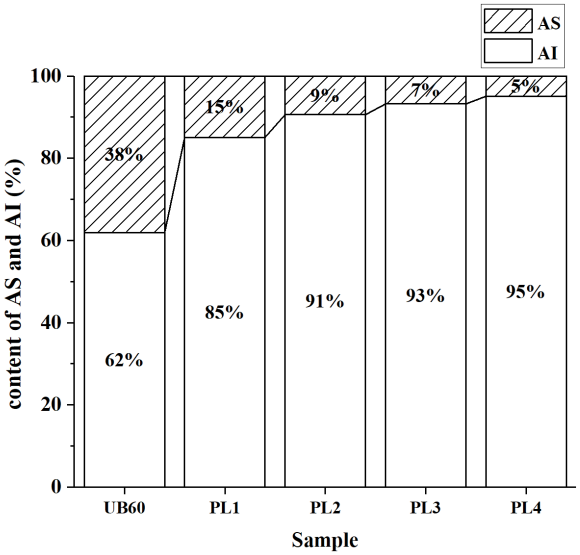

Figure 1. Changes of Contents of AI and AS in Phospholipids

(3 times washing), PL4 phospholipid (4 times washing) and acetone soluble substances (AS) respectively. The AI and AS content, acid value and iodine value of phospholipids were tested.

Content and acid value of AS and AI

With the increase of acetone washing times, the color of phospholipids gradually became lighter and the fluidity was lost. After 4 times of washing, PL4 phospholipids obtained was a yellow powder. The changes of AS and AI contents in phospholipids with washing times are shown in Figure 1.

Figure 1 shows that during acetone washing, components in concentrated soybean phospholipid, such as soybean oil and pigments, were dissolved in acetone, and concentrated soybean phospholipids were purified. The content of AI in phospholipids were increased with the increasing of washing times. The AI content of PL4 phospholipids reached up to 95% after 4 times of washing.

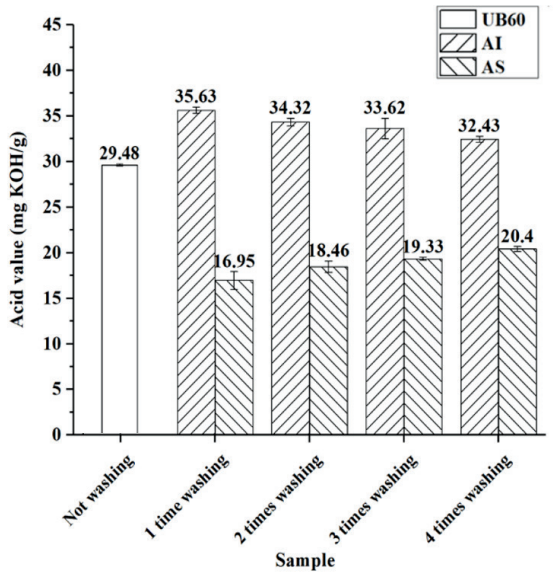

Figure 2. Acid values of main components of phospholipids

The acid values of AS and AI components obtained after different washing times were further determined. The results are shown in Figure 2.

The acid value of concentrated soybean phospholipid mainly comes from the acidic groups of phospholipid molecules and FFAs in non-phospholipids. Figure 2 shows that the acid value of UB60 is 29.48 mg KOH/g, the acid values of phospholipid component (AI) obtained after acetone washing are significantly higher than that of non-phospholipid component (AS). It indicates that the acid value of concentrated soybean phospholipid is mainly caused by phospholipid component, and the content of fatty acid is not high. With the increase of acetone washing times, the acid value of AI component gradually decreased, while the acid value of AS component increased. This phenomenon indicates that the free fatty acids in soybean phospholipids would gradually dissolve in acetone and eventually enrich in AS.

Iodine value of AS and AI

The higher the unsaturation degree of oil, the easier oxidation occurs. The iodine value is often used as an index to measure oil unsaturation degree. The iodine values of AS and AI in concentrated soybean phospholipid were determined. The results are shown in Figure 3.

