Quality Enhancement of Low Grade Wet Blue Leathers: Up-grading of Thin Substance in the Wet End Process

by

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Abstract

Various factors control the quality of the raw materials (hides/skins) used for leather processing. Leathers made from such varied quality of raw materials also have very varied grading. Leathers of higher grades are processed conventionally and finished to the desired effect and the required end product. However, processing and manufacturing of lower grade leathers and improving their properties to make them more useful for high quality products is a big challenge for the leather industry. Conventional up-grading of low quality leathers is brought about by surface modifications. However, such surface modifications significantly affect the natural look of the leathers and hence find use in products applications of low value. This study attempted to improve the grade of the leathers by suitably modifying the post tanning operations without affecting the natural feel of the leathers. One of the major defects, thin substance, has been selected for up-grading. The post tanning auxiliaries have been selected so as to enhance the substance of the leather. Different types of leathers (upper, glove and lining) were made from thin substance raw material. The physical strength properties of these leathers match that of the conventionally processed leathers. The organoleptic properties of the leathers made in this study are also on par with that of the conventional leathers. The cost of chemicals can be easily offset with the additional value realized by following this process of up-grading.

Resumen

Varios factores controlan la calidad de las materias primas (cueros/pieles) utilizados para el proceso del cuero. Cueros elaborados a partir de una calidad tan variada de materias primas también tienen calificaciones muy variadas. Los cueros de grados más altos se procesan convencionalmente y se acaban con el efecto y el producto final deseado. Sin embargo, el procesamiento y la fabricación de cueros de calificaciones de menor grado y el mejoramiento de sus propiedades para que sean más útiles para los productos de alta calidad es un gran reto para la industria del cuero. La mejora convencional de las pieles de baja calidad se produce por modificaciones en la superficie. Sin embargo, dichas modificaciones superficiales afecta significativamente el aspecto natural de los cueros y por lo tanto, encuentran uso en aplicaciones de productos de bajo valor. Este estudio intenta mejorar el grado de los cueros modificando adecuadamente las operaciones post-curtido sin afectar el toque natural de las pieles. Uno de los defectos importantes, el espesor fino, ha sido seleccionado para mejorar la calificación. Los auxiliares de post-curtido han sido seleccionados a fin de aumentar el espesor de la piel. Los diferentes tipos de cueros (calzado, guante y forro) se hicieron a partir de materia prima de espesor fino. Las propiedades de resistencia física de estos cueros coinciden con el de los cueros procesados convencionalmente. Las propiedades organolépticas de los cueros realizados en este estudio se encuentran también a la par con la de los cueros convencionales. El costo de los productos químicos puede ser fácilmente compensado con el valor adicional obtenido siguiendo este proceso de mejora de clasificación.

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INTRODUCTION

Raw material quality affects the final value of the leathers made. One of the defects, which reduce the value of the skin, is thin substance. Physical properties of the leathers are directly related to the thickness of the skin (and weight), grain to corium ratios and corium collagen structure. The thickness decreases due to reasons like death at early stage, under nourishment, animals burning their fat to resist cold in winter season etc. It has been shown previously that quality of raw material can be influenced by factors such as sex,[1] the age,[2,3] the live weight of the animal,[4,5] the breed[5-7] as well as by feeding and environmental conditions.[1,4,8,9] Gouges are caused during flaying, where unintentional cutting of flat pieces of skin out of the reticular layer occurs. These result in thinner quality of the finished leather. Soaking temperatures exceeding 28°C can also lead to undesired high bacterial growth and furthermore to greater hydrolytic degradation of skin substance, resulting in a flat and tinny leather quality. Inadequate liming leads to tinny type leathers.[10]

The grading of skins is done by experienced tanners using the following grading patterns and the respective articles conventionally made from goat skins is also given below.

- Leathers, which are assorted between grades **I to VIII** go for **upper**
- Leathers, which are assorted between **IX** to **X** grades go for **upper**, which are rejected in I to VIII **upper**
- Flesh side finished articles go as **suede**
- The articles with less value than suede goes for **heel grip**
- Leathers, which are not suitable for **upper** are taken as **lining-I** material
- Leathers rejected in **lining-I** go as **lining-II** grade
- Leather with severe damage and defects goes for **rejection** grade

The up-grading of leather is done to mask the defects and to increase its unit value (per sq.ft). The value of leather, though being increased through the various processing until the crust stage, can find its absolute value only when its aesthetic appeal is improved through finishing. General up-grading methods are done in finishing using pigments to mask the defects.[11] Though it adds a certain value to the final product there is still growing demand for quality leather. A consumer generally prefers to choose a leather equivalent material in feel in terms of cost affordability. Hence, considering the factor that finishing upgradation affects the feel and downgrades the value of leather, it is better if up-grading could be achieved through post tanning processes.

