STUDIES ON SOLUBILIZED SULFUR DYES FOR COLORING LEATHER

by

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ABSTRACT

Cow wet blue stock was colored with solubilized sulfur dyes in a systematic study to unravel the color yield quality of dyeing and fastness of the dyes. These dyes penetrated the leather cross-section well and this performance resulted in a beneficial tone-in-tone dyeing, which means that the color of the grain, flesh and cross section of leather was almost the same tone. The levelness and uniformity of dyeing were excellent. Their fastness performance was generally very good. The resultant shades suggested that the sulfur dyes were best suited for light, pastel and medium shades, which require a high degree of levelness, penetration and fastness properties. An intense shade resulted from offering the sulfur dyes ahead of the retanning and fatliquoring process steps with a trivial reduction in penetration through the leather cross section for all the ten dyes studied. These findings favor the profitable production of light, medium to dark dye shades on leathers.

INTRODUCTION

Sulfur dyes are mostly used in the textile industry, but seldom in leather coloration. The main reason for their limited application in leather is their poor water solubility in neutral pH conditions.[1] In textile dyeing, they are used in alkaline pH conditions and are solubilized with sodium hydroxide and sodium sulphide. In cotton-based substrates, they provide a wide range of shades, good fastness to washing and light at less expense than other dyes.[2-8] However, their shades are generally dull and brilliant shades are not commonly available. Black and navy blue are the most important members of the sulfur dyes family.[4-5]

Conventional sulfur dyes are insoluble in water, and need to be chemically reduced with sodium sulfide (alkali reduction) by cleaving the disulfide bonds.[6-12] In the 1970's, the use of sodium sulfide has been restricted by different legislations due to high residual content.[13-15] However, even in 1990's, sulfur dyes still represented 10% of all the manufactured synthetic dyes.[16-17] In mid 1980's, modified sulfur dyes with lower amount of sulfur were introduced and now, a new range of sulfur dyes having only traces of free sulphide, and good solubility in water around neutral pH conditions are available for textile dyeing.

With increasing demand for high degree of fastness to washing and dry cleaning, reactive dyes are also being used in the recent times for leather dyeing but the cost of dyeing increases with the use of such class of dyes. Of late, there has been increasing demand for highly uniform and level dyeing with the cross section being in tone with the surface color. This is very difficult to achieve with conventional dyes. To date, there is a long felt need for the production of colors with high degrees of fastness but at reduced cost. In this context, sulfur dyes are attractive alternatives especially for the production of light and pastel shades.

Despite advances in the chemistry of sulfur dyes, their use in leather coloration did not receive serious attention, though there had been some patents filed in USA for the application of sulfur dyes in leather dyeing.[18-19] The main reason for this is the lack of knowledge on how this class of modified dyes, though ready to use as such, will behave on leather. Hence, the present systematic study assessed the usefulness of this range of sulfur dyes in leather dyeing.

The modified sulfur dyes used in this study are water soluble and are presented using the symbolic form of Col-S-SO_3Na. They were made by treating the parent sulfur dye with sulphite and bisulfite in the presence of atmospheric oxygen (Equation 1).

$$\text{Col-S-S-Col} + 2\,HSO_3^- + \tfrac{1}{2}O_2 \longrightarrow 2\text{Col-SSO}_3^- + H_2O \qquad (1)$$

The modified dyes have sulfonic acid groups, which impart water solubility and offer the chance for ion-pair linkages with positively charged side chain amino groups in leather. The physical adsorption of the dyes on the leather fibers coupled with ionic interaction can result in a high degree of fastness characteristics of the resultant shades.

The solubility and spectral characteristics of the dyes were studied, and leather application trials were carried out on chrome-

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tanned cow hides. The methodology followed for dyeing with sulfur dyes was the same as used for conventional leather dyes.

MATERIALS AND METHODS

Materials

Ten solubilized sulfur dyes, *viz.,* Green TBY, Black LSG (C.I. Black 1), Chocolate Brown LFP (C.I. Brown 14), Snuff Brown LG, Brown LRV, Maroon TBB, Golden Yellow TGG, Green Blue LCV(C.I. Blue 15), Blue LSR (C.I. Blue 4), Grey LNC (C.I. Blue 21) from SF Dyes, Bangalore, India were used in this systematic study. Other chemicals used in the leather processing are of technical grade and auxiliaries are proprietary products from Multinational Leather Chemical Supply houses. Dyeing study was carried out with chrome tanned cow leathers.

Methods

Studies on Solution Characteristics of Dyes

The solubility of each sulfur dye was determined by using the official method SLF 201. The spectral characteristics of the dyes were studied using a Hitachi UV- visible spectrophotometer (U-2000 Model). The spectra for all the dyes were recorded in the visible range of 350-700 nm for solutions of suitable concentration and the respective absorption maxima (λ_{max}) for each dye was noted.

Fastness of color and the stability of the dye's solution in mild and strong acids were studied using procedures SLF 202 and 203 respectively. Stability of dye solutions in hard water and in the presence of mild and strong alkalis was studied by using procedures SLF 442 and 204 respectively.

Leather Application Trials with Sulfur Dyes

The application trials used the same approach or methodology for conventional anionic dyes. The cow blue stock was offered 2.5% dyestuff based on its shaved weight. The process used for the coloring, retanning and fatliquoring is shown as Appendix I.

The dyed leathers were assessed visually by a dye expert who used a subjective scale of 1-5, with 1 as the lowest and 5 as the best rating. The resultant performance profile embodied ratings of dye penetration through the cross section of leather, its exhaustion or uptake from the dye bath, its levelness, uniformity and depth of the shade on the surfaces of leather. The fastness of leather color was assessed for the following tests.

