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The effects of finish type on permeability and organoleptic properties of python (*Python reticulatus*) skin finished leather

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ABSTRACT

In the leather industry, there are many different types of finish, i.e. two-tone, transparent, semi aniline and opaque/solid color. The composition formulation of each finish type is different so each will impact not only on the performance but also on the properties of the finished leather. The objective of this research was to investigate the effects of finish type (natural, aniline, semi-aniline, and two-tone) on permeability and organoleptic properties of python skin finished leather. This research focused on the finishing process with various finish types. The results showed that the effect of semi-aniline (I,II) finish type on water vapor permeability reduction is the highest when compared with natural (I, II); aniline (I,II) and two-tone finish types. Otherwise, the effect of semi-aniline (I,II) finish type on organoleptic properties is the lowest compared with natural (I, II); aniline (I,II) and two-tone finish types. The aniline I finish type has better organoleptic properties.

Keywords: finish type, natural, aniline, semi-aniline, two-tone, python skin.

INTRODUCTION

The python (*Python reticulatus*) skin, known as Sanca skin, is included on Appendix II of CITES (Convention on International Trade in Endangered Species of Wild Fauna and Flora). It is one of the snakes that is not protected and can be traded (Menteri Perdagangan, 2013).

Generally, reptile skin finished leather only used protein/casein binder or nitrocellulose lacquer emulsion as the top coat, without pigment, so the leather grain will look like the original (Sumarni *et al.*, 2013). In general, the coating composition includes pigments, binders, dyes, wax, plasticizer, filler, and penetrator (Niculescu *et al.*, 2012; Gumel & Dambatta, 2013) and the top coat uses nitrocellulose lacquer emulsion (Niculescu *et al.*, 2015). Plating treatment will help flatten the formed film coating so that the layer of the film becomes compact, permanent and resistant to rubbing using either dry or wet cloth (Kasmudjiastuti, 2014). In the leather industry, there are many different types of finish i.e. two-tone, transparent, semi-aniline, and opaque/solid color. Two-tone finish is the second color either sprayed lightly or wiped over the original color or the lighter color

wiped first before darker color is applied over it. Transparent finish is found on aniline and natural finish types. Aniline and natural finish types are the most natural look leather with unique surface characteristics. Aniline finish type is applied on dyed crust leather and natural finish type is applied on crust without dyestuffs. Both allow natural marking and grain of the leather to show through. The materials for coating usually use casein or protein binder. Casein binder is a binder that comes from milk, available as water-soluble colloid and one of natural components of milk. Casein binder is an easily degraded material of natural polymers, has good adhesive properties and resistant to high temperatures (Ma *et al.*, 2012). Casein binder is used in small quantities because of its hardness, which could cause dry wrinkled folds and gives them more brightness and transparency. Nitrocellulose lacquer emulsion, when used for the top coat, can provide a transparent coating on the surface of the leather (Gumel & Dambatta, 2013) as well as protein and casein binder. Protein binder gives a fine grain pattern, good breathability, and natural feel. Semi-aniline finish contains a small amount of pigment. Opaque color finish contains a

big amount of pigment. It is not satisfying for finish on reptile skin. The finish must stick when it is applied, otherwise it will peel or crack. Good finish ensures good rub fastness and adhesive strength of paint cover. The top coat gives properties like appearance, handle, fastness to wet and dry rub resistance against hot plating and reduces the tackiness of binders used in the top coat (Wakaso, 2014).