The objective of this work is to improve the value of thin substance wet blue leathers in post tanning processes and mechanical operations rather than in finishing, so that the natural look and feel of leather is unaltered. This would minimize the effort and money spent in finishing process and paves a new way in the leather market and trend.

EXPERIMENTAL

Post Tanning Operations

Thin substance wet blue (goat skin) was taken as raw material. Three different end products viz. upper, lining and glove leathers were made using thin substance wet blue leathers. The post tanning recipes followed are given in Table I-III for upper, lining and glove leathers, respectively. Control leathers were made using conventional post tanning recipe for each product.

Physical Testing of Leather Samples

The samples for physical testing were obtained as per IULTCS methods.[12] The samples were conditioned at 80±4°F and 65±2% R.H. for 48 hrs. Physical properties such as tensile strength, tear strength and grain crack strength were investigated as per standard procedures.[13-15] Each value reported is an average of four (2 along the backbone, 2 across the backbone) experiments on each skin.

Evaluation of Organoleptic Properties

Crust leathers were assessed for softness, grain smoothness, grain tightness, fullness and general appearance by tactile evaluation. Experienced tanners rated the leathers in a scale of 0-10 points for each functional property.

Wet and Dry Rub Fastness

Samples of appropriate size (5 x 14 cm) were cut from the official sampling position and after conditioning as mentioned before were tested according to IS 6191-1971 (LF:10)31 using SATRA Crockmeter.[16]

Scanning Electron Microscopic Analysis

Wet blue thin substance sample was dehydrated by gradual dehydration process using methanol and acetone.[17] The specimens were then coated with gold using Edwards E306 sputter coater. A Leica Cambridge Stereoscan 440 scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 20 KV with different lower and higher magnification levels.

RESULTS AND DISCUSSION

In order to improve the grading of the thin substance wet blue, changes were made in the post tanning recipe by choosing appropriate chemicals (both syntans and fatliquors). The properties expected to be imparted by the specialty chemicals used in the processes viz., the syntans and fatliquors are given on page 298.

TABLE I
Process recipe for upper leather from wet blue thin substance.

Chemicals	% offer	Time (min)	Remarks
Water	200	60	
Dispersing agent	0.5		
Degreasing agent	0.5		Drain/Wash
Water	150		
Cationic fatliquor	1	60	pH: 3.0-3.2. Drain/Wash
Water	150	30	
Synthetic fatliquor	2	20	
Chrome syntan	4	60	
Sodium formate	0.5		
Protein syntan	4	30	
Acrylic syntan	4	40	
Oxozolidin based syntan	2	60	Basification pH:4.0 Drain/Pile Over night
Water	150	20	
Sodium formate	1.5		
Neutralising syntan	1		
Ammonium Bicarbonate	1	30	
Synthetic fatliquor	2	45	
Water	50		
Sequestering agent	0.3	10	
Acrylic syntan	4	30	
Synthetic fatliquor	2	20	
Naphthalene sulphone based syntan	3	20	
Wattle extract	2	30	
Melamine syntan	3		
Lanoline base fatliquor	2	20	
Wattle extract	8	120	
Quebracho	6		
Dicyandiamide based syntan	3		
Phenolic syntan	4		
Water	200	20	Leave Over Night Next day run for 20 min
Oxozolidine based syntan	1	30	
Oxalic acid	1	30	Drain/ Wash
Water	50		
Dye leveling syntan	1		
Dye (Brown CRL)	2	30	
Brown BR	2		Check pH
Hot water	100	20	
Protein syntan	3		
Ester based fatliquor	2	60	
Lanoline base fatliquor	3		
Neatsfoot oil	1		
Ester based fatliquor	2		
Synthetic fatliquor	3		
Pastosol F	0.5		
Formic Acid	4	4x10+30	Drain/Wash/Pile Over Night

TABLE II
Process recipe for lining leather from wet blue thin substance.