Figure 3 shows that with the increase of acetone washing times, the iodine value of phospholipid component (AI) decreases continuously. The iodine value of unwashed concentrated soybean phospholipid (UB60) is 91.93 g I_2/100 g after four times of washing, the iodine value of AI component (PL4) decreases to 71.63 g I_2/100 g, while the average value of AS component (the iodine values of AS-40 and AS-80 is about 126 g I_2/100 g) is 126.18 g I_2/100 g, which was close to that of soybean oil (128.66 g I_2/100 g).

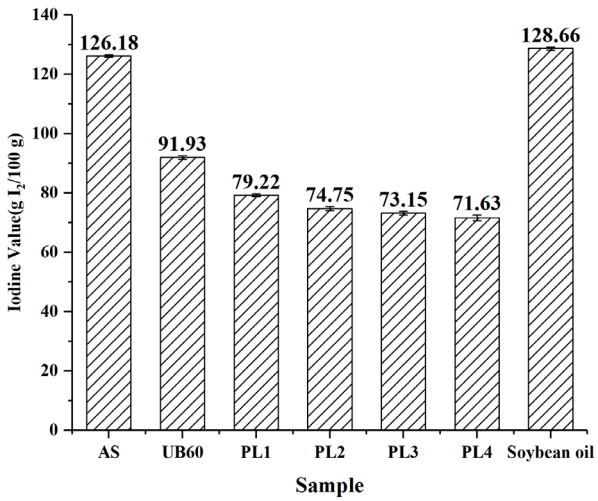

Figure 3. Iodine values of different phospholipids

The unsaturation degree of concentrated soybean phospholipids is high, and the iodine values of the AS and AI components are quite different. Therefore, the effect of the main components of phospholipids on the properties of phosphatidylcholine fatliquoring leather should be further investigated.

Effect of different components on leather properties

Phospholipids can influence the physical characteristics of leather, such as softness and wetting properties, but leather made with phospholipid fatliquors is prone to problems such as yellowing, elevated hexavalent chromium content, and undesirable odor in its storage, transport and use process. High unsaturation of concentrated soybean phospholipid and its free fatty acids, pigments, soybean oil and other factors may be the primary sources for the abovementioned problems. Therefore, different phospholipid components are compounded into different fatliquors according to the same formula, and the hexavalent chromium content, yellowing resistance and odor change of leathers fatliquored with those fatliquors were tested.

Effect of different components on hexavalent chromium content

The autoxidation of lipids in leather will produce hydroperoxides and so on. These substances are very active and have strong oxidizability, which can oxidize the free Cr (III) to Cr (VI).[29-30] In order to explore the influence of the main components of soybean phospholipid on the formation of hexavalent chromium, the hexavalent chromium contents in fatliquored leathers were determined after storage (7 days at room temperature) and dry heat treatment (80°C, 12 h). The results are shown in Figure 4.

Figure 4 shows that no Cr (VI) has been detected in the control sample (a synthetic emulsifier with saturated fatty alcohol as raw material, used for compounding phospholipid fatliquor), UB60 and AS-40 (distilled acetone at 40°C) fatliquored leathers after one week storage at room temperature. The hexavalent chromium content in the control sample after dry heat treatment is only 1.67 mg/kg. High hexavalent chromium content was detected in purified phospholipid (PL1-PL4) and AS-80 (distilled acetone at 80°C) fatliquored leathers after one week storage and dry heat treatment. Among them, the hexavalent chromium content in PL4 fatliquored leather was the highest, which is more than 110 mg/kg after one week storage or dry heat treatment. Figures 1 and 4 shows that with the increase of acetone washing times, the increase of phospholipid content (AI) and the decrease of non-phospholipid content (AS) in the samples (PL1-PL4) can lead to the increase of hexavalent chromium content. This phenomenon indicates that the improvement of phospholipid purity cannot solve the problem of elevated hexavalent chromium content.