The leather is an excellent three-dimensional matrix porous network, so it has the ability to blow (breathe). Porosity is an important parameter, which allows the leather to blow air (breathability) (Fathima *et al.*, 2010). Water vapor permeability (WVP) is the amount of moisture that can penetrate the leather in the area and at a certain time that is expressed in the unit of mg/cm².h (BSN, 1998). WVP is its ability to allow moisture to pass through it. WVP is one of the most valuable physical properties of leather, which may greatly affect the breathability and comfort of leather goods (Tang *et al.*, 2013). The properties of materials for leather goods is mainly associated with the softness and WVP (Smiechowski *et al.*, 2014). Leather has better WVP compared to synthetic leather. Unfinished leather has better WVP than finished leather (Tang *et al.*, 2013). Leather treatment at high temperatures (100-150°C) will lower the WVP. Mechanism of WVP is only transporting water molecules through capillaries in leather driven by water pressure difference between two sides of the leather sample (Tang *et al.*, 2013). The spread of water vapor velocity decreases after heat treatment, most likely due to a reduction in the number of macromolecular hydrophilic group of collagen and decreases the porosity of leather (Smiechowski *et al.*, 2014). WVP is influenced by the retanning process and the fatliquoring, but very important for finishing process is including chemical structure of the finishing solution (Smiechowski *et al.*, 2014; Tang *et al.*, 2013). In the finishing process, some finishing agents are applied to the surface of the leather to add aesthetic value to the leather finish, while reducing air permeability (Sathish *et al.*, 2015). Thick leather does not affect WVP, but thick layer affects WVP. The thicker the layer, the lower the WVP (Smiechowski *et al.*, 2014). According to Gulbiniene *et al.* (2007), transfer of water vapor depends on the number of binders and pigments, and each affects WVP and layer thickness will reduce the permeability of the leather. The thinner the film, the better the breathability

of the leather (Bekele, 2014). Leather is a unique material with the ability to breathe through porous network. Breathability and leather permeability and porosity are associated with the chemicals on the leather surface (Gil *et al.*, 2013).

The aim of this study was to investigate the effect of finish type (natural, aniline, semi-aniline, and two-tone) on permeability and organoleptic properties of python (*Python reticulatus*) finished leather. A research related to the type of finish has been undertaken by Kasmudjiastuti *et al.* (2015) on lizard (*Varanus salvator*) skin, with a discussion on mechanical tests, organoleptic, and observation of the photomicrograph. This study focused on the observation of permeability and organoleptic properties of python skin finished leather.

MATERIALS AND METHODS

Materials

Experiments were conducted with 14 (fourteen) dried python skins obtained from Sumatera island in Indonesia, wetting agent, sodium sulfide, slaked lime, degreasing agent, bating agent, ammonium chloride, formic acid, sulfuric acid, sodium bicarbonate, mimosa powder (Brand Extract from Czechoslovakia), white syntan, fatliquors, dyestuffs, fungicide, liquid dyestuffs, pigments, protein binder, casein binder, urethane and acrylic resin binder, thinner and nitrocellulose lacquer.

Methods

Apparatuses

The apparatuses used were rotary drum: Otto Specht serial number 80304, easel, hand sprayer, hand staking tool, toggling machine, glazing machine, plating machine, thickness gauge, pH stick, tensile strength tester: Zwick Roell ZO20 type KAP-TC serial number 07 4170 made in Germany, crockmeter tester: AATCC, model M238 AA serial number 708B0086, adhesion of finish tester: STD 112 serial number 11446, water vapor permeability apparatus: Wallace REF W2 serial number C 73097/2 made in England, and Scanning Electron Microscopy: SEC type SNE 3200 M.

Tanning process

The tanning, carried out in processing dried python skin, used mimosa powder. The formulation of tanning process shown in Table 1 (Kasmudjiastuti *et al.*, 2015).

Finishing process

Table 1. The formulation of tanning process from dried raw python skin.