Chemicals	%	Time (mins)	Remarks
Water	300		
Emulsifier	0.2	15	Drain
Water	75		
Acrylic syntan	6	30	
Hydrocarbon derivative	2		
Formic acid	0.5	15	Check pH 3.0-3.2
Ester based fatliquor	2	60	
Activation derivative	1		
Acrylic syntan	5		
Chrome syntan	5		
Polymeric syntan	3	60	
Glutaraldehyde based syntan	2	60	
Water	75	10	
Sodium formate	1	2*15+30	
Sodium bicarbonate	0.5		Check pH 4.0 Leave Over Night
Water	100		
Neutralising syntan	1		
Sodium formate	0.5		
Sodium bicarbonate	0.5		
Water	50		
Polymeric syntan	5	30	
Melamine syntan	4	30	
Wattle extract	4	60	
Phenolic syntan	5		
Naphthalene sulphone based syntan	2		
Dye leveling agent	0.5		
Dye (beige)	0.1		Check penetration
Ester based fatliquor	3		
Synthetic fatliquor	4		
Phosphorylated fatliquor	2	60	
Acrylic syntan	5	30	
Polymeric syntan	5	60	
Water	200	10	
Formic acid	3	30+30	Drain/Wash/Pile

TABLE III
Process recipe for glove leather from wet blue thin substance.

Chemicals	% offer	Time (mins)	Remarks
Water	100		
Emulsifier	0.2	20	Drain
Water	50		
Acrylic syntan	6	30	
Hydrocarbon derivative	2		
Formic acid	0.5	15	Check pH 3.2
Glutaraldehyde based syntan	2	30	
Chrome syntan	5	40	
Ester based fatliquor	2	40	
Chrome	2	60	
Polymeric syntan	3		
Water	100	10	
Sodium formate	1	2x15+30	
Sodium bicarbonate	1		Check pH 3.8-4.0
Water	100	10	Leave over night
			2 days ageing and taken for crusting
Water	200		
Neutralising syntan	2	20	
Sodium bicarbonate	1.5	60	
Ammonium bicarbonate	1.5		Check pH 6.0-6.5
Synthetic fatliquor	2	40	
Ester based fatliquor	1	60	
Phosphorylated fatliquor	1		
Emulsifier	0.1		Drain/Wash/Drain
Water	100		
Acrylic syntan	4	20	
Polymeric syntan	10	40	
Synthetic fatliquor	3	90	
Vegetable based fatliquor	4		
Ester based fatliquor	4		
Phosphorylated fatliquor	4		
Emulsifier	0.25		
Water	100	10	
Formic acid	3	30+30	Drain/Wash/Pile
			Sam, hook dry, buff and taken for dyeing based on crust weight
Water	300		
Wetting agent	2	60	
Emulsifier	1		Drain/Wash/Drain
Water	50		
Ammonium bicarbonate	2	30	Check pH 6.0
Synthetic fatliquor	2	30	
Ester based fatliquor	2	60	
Water	200	10	Drain/Wash/Drain
Water	100		

Table III continues on following page.

Table III continued.

Naphthalene sulphone based syntan	1	40	
Dye (Luganil blue NGR)	4		Check penetration
Ester based fatliquor	5	30+60	
Phosphorylated fatliquor	5		
Ester based fatliquor	10		
Emulsifier	0.5		
Water	100	10	
Formic acid	4	30+30	Drain/Wash/Drain
Water	100		
Naphthalene sulphone based syntan	1	20	
Dye (Luganil blue NGR)	2		
Synthetic fatliquor	2		
Emulsifier	0.1		
Formic acid	2	20+20	Drain/Wash/Drain
Water	150		
Cationic fatliquor	1	20	Drain/Rinse/Pile

Syntans

- Acrylic syntan: grain tightness and soft feel
- Protein syntan: for belly filling and flexibility
- Oxazolidine based syntan: provides fullness
- Phenolic syntan: produces full and resilient leathers
- Melamine based syntan: Grain tightness and improved fullness
- Dicyandiamide based syntan: Grain tightness and improved fullness
- Naphthalene sulphone based syntan: light fastness, good dyeability, level shades, tight fine pored grain
- Glutaraldehyde based syntan: soft, full handle, wash fastness and perspiration resistance
- Polymeric syntan: filling, grain tightness and medium mellow feel, good selective filling in tightening loose belly and flank areas