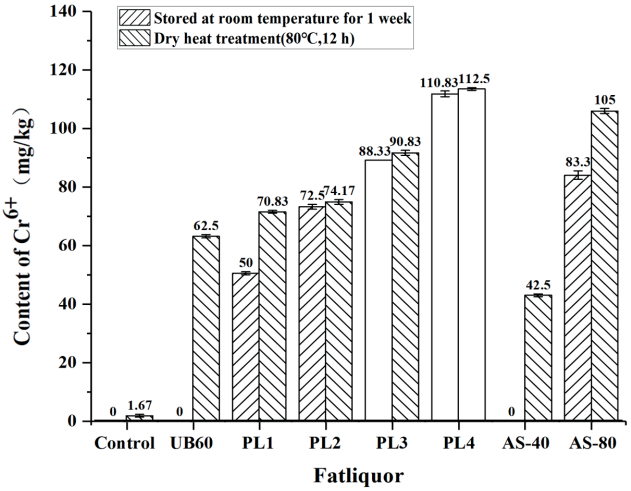

Figure 4. Hexavalent chromium content

The oxidation of the fatliquor is one of the main reasons for the hexavalent chromium increase. The hexavalent chromium content can reflect the oxidation degree of fatliquor in leather. The unsaturation of phospholipid is high. After four times of acetone washing, the iodine value of PL4 with 95% phospholipid content is still above 71 g/100 g (Figure 2). Therefore, the removal of non-phospholipid components (AS) in concentrated soybean phospholipid by acetone washing cannot solve the oxidation problem of phospholipid fatliquor.

It is worth mentioning that the content of non-phospholipid component (AS) in UB60 (38%) is much higher than that of PL4 (5%) (Figure 1), and the iodine value of UB60 is also higher than that of PL4. After one week storage and dry heat treatment, the hexavalent chromium content in the UB60 fatliquored leather is significantly lower than that in the PL4 fatliquored leather. This phenomenon indicates that the antioxidant activity of concentrated soybean phospholipid is higher than that of purified phospholipid. In addition, although the iodine value of AS is significantly higher than that of UB60 and PL1-PL4 (Figure 4), the AS-40 (distilled acetone at 40°C) has the strongest antioxidant activity. No hexavalent chromium was found in the AS-40 fatliquor leather after one week storage at room temperature. Even after dry heat treatment, the hexavalent chromium content in that is the lowest. However, the oxidation resistance of AS-80 (distilled acetone at 80°C) decreased significantly, and the hexavalent chromium content in the AS-80 fatliquored leather is significantly higher than that of AS-40 and UB60 fatliquored leathers. The reason for the above phenomenon may be that concentrated soybean phospholipid contains natural antioxidants. With the increase of acetone washing times, although the purity of phospholipid increases and its iodine value decreased, the antioxidants were dissolved by acetone. Therefore, the antioxidant activity of purified phospholipid becomes less, and the antioxidant activity of AS is enhanced with the increase of antioxidant concentration. After high temperature distillation at 80°C, the antioxidants in AS-80 destroyed and decomposed, resulting in the oxidative stability of AS-80 was significantly lower than that of AS-40. The existence and role of antioxidants in phospholipids will be discussed in detail in the following section.

Table I

Odor scores of fatliquored leathers stored at room temperature for 1 week

Sample	Evaluator				Average score
	No.1	No.2	No.3	No.4	
Control	1	2	1	2	1.5
UB60	1	2	1	2	1.5
PL1	6	6	6	5	5.8
PL2	6	6	5	6	5.8
PL3	6	7	6	6	6.3
PL4	9	8	8	7	8
AS-40	1	1	1	1	1
AS-80	9	7	9	9	8.4