Process	Product	%	pH	Duration (minutes)
Soaking	Water	800	9-10	
	Wetting agent	0.5		
	Soda ash	0.3		30
	Cismolan UAL	0.5		30
Washing	Water	300		10
Liming	Water	300	11-12	
	Slaked lime	5		
	Sodium sulfide	2		
Washing	Water	300		10
Scales removing				
Washing	Water	300		10
Fleshing				
Weighing				
Deliming	Water	400	7 – 8	
	Ammonium chloride	1.5		
Washing	Water	300		10
Bating	Water	100	7 – 8	45
	Bating agent	0.5 - 1		
Degreasing	Wetting agent	0.5 - 1		60
Washing	Water	300		10
Pickling	Water	100	2.5 – 3	
	Salt	10		
	Formic acid	0.5		
	Sulfuric acid	0.5		
Pretanning	Pamol	2		30
Tanning	Mimosa powder	6		45
	Mimosa powder	6		45 +180
	Alum	2		60
Washing	Water	300		10
Neutralization	Water	150		60
	Sodium bicarbonate	1		
Washing	Water	300		10
Retanning	Water	100		
	PWB	2		45
	Retingan R7	3		45
	Novaltán PF	3		45
Fatliquoring and dyeing	Water	100		
	PWB	3		60
	<i>Leveling agent</i>	1		10
	Dyestuffs	2		60
	Lipoderm liquor SPE	2		60
	Lipoderm liquor SAF	2		
	Sandolix WWL	2		
	Formic acid	1		
	Fungicide	0.02		30
Washing	Water	300		10
Pile				
Staking				
Toggling				

There were seven variations performed in the finishing process with the formulation as shown in Table 2. They were natural I finish type (with casein binder), natural II finish type (with protein binder), aniline I finish type (with casein binder), aniline II finish type (with protein binder), semi-aniline I finish type (with liquid dyestuffs), semi-aniline II finish type (with liquid dyestuffs + pigment) and two-tone finish type. The formulation of finishing refers to Kasmudjiastuti *et al.* (2015). The treatments of finishing operation for natural I and aniline I finish types were brushing by pillowcase, glazing, and kiss plating; for natural II and aniline II finish types were spraying, glazing, and kiss plating; for semi-aniline were spraying and plating with pressure of 50-75 Bar, temperature 80°C for 2 seconds; and for two-tone were spraying with effect (not homogenous) and plating with pressure of 50 Bar, temperature 80°C for 1 second.

Testing

The test parameters of the results of the study focused on the effect of finish type on permeability and organoleptic properties of phyton leather, which included measurement of film thickness, water vapor permeability (WVP), rub fastness (dry, wet), and the adhesive strength of cover paint (dry, wet).

The thickness of film coating was measured by scanning electron microscopy technique using

300X magnifications.

WVP test method (BSN, 1998): Leather was cut into 5 x 5 cm rectangular pieces of test piece and conditioned at 70% RH with minimum temperature for 24 hours. Test piece was rubbed lightly with sand paper in all directions 10 times with maximum load of 200 grams and cut circular with a diameter of 36.0 mm. Tes bottle was filled approximately ½ of it with silica gel, put in dryer cabinet at 102-105°C for minimum 2 hours, and cooled in decicator.

Test piece was then placed with grain inside the mouth of bottle cap, the lid was tighten and then was weighed. The bottle and the test piece were mounted on WVP test equipment and spinned for minimum 7 hours. After that, the bottle and the test piece were weighed and the time from the first to second weighing was recorded.

WVP was calculated with equation (1):

$$WVP (mg/cm^2h) = 7639 \cdot m / (d^2 \cdot t) \quad (1)$$

Where m was the difference of weight before and after test (milligram), d was the average diameter of bottle mouth (mm), t was the time of the test (minute), and 7639 was conversion of unit

Organoleptic test method

Organoleptic test was conducted by 10 panelists, who are competent in the area of leather, to assess softness and appearance. The assessment criteria were as follows: very good with a score of

Table 2. The formulation of finishing for different finish type

Finishing auxiliaries (gram)	Natural (crust)		Aniline (dyed crust)		Semi-aniline (dyed crust)		Two-tone (dyed crust)
	I	II	I	II	I	II	
Water	1000	750	1000	750	575	575	550
Casein binder	30	-	30	-	-	-	-
Ammonia	40	-	40	-	-	-	-
Cationic fatliquor	10	-	10	-	-	-	-
Fixing agent:							
Formaldehyde	200	-	200	-	-	-	-
Water	800	-	800	-	-	-	-
Protein binder	-	250	-	250	-	75	75
Urethane resin	-	-	-	-	50	50	50
Acrylic resin	-	-	-	-	250	250	250
Liquid dyestuffs	-	-	-	-	50	30	75
Pigment	-	-	-	-	-	20	-
Top coat:							
Nitrocellulose	-	-	-	-	200	200	200
Thinner	-	-	-	-	800	800	800

91-100; good with a score of 81-90; adequate with a score of 71-80.