Fatliquors

- Ester based- imparts softness, fine grain, perfect firmness
- Synthetic fatliquor- gives softness without loading
- Phosphorylated fatliquor- gives good softness with fire retard property
- Vegetable fatliquor- gives softness with loading, for producing firm and dry leathers with non- greasy handle
- Cationic fatliquor: improves the handle and lustre of suedes, rich surface feel on retanned leathers, good lightfastness
- Lanoline based: reduces water absorption and wettability, gives a tight grain and greasy handle
- Lecithin based: excellent softness, fluffy character with a mellow and silky feel
- Sperm oil based: waxy touch, smooth grain
- Fish oil based: gives very soft leathers
- Neatsfoot oil: gives full, supple handle and smooth fine grain

The above chemicals have been used in different combinations for making upper, lining and glove leather and the optimized recipes are presented in Table I-III. The comparison of the post tanning chemicals used in conventional and experimental leathers are shown in Table IV-VI for upper, lining and glove leathers, respectively. Generally, the thickness of the leathers during post tanning can be improved through the proper choice and amount of syntans and fatliquors. It can be seen from the tables that the offer of syntans given in experimental leathers is higher compared to control leathers. An increase of about 20% for upper, 24% for lining and 17.5 % for glove leather in the offer of syntans is seen. Though there is an increase in the amount of post tanning chemicals used, which in turn would result in the increase in cost, this can be offset by the gain obtained in value addition through up-grading of grade by one unit.

Up-Grading in Thin Substance

There is a thickness increase of 0.4-0.6 mm achieved by following the process recipe designed for glove leather and the substance increase of lining leather is from 0.3-0.5mm to 0.6-0.7 mm. Table VII shows the improvement in grading obtained by this up-grading technique. It can be seen that significant improvement in the type of end leathers has been achieved using this up-grading process recipe.

TABLE IV
Comparison of post tanning chemicals for conventional and experimental upper leathers from wet blue thin substance.

Chemical	Conventional	Experimental
Syntans	Acrylic syntan (Oratan 540)a: 5% Vegetable: 10% Oxazolidin based syntan (Orgtan ZE50)b: 3% Protein syntan (Tergotan RA)f: 2% Phenolic syntan (Basyntan DI)a: 5% Melamine based syntan (Basyntan FFS)a: 4% (Total composition: 29%)	Protein syntan (Tergotan RA)f: 7% Acrylic syntan (Oraton 540)a: 8% Oxazolidin based syntan (Orgtan ZE50)b: 3% Naphthalene sulphone based syntan (Basyntan DLE)a: 3% Melamine based syntan (Basyntan FFS)a: 3% Dicyandiamide based syntan (Intan EMS)d:3% Phenolic syntan (Basyntan DI)a: 4% Vegetable: 16% (Total composition: 49%)
Fatliquors	Fish oil (Lipsol E)a: 2% Synthetic fatliquor (Coripol SBL)c: 4% Lecithin fatliquor (Ossipal LN)e: 5% Lanoline based (Lipoderm liquor WF)a: 4% Vegetable based fatliquor (Lipoderm liquor 2FB) a: 3% (Total composition: 18%)	Cationic fatliquor (Catalix GSliquid)f: 1% Synthetic fatliquor (Coripol SBL)c: 9% Ester based (Lipoderm Liqo AS)a: 4% Lanoline based (Lipoderm liquor WF)a: 5% Neatsfoot oil (Lipoderm oil N1)a: 1% (Total composition: 20%)

a: BASF; b: GG Organics; c: TFL; d: ALPA; e: Schill and Seilacher; f: Clariant

TABLE V
Comparison of post tanning chemicals used for conventional and experimental lining leathers from thin substance.