Note: 1 point = no peculiar smell; 5 = moderate odor; 9 = strong odor

Effect of different components on leather odors intensities

The oxidation of oil in leather can produce small molecule volatile substances, which can make leather confer offensive odors. It is one of the most serious problems of leather products. As mentioned above, the undesirable odor is a common problem of phospholipid fatliquors. As shown in Table I, the odor intensities of the fatliquored leathers after one week storage are different. The UB60 fatliquored leather has a slight smell (beany smell). The phospholipids (PL1-PL4) fatliquor leather purified by acetone washing have moderate undesirable odors, and with the increase of acetone washing times the odor of leathers is stronger, because the antioxidants in concentrated soybean phospholipid were washed out after acetone washing. The AS-40 fatliquored leather also has a slight smell, while the AS-80 fatliquored leather has a strong undesirable odor, which is due to the high unsaturation of AS, and the antioxidants decompose at high temperature (80°C). Figure 4 and Table I shows that odor sensory and hexavalent chromium test data show a strong correlation. The higher the hexavalent chromium content, the higher the odor concentration.

With the prolongation of storage time, the peculiar smell of leathers was aggravated. After one month storage, UB60 and AS-40 fatliquored leathers conferred offensive odors (5 points); The oiliness, softness of leather decreased significantly. As mentioned above, natural antioxidants in UB60 and AS-40 delay the oxidation of the lipids.

The following experiments were planned to further confirm that the odor in leather was caused by oil oxidation. The volatile compounds in the control sample and AS-80 fatliquored leathers were collected and studied by HS-SPEM-GC-MS. The volatile compound mass spectrum data was automatically vetted through the atlas library and the components with low content and low confidence were discarded. Lastly, the relative percentage content of volatile compounds was determined by gas chromatography peak area percentage method.

Through GC-MS analysis found that there is a significant difference in the composition of volatile gas between the control sample and AS-80 fatliquored leathers. As shown in Table II, 41 volatile substances were detected in the control sample, and 67 substances were detected in the AS-80 fatliquored leather. Although there are 32 types of the same substances in the two kinds of fatliquored leathers, there are 29 types of aldehydes, esters, ketones and ethers (their thresholds are low) in the volatile components of the AS-80 fatliquored leather, and the relative total content is 45.94%. The types and relative contents of that volatile components in the AS-80 fatliquored leather are higher than those in the control samples (9 kinds, 37.56%).

The volatile compounds produced by oil oxidation mainly include aldehydes, ketones, acids, esters, furans, alcohols and hydrocarbons. The content of linoleic acid in soybean oil and phospholipids is about 50%, and aldehydes are mostly the oxidative degradation products of linoleic acid. The odor characteristics of saturated aldehydes are related to concentration. The odor threshold of aldehyde is very low. The odor characteristics of saturated aldehydes are related to concentration. When the concentration is low, it will present a sweet and fruity odor, and when the concentration is high, it will produce a pungent odor.[31] Table III shows the types and contents of volatile aldehydes in the control sample and AS-80 fatliquored leathers. It can be seen from Table III that the types of aldehydes in the AS-80 fatliquored leather are obviously more than that in the control sample fatliquored leather. In addition, the contents of trans-2-octenal, trans-2-decenal, nonanal and N-octyl aldehyde (these substances are the typical odiferous substances of oil oxidation.) in the AS-

Table II

Types and relative contents of volatiles in leathers

		alcohol	ester	ether	ketone	alcohol	alkane	others	total
Control sample	types	3	4	1	1	12	17	3	41
	Relative content %	3.22	30.32	1.53	2.49	43.79	15.48	2.79	99.62
AS-80	types	13	9	2	4	17	19	4	67
	Relative content %	17.96	23.14	1.00	3.84	38.14	11.89	2.08	98.05