RESULTS AND DISCUSSION

Properties of Python Leather

The properties of the leather may include film thickness of coating, WVP, rub fastness (dry, wet), the adhesive strength of cover paint (dry, wet) and organoleptic. The film thickness of coating is shown in Figure 1. The data of WVP, rub fastness (dry, wet), and adhesive strength of cover paint (dry, wet) are shown in Table 3. The reductions of WVP of various types of finish are shown in Figure 2 and organoleptic properties are shown in Figure 3.

Film Thickness

The film forming in various finish types were not uniform. Therefore, it was important to measure the thickness of the film formed. The film thickness of each finish types was measured by scanning using electron microscopy technique at 300 X magnifications. The film thickness of each finish type on python leather surface was measured and shown in Figure 1.

Figure 1 shows that the thickness of natural I (Figure 1(a)) coated surface was 53.85 microns; natural II (Figure 1(b)) was 58.15 microns; aniline I (Figure 1(c)) was 42.0 microns; aniline II (Figure 1(d)) was 44.7 microns; semi-aniline I (Figure 1(e)) was 48.8 microns; semi-aniline II (Figure 1(f)) was 104.0 microns; and two-tone finish (Figure 1(g)) was 38.9 microns. Unfinished (control) sample without coated surface (Figure 1(h)) had no thickness. Differences in film thickness were due to material compositions of finishing and coating, meaning that each type of finish was different.

The thinnest film was two-tone finish type with a film thickness of 38.9 microns. The thickest film was semi-aniline finish type II with a film thickness of 104.0 microns. According to Gulbiniene *et al.* (2007), transfer of water vapor depends on the surface of coating thickness (amount of binder and pigment) and film thickness will reduce the permeability of leather. WVP of the leather depended on the numbers of binders and pigments. The thickness of coating affects WVP. The thicker the film, the lower the WVP (Smiechowski *et al.*, 2014). Otherwise the thinner of film, the higher the WVP (Bekele, 2014). The test results of WVP, rub fastness, and the adhesive strength of the cover paint are presented in Table 3.

WVP and Reduction of WVP on Various Finish Types

WVP, in general, is measured by air volume pass through the leather of unit area in unit time. Its unit is mg/cm².h. The results of WVP are given in Table 3. According to Smiechowski *et al.* (2014), the value of WVP of unfinished leather is higher than WVP of finished leather. It is evident in Table 3 that the WVP of control (unfinished) was 15.95 mg/cm², which was higher than the finished leather. The WVP value of two-tone finish type (12.38 mg/cm².h) was higher than the other finish types. The spread of water vapor velocity decreased after heat treatment, most likely due to a reduction in the number of macromolecular hydrophilic group of collagen and decreased the porosity of the leather (Smiechowski *et al.*, 2014). The two-tone finish coating on the surface of the leather used a mix of base coat and liquid dye-stuffs with thin spray to give a two-tone effect so that the coating film was thinner than the other.

Table 3. WVP, rub fastness, and the adhesive strength of the cover paints of various finish types on python leather.

Type of finish	WVP (mg/cm ² .h)	Rub fastness		The adhesive strength of cover paint (g/cm)	
		Dry	Wet	Dry	Wet
Control (unfinished)	15.95	-	-	-	-
Natural I	12.18	4/5	4/5	400.83	75.00
Natural II	11.45	4/5	4/5	258.33	150.00
Aniline I	11.63	4/5	4/5	350.00	75.00
Aniline II	11.56	4/5	3/4	541.67	75.00
Semi-aniline I	10.07	4/5	4/5	533.33	216.67
Semi-aniline II	9.60	4/5	4/5	245.83	129.17
Two-tone	12.38	4/5	4/5	275.00	175.00