Chemical	**Conventional**	**Experimental**
Syntans	Acrylic syntan (Oratan 540)[a]: 5% Polymeric syntan (Tergotan PMB liquid)[f] : 3% Melamine syntan (Basyntan FFS)[a]: 3% Vegetable: 5% Glutaraldehyde based syntan Relugan GT50)[a]: 2% (Total composition: 18%)	Acrylic syntan (Oratan 540)[a]: 11% Polymeric syntan (Tergotan PMB liquid)[f]: 14% Melamine syntan (Basyntan FFS)[a]: 4% Vegetable: 4% Phenolic syntan (Basyntan DI)[a]: 5% Glutaraldehyde based syntan (Relugan GT50)[a]: 2% Naphthalene sulphone based syntan (Basyntan DLE)[a]: 2% (Total composition: 42%)
Fatliquors	Cationic fatliquor (Catalix GS liquid)[f]: 1% Fish oil (Lipsol E)[a]: 1.5% Phosphorylated fatliquor (Derminol SF liquid)[f]: 2% Vegetable fatliquor (Lipoderm liquor 2FB)[a]: 2% Synthetic fatliquor (Coripol SBL)[c]: 1% (Total composition: 7.5%)	Ester based fatliquor (Lipoderm Eco AS)[a] : 5% Synthetic fatliquor (Coripol SBL)[c]: 4% Phosphorylated fatliquor (Derminol SF liquid)[f]: 2% (Total composition: 11%)

a: BASF; b: GG Organics; c: TFL; d: ALPA; e: Schill and Seilacher; f: Clariant

TABLE VI
Comparison of post tanning chemicals used for conventional and experimental glove leathers from wet blue thin substance.

Chemical	Conventional	Experimental
Syntans	Glutaraldehyde based (Relugan GT50)a: 2% Acrylic syntan (Relugan RE)a: 2% Polymeric syntan (Tergotan PMB liquid)f: 3% Protein syntan Tergotan RA)f: 3% (Total composition: 10%)	Glutaraldehyde based (Relugan GT50)a: 2% Acrylic syntan (Relugan RE)a: 10% Polymeric syntan (Tergotan PMB liquid)f: 13% Naphthalene sulphone based syntan (Basyntan DLE)a: 2% (Total composition: 27%)
Fatliquors	Semi synthetic fatliquor (Derminol KB liquid)f: 10% Lecithin fatliquor (Ossipal LN)e: 8% Fish oil (Lipsol E)a: 5% Sperm oil based fatliquor (Derminol SPE liquid)f: 2% (Total composition: 25%)	Ester based fatliquor (Lipoderm Eco AS)a: 24% Phosphorylated fatliquor (Derminol SF liquid)f: 10% Synthetic fatliquor (Coripol SBL)c: 9% Vegetable based fatliquor Lipoderm liquor 2FB)a: 4% Cationic fatliquor (Catalix GS liquid)f: 1% (Total composition: 48% of which 22% is based on crust weight)

a: BASF; b: GG Organics; c: TFL; d: ALPA; e: Schill and Seilacher; f: Clariant

TABLE VII
Up-grading achieved for different types of leathers from wet blue thin substance.

Product	Grade at Wet Blue Stage	Final Grade Improvement
Upper	Lining-II	Upper
Lining	Rejections	Lining-I
Glove	Rejections	Glove

TABLE VIII
Physical strength characteristics of various leathers made from wet blue thin substance.

Leather	Tensile strength (Kg/cm^2)		Tear strength (N)		Load at grain crack (Kg)		Distention at grain crack (mm)	
	Control	Exp.	Control	Exp.	Control	Exp.	Control	Exp.
Upper	220±5	240±5	42±2	46±1	23±1	21±2	9.0±0.2	11.7±0.4
Lining	165±2	172±2	39±2	31±3	-	-	-	-
Glove	186±2	195±2	38±3	45±1	-	-	-	-

TABLE IX
Rub fastness characteristics of various leathers made from wet blue thin substance.

Leather	Rub Fastness	
	Dry fastness	Wet fastness
Upper	4	3\4
Glove	4\5	4
Lining	4	3

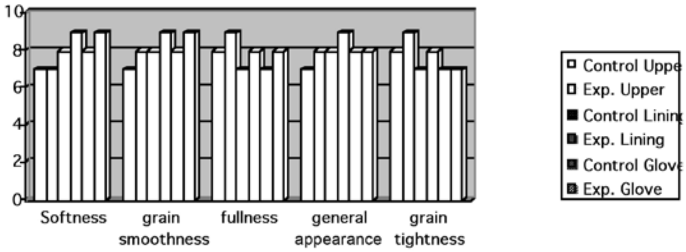

Figure 1. Organoleptic properties of control and experimental leathers.