Table III

GC-MS detection of main volatile aldehydes

No.	Name of components	Relative content %	
		Control sample	AS-80
1	Trans-2-decenal	-	3.15
2	Trans-2-octenal	1.39%	3.25
3	Nonanal	1.47%	3.18
4	2- undecylenic aldehyde	-	2.03
5	Trans (E)-nonenal	-	1.99
6	(E, E)-2, 4-nonadienal	-	1.37
7	N-octyl aldehyde	-	1.13
8	Trans-4, 5-epoxy-(E)-2-decanal	-	0.64
9	(2E)-2-hexadecenal	-	0.36
10	4-ketoaldehyde	-	0.30
11	Benzaldehyde	-	0.28
12	7, 11-hexadecadienal	-	0.28
13	2-heptanal	0.36%	-

80 fatliquored leather are higher than that in the control sample fatliquored leather. Therefore, the volatile aldehydes produced by oil oxidative rancidity in the fatliquor is the main reason for the odor increase in the fatliquored leather.

(α) Tocopherol Content and Antioxidant Activity of (α) Tocopherol

Figure 4 shows that there are antioxidant substances in phospholipids which can inhibit phospholipid oxidation, thus reducing the hexavalent chromium. Among them, tocopherol (VE) is the most important antioxidant in soybean phospholipids.[32] Thus representative natural antioxidant (α) tocopherol became a research

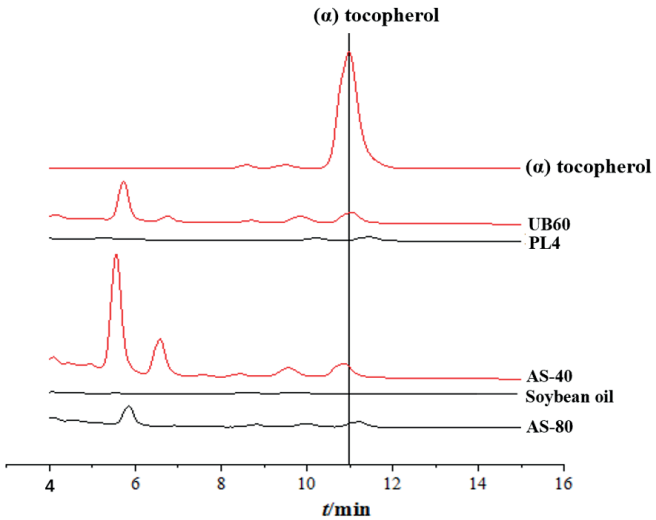

Figure 5. (α) Tocopherol Liquid Chromatogram curve

Table IV

(α) tocopherol contents in samples

Sample	Content (mg/g)
UB60	0.064
PL4	0
AS-40	0.159
AS-80	0
Soybean oil	0

focal point. The content of (α) tocopherol in the main components of phospholipids was detected, and its antioxidant properties to phospholipids were investigated.

Figure 5 shows that (α) tocopherol appears in both UB60 and AS-40, but not in PL4, AS-80 and soybean oil. (α) tocopherol is not resistant to high temperature. After long time distillation at 80°C, (α) tocopherol in AS was decomposed and destroyed.[32-34] Therefore, the presence of (α)tocopherol is almost undetectable in AS-80.

The concentration of (α) tocopherol was further determined. It can be seen from the results in Table IV that the (α) tocopherol concentration in AS-40 (0.159 mg/g) is much higher than that in UB60 (0.064 mg/g), while the tocopherol contents in PL4, soybean oil and AS-80 are 0. This phenomenon indicates that there is tocopherol in concentrated phospholipid (α) tocopherol, after repeated acetone elution, (α) tocopherol, a fat soluble substance, will flow out with acetone and finally enrich in AS.