- Wet and dry rub fastness
- Light fastness
- Perspiration fastness
- PVC migration
- Wash fastness

Study on the Fastness Characteristics of the Dyed Leathers

The dyed leathers were conditioned at $20^0 \pm 2^0$C and 65± 5% RH for 48 hours, and then tested with standard procedures for fastness characteristics. The wet and dry rub and perspiration fastness characteristics and the respective color staining fastness were tested by methods SLF 450/1965, the light fastness was assessed by SLF 1, PVC migration by SLF 442 and wash fastness by SLF 423 respectively.

All the fastness characteristics were assessed on a grey scale of 1-5 with 1 as the lowest and 5 as the best ratings; except for light fastness which was assessed on a blue scale of 1-8 with 1 as the lowest and 8 as the best rating.

Study on the Effect of Process Parameters on Color Intensity

The effect of changing the sequence of coloring in wet end processing was studied to understand the intensity of the resultant shades. Thus, in this new set of experiments, and after the neutralization of blue stock to pH 5.0 and its subsequent washing, its dyeing was carried out in a separate bath before offering retanning and fatliquoring auxiliaries. This process is described in [Appendix I]

Color Strength or Color Yield analysis was carried out based on the measurement of reflectance using a reflectance spectrophotometer.[20] Leather samples from conventional dyeing were used as standard for comparison of color intensity. Relative color strength calculation was carried out using three different methods based on the calculation of Chromatic color Strength, Apparent color Strength and Integrated Wavelength color strength and all of them make use of the reflectance data obtained from the spectrophotometer, which measures reflectance for the dyed samples at 10 nm intervals in the visible wave length range of 400-700 nm using D_{65} illuminant and 10° deg observer.[21]

Chromatic color strength (Equation 2) represents the ratio based on the K/S-value of the sample in relation to the K/S value of the standard at the wavelength of maximum absorption (λ_{max}).

$$\text{Chromatic color strength\%} = 100\,X\,\frac{\left(\frac{K}{S}\right)_{Sample}}{\left(\frac{K}{S}\right)_{Std}} \qquad (2)$$

Where, K/S is called Kubelka-Munk function (Equation 3), which is the ratio of absorption co-efficient to scattering co-efficient and calculated at a wavelength from the reflectance value, R using the equation

$$\frac{K}{S} = \frac{(1-R)^2}{2 * R} \qquad (3)$$

Apparent color strength (Equation 4) represents the ratio of sum of K/S-values at all wavelengths in the visible range measured at 10 nm interval for the sample to that calculated for the standard.

$$\text{Apparent color strength\%} = 100\ X\ \frac{\sum_{700}^{400}(\frac{K}{S})_{Sample}}{\sum_{700}^{400}(\frac{K}{S})_{Std}} \quad (4)$$

Integrated wavelength color strength (Equation 5)represents the ratio of sum of K/S data multiplied by the sum of weighted observer/illumination at all wavelengths for the sample in relation to the standard. In this study, we have used D_{65} illuminant and 10^{o} deg observer data.

$$\text{Integrated color strength\%} = 100\ X\ \frac{\sum_{700}^{400}(\frac{K}{S})(f_X + f_y + f_z)_{Sample}}{\sum_{700}^{400}(\frac{K}{S})(f_X + f_y + f_z)_{Std}} \quad (5)$$

RESULTS AND DISCUSSIONS

Study on the Solution Characteristics

The spectral characteristics of the sulfur dyes are shown in Fig. 1(a&b). The results of the solution studies are presented in Table I.

Spectral graphs for the sulfur dyes maroon TBB, Green Blue LCV, black LSG, Blue LSR, green TBY and Green LNC show clear peaks each with distinct absorption maxima λ_{max} indicating better spectral purities of the dyes compared to the dyes, Snuff Brown LG, Golden Yellow TGG, Chocolate Brown LFP and Brown LRV, which exhibited broader peaks.

All of the sulfur dyes studied dissolved well in water with a solubility of 50 G./L or more(Table I). The fastness of dye solution in formic acid was good with all the dyes rated at 4 and above except Yellow TGG which had a rating of 3-4. In sulfuric acid, all the dyes except Green Blue LCV, Green TBY and Golden Yellow TGG had the rating of 4-5. Golden Yellow TGG had the poorest rating of 1-2 indicating this dye was sensitive to acid (both formic and sulphuric acid) in general and changed color appreciably on addition of acid; like during the lowering of pH with formic acid in wet end processing.

The results of the study on the stability of dye solution to acid and alkali addition are given in Table I. Maroon TBB, Snuff Brown LG, Black LSG, Chocolate Brown LFP and Brown LRV exhibit excellent stability on acid addition with the rating of 5 whereas Green Blue LCV, Green TBY, Grey LNC and Golden Yellow TGG register poor stability of 3 or below. All the solubilized dyes except Snuff Brown LG had good stability on alkali addition with the rating of 4. All the dyes have excellent stability in hard water with the perfect rating of 5.

Visual Assessment of the Dyeing Characteristics of Sulfur Dyes

Visual assessment data on the dyeing characteristics of sulfur dyes are presented in Table II. All of the dyes penetrated the leather cross section when conventional process was followed and were rated 4-5. The uptake out of the dye bath was moderate and was rated 3-4. The dyes gave full-chrome leather a good level dyeing. The intensity of shade as assessed visually was moderate for six of the ten dyes. Four dyes, Snuff Brown LG, Black LSG, Chocolate Brown LFP and Brown LRV, only dyed to light shades. These results showed that sulfur dyes are more suited to produce light and medium shades with and an attendant high degree of penetration, uniformity and level dyeing. Another interesting observation is that all the dyes gave good tone-in-tone dyeing which means the grain, flesh and cross section were colored to almost the same shade.

Fastness