Physical Strength Characteristics, Organoleptic Properties and Rub Fastness Measurements

Tensile, tear strength and grain crack strength for various leathers processed using the modified post tanning recipe are given in Table VIII. It is seen that the physical properties of leathers made using the modified recipe are comparable and/or better than the control leathers. Generally, increase in the offer of syntans may affect the physical strength properties negatively. However, the process recipe followed for all the three products have resulted in better strength characteristics. The bulk properties of the control and experimental leathers were assessed by standard tactile evaluation by experienced tanners. The comparative ratings for each property are given in Fig. 1. The figure shows that leathers made using the designed process recipe fare well in all the organoleptic properties. Rub fastness measurements were carried out on the three types of leathers made from thin substance wet blue and the same is given in Table IX. An average rub fastness of about 4/5 has been achieved for the different types of end leathers made.

CONCLUSIONS

Three end products viz. lining, upper and glove have been made from thin wet blue substance. Post tanning recipes for various leathers have been optimized. Sheep like softness achieved using goat skins resulting in further value addition. Physical strength and organoleptic properties are on par with that of the control leathers.

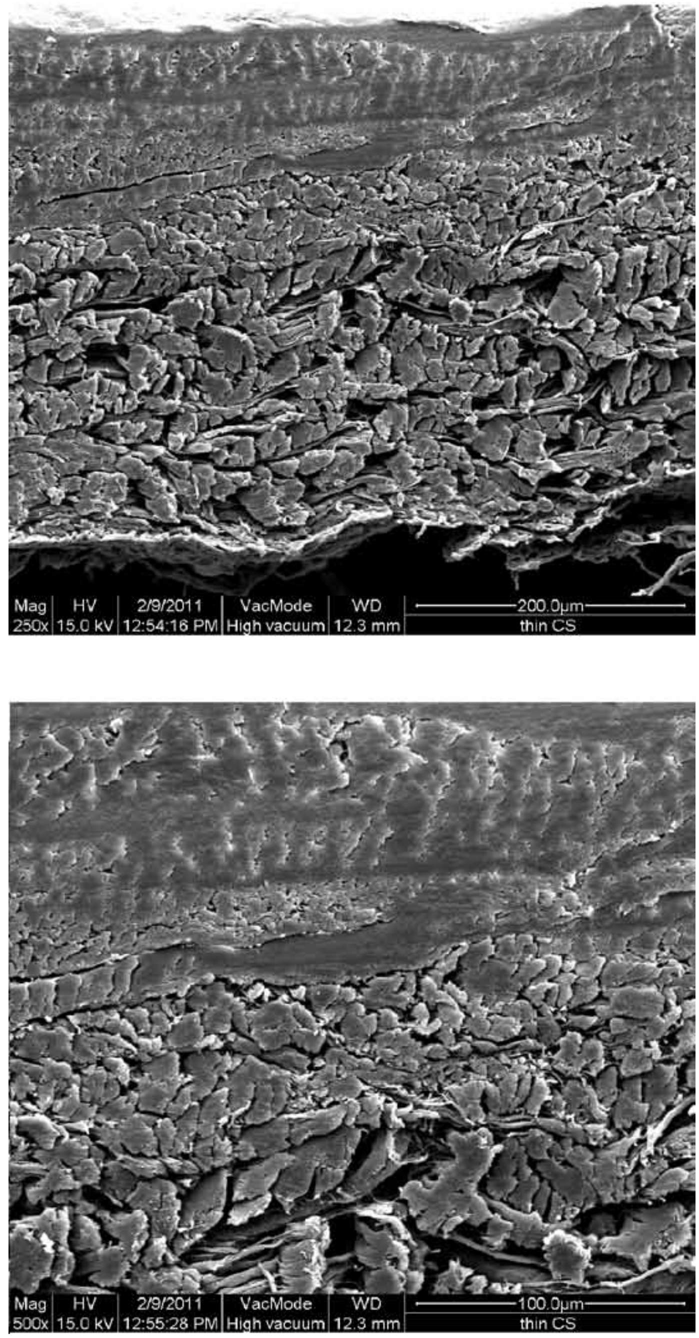

Figure 2. Scanning electron micrographs showing the cross section of the thin substance wet blue raw material at different magnification (a) X250 (b) X500.

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