Figure 4 and Table IV shows that the (α) tocopherol content in phospholipids and hexavalent chromium test data show a strong correlation. The presence of (α) tocopherol can inhibit the oxidation of phospholipids obviously. Therefore, adding antioxidants to phospholipids is an effective way to solve the problem of hexavalent chromium and peculiar smell caused by oxidation of phospholipid fatliquors. The antioxidant effect of (α) tocopherol on phospholipid fatliquor was further investigated. It was found that when 1% (α) tocopherol was added to UB60, the UB60 fatliquored leather had no undesirable odor after one week, but still appeared a strong undesirable odor after one month. After dry heat treatment (80°C, 12 h), the hexavalent chromium content of leather was still as high as 58.3 mg/kg, which indicated that (α) tocopherol was not strong in improving the antioxidant ability of soybean phospholipid. In addition, (α) tocopherol is not resistant to high temperature. Therefore, it is necessary to further optimize the antioxidant.

Effect of phospholipid saturation on leather properties

It can be seen from the previous experimental results that tocopherol can effectively reduce but not completely prevent the formation of hexavalent chromium caused by oxidation of phospholipid. The

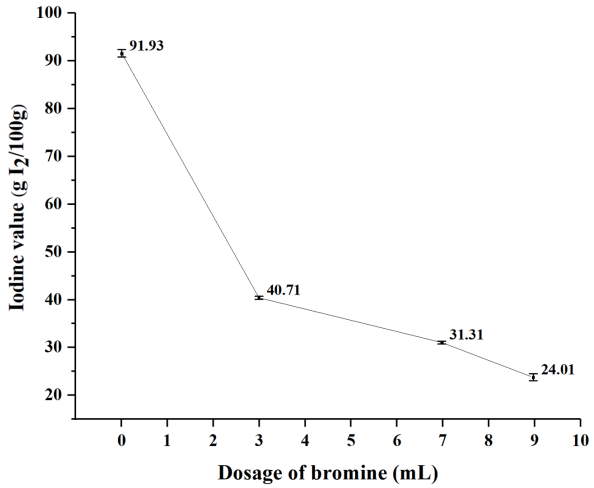

Figure 6. Iodine values of modified phospholipids

high unsaturation is the main reason for the low oxidation stability of soybean phospholipids. Therefore, bromine was used to modify UB60 in different degrees, and the effect of phospholipid saturation on the properties of fatliquored leathers was investigated.

The iodine value of bromine-modified phospholipids in different degrees

Different amounts of bromine were used for the addition reaction of 15 g UB60 to obtain phospholipids with different saturations. The iodine values are shown in Figure 6.

Figure 6 shows that the iodine value of phospholipid after brominated modification decreases with the increase of bromine dosage, but the bromine dosage is not completely proportional to the decrease of iodine value of phospholipids. The main reason is that not only the addition reaction but also the substitution reaction will occur when bromine is added to the phospholipid.

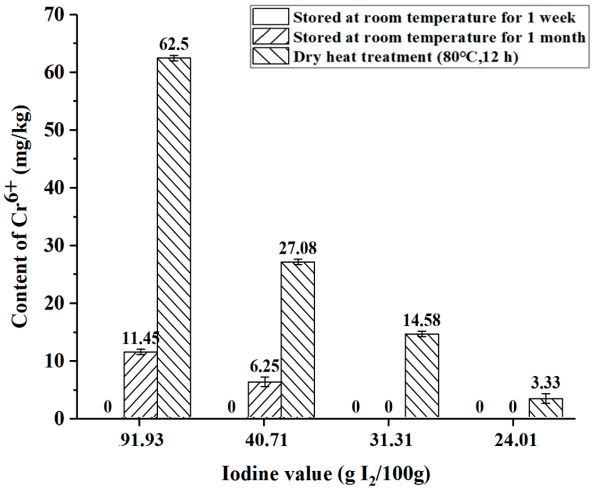

Figure 7. Hexavalent Chromium Content in modified phospholipid fatliquored leathers

Effect of phospholipid saturation on hexavalent chromium

The hexavalent chromium content in leather fatliquored with phospholipids with different Iodine value after storage (7 days and 1 month at room temperature) and dry heat treatment (80°C, 12 h) is shown in Figure 7.