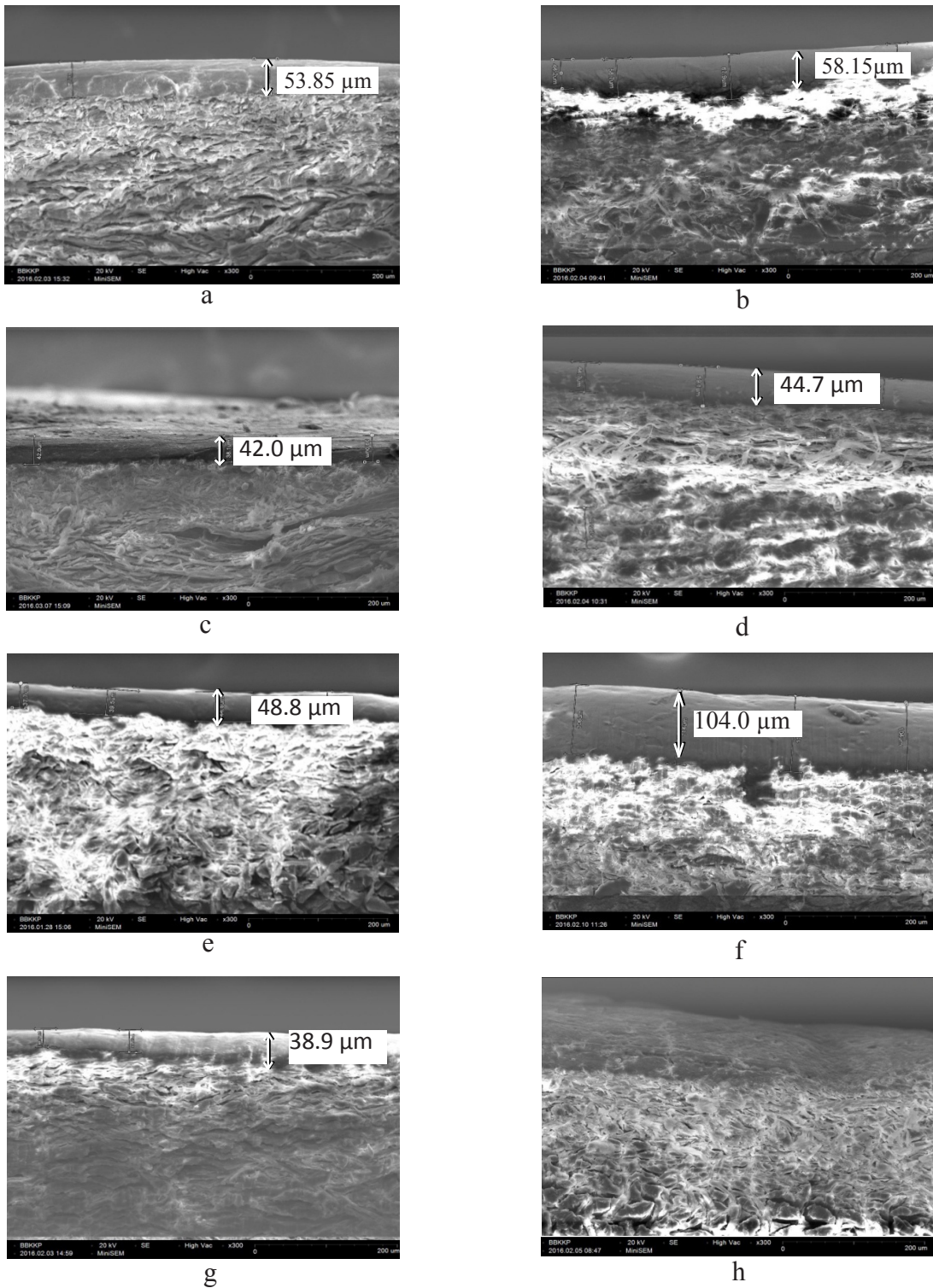


Figure 1. Film thickness of (a) natural I; (b) natural II; (c) aniline I; (d) aniline II; (e) semi-aniline I; (f) semi aniline II; (g) two-tone; and (h) unfinished.

The WVP value of natural I finish type was higher than the natural II finish type (12.18 and 11.45 mg/cm².h). This was due to the differences in material composition and viscosity of the solution, so the leather surface porosity was affected. Natural

I finish type used casein binder, which dissolved in water (30g/1000g), used more dilute solution compared with the natural II finish type, which used a protein binder material dissolved in water (250/750g). Similarly, the value of WVP aniline I

finish type was higher than aniline II (11.63 and 11.56 mg/cm².h), due to the material composition. The viscosity was the same type as natural finish. The difference was aniline finish type which used dyed crust raw materials, while natural finish type used natural crust raw materials. The WVP value of semi-aniline II finish type was lower than the semi-aniline I (9.60 and 10.07 mg/cm².h). It was also because the composition of the coating material of semi-aniline II was more solid than semi-aniline I as the composition of the coating material of semi-aniline II also contained pigment, thereby affecting the porosity of the surface of the leather and caused reduction in WVP. The highest WVP was the two-tone finish (12.38 mg/cm².h), which had the thinnest film (38.9 microns). The WVP value is influenced by the retanning and fatliquoring process, but the most important process is finishing process, including chemical structure of the finish (Smiechowski *et al.*, 2014). In the finishing process, some finishing agents were applied to the surface of the leather to add aesthetic value to the leather finish, but it will reduce WVP (Sathish *et al.*, 2015). To see the effects of various types of finishing in reducing WVP, equation (2) was used to calculate it and the graphic images are shown in Figure 2.

$$WVP_R = \frac{WVP_{BC} - WVP_{AC}}{WVP_{BC}} \times 100 \quad (2)$$

Where WVP_R is WVP reduction in percentage, WVP_{BC} is WVP before coating (crust leather), and WVP_{AC} is WVP after coating (finish leather).

The percentage of WVP reduction of each finish type can be seen in Figure 2. The highest WVP reduction was in semi-aniline II finish type with 39.8% reduction. The lowest WVP reduction was in two-tone finish type with 22.38% reduction. The reduction of WVP was due to the chemical substance applied to the surface of the leather in the finishing process (Smiechowski *et al.*, 2014; Tang *et al.*, 2013). It does not only consist of polymer as binder but also a wide range of additional materials which can close the pores of the leather surface. Moreover, due to the effects of heat treatment (glazing or plating treatment), the number of hydrophilic groups of macromolecule collagen were reduced and decreased the porosity of the leather (Smiechowski *et al.*, 2014). Chemical substance for coating consisted not only of polymer

as binder but also of various auxiliaries. Each of them might have covered the surface porosity of leather, which reduced the WVP of leather. The reduction of WVP by semi aniline (I, II) finish type was higher compared with natural (I, II); aniline (I,II) and two-tone finish types.

Rub Fastness

The values of wet and rub fastness of the finished leather are given in Table 3. The results indicated that finish type did not affect the rub fastness. The results of all finish type showed good dry and wet rub fastness with score 4/5, indicating that sufficient binder or lacquer emulsion was used and the bonding between the pigment and the binder was strong. This showed that the formula of the top coat was compatible with the system/treatment, so that when it dried it formed a strong glue film coating on the surface of the leather. Top coat determined the final appearance and the handle of leather surface and it had decisive influence on the fastness proportion of finish. Moreover, heat and pressure treatments (plating/glazing) helped flatten the formed film coating, so that a layer of film became compact and permanent and resistant to rubbing with a dry cloth or wet cloth (Kasmudjastuti, 2014).