Figure 7 shows that there is no hexavalent chromium in the leathers after one week storage; After one month storage, the hexavalent chromium contents in the leathers fatliquored with phospholipid fatliquors with high iodine value (about 92 and 41 g I_2/100 g) were 11.45 and 6.25 mg/kg respectively; However, no hexavalent chromium was found in the leathers fatliquored with phospholipid fatliquors with low iodine value (less than 32 g I_2/100 g); After dry heat treatment (80°C for 12 h), the hexavalent chromium content decreased with the decrease of phospholipid iodine value; It is worth noting that when the phospholipid iodine value was reduced to about 24 g I_2/100 g, the phospholipids had excellent antioxidant properties, and the hexavalent chromium content is only 3.33 mg/kg after dry heat treatment.

The odor of different modified phospholipid fatliquored leathers during storage was evaluated. It was found that the leathers with phospholipid fatliquors with the lowest iodine value had no undesirable odor after one month storage, while the others had different degrees of undesirable odor.

According to the above results, it can be concluded that the high unsaturation of soybean phospholipid is the main reason for poor oxidation stability of soybean phospholipid. The antioxidant activity of phospholipids could be enhanced with the decrease of unsaturation of phospholipids. When the iodine value of phospholipid is reduced to about 20 g I_2/100 g, the problem of elevated hexavalent chromium content and undesirable odor can be completely solved.

Effect of phospholipid saturation on yellowing resistance

Yellowing resistance is an important index to evaluate leather products, and fatliquor is one of the main factors affecting the yellowing of leather. Oil, pigment and other substances can accelerate oxidative browning under light and high temperature conditions, resulting in yellowing of leather. The light and heat yellowing resistance of leathers fatliquored with several phospholipid fatliquors with different iodine values was further studied. The color difference values of leather before and after illumination (300 W xenon lamp, 50°C, 24 h) and dry heat treatment (120°C, 24 h) were measured by a colorimeter, and ΔE (comprehensive deviation of color difference) represents the yellowing degree of leather.

It can be seen from Table V that with the decrease of modified phospholipid iodine value, the light-resistance and heat-resistant yellowing properties of fatliquored leather are improved, especially

Table V

ΔE of modified phospholipid fatliquored leathers

Iodine value (g I_2/100g)	ΔE	
	Illumination (50°C, Xenon lamp, 24 h)	Dry heat treatment (120°C, 24h)
91.93	1.46	10.97
40.71	1.37	5.86
31.31	1.36	3.25
24.01	1.29	2.58

the heat-resistant yellowing properties. The heat-resistant yellowing was significantly enhanced with the decrease of iodine value of modified phospholipid. The color difference value of unmodified phospholipid (UB60) fatliquor leather before and after dry heat treatment is as high as 10.97, and the leather appearance is seriously yellowing, and the handle is dry and hard. The heat-resistant yellowing ability of the leather with modified phospholipid (Iodine value= 24.01 g I_2/100 g) fatliquors is the best, and the color difference value before and after dry heat treatment is only 2.58, the leather can still maintain good softness.

Conclusion

Leather made with soybean phospholipid fatliquors is prone to problems such as yellowing, elevated hexavalent chromium content, and undesirable odor, which are mainly caused by the oxidation of phospholipid. The volatile aldehydes produced by lipid oxidative rancidity are the main components of the undesirable odor. The purification of natural soybean phospholipid through simply removes the non-phospholipid components cannot solve the problems caused by oxidation of phospholipid. as a typical natural antioxidant existing in natural soybean phospholipid, tocopherols can restrain the oxidation of phospholipid to a certain degree, however, the dissolving out and destruction of tocopherols at high temperature in the phospholipid purification process can lead to more obviously oxidation of phospholipids. Additionally, the oxidation defects of phospholipid cannot be completely resolved by adding extra tocopherols, even at high dosages. The research finds that the defects of soybean phospholipid fatliquors can be thoroughly solved by increasing the saturation degree of lipid through addition reaction, the suggested iodine value of phospholipid products is lower than 20 g I_2/100 g.

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