Adhesive Strength of Cover Paint

The values of the effects of the finish types on the adhesive strength of the cover paint of the finished leather are shown in Table 3. The results indicated that the value of adhesive strength of cover paint (dry) was in a range 245.83-541.67 g/cm and 75.00-216.67 g/cm (wet). The highest value of adhesive strength of cover paint (dry)

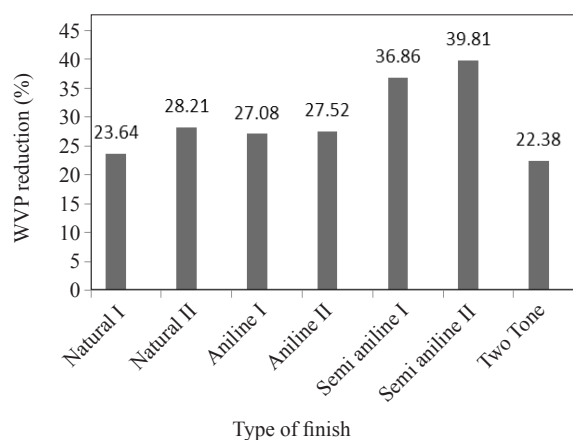


Figure 2. Percentage reduction of WVP on various finish types.

was achieved by the aniline II finish type (541.67 g/cm) and 216.67 g/cm for adhesive strength of cover paint (wet).

The finish coat must stick when applied on leather surface. Otherwise it will peel or crack. Adhesion is the degree of binding to the surface of the leather of a finishing layer, which used to improve the leather's physical characteristics. This showed that the composition of the material for the base coat was compatible with the composition of the material for the top coat, so it could become a powerful glue on the surface of the leather when coupled with plating treatments that enhanced adhesion to the surface of the leather due to their thermal energy.

Organoleptic Properties of Leather (Performance of Leather)

The finished leathers of all finish types had been evaluated for organoleptic properties by hand and visual evaluation. The average of rating for the leathers is given in Figure 3. Higher numbers indicated a better property.

Organoleptic test was intended to determine the extent of the softness and appearance of the python leather which used vegetable tanning with various types of finish. Organoleptic testing was judged by 10 panelists with average values as shown in Figure 3. The results showed the highest organoleptic test on the python leather was produced by aniline I finish type with a value of 92.6. It means that aniline I finish type had better softness and appearance than the other finish types. Semi aniline (I, II) finish type had lower organoleptic properties when compared with natural (I, II); aniline (I,II); and two-tone finish types.

The purpose was to produce finished ani-

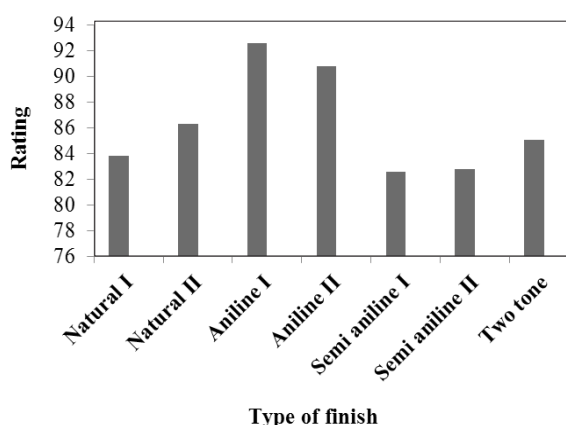


Figure 3. Organoleptic properties of the python leathers.

line leather that had a natural appearance (natural look). It was evident that the selected panelists considered the best leather was the one that used aniline finish. For reptile leather finishing, the most important thing is the beauty of the grain and retaining of its original color and not being covered by the cap when using a paint pigment. To achieve this, the layer of film that is formed should be transparent. Reptile leather at the finish uses a protein or casein binder, finished leather looks transparent, and the grain look like the original (Sumarni *et al.*, 2013).

CONCLUSIONS

Any type of finish affected the WVP and reduced WVP, film thickness, adhesive strength of cover paint, and organoleptic (performance) of leather finish, but did not affect the rub fastness properties. The aniline I finish type was the optimum treatment in this trial to produce python leather with the properties as follows: WVP of 11.63 mg/cm².h; rub fastness of 4/5 (dry and wet); the adhesive strength of cover paint of 350 g/cm (dry), 75 g/cm (wet), WVP reduction of 27.08% and organoleptic value of 92.6 (very good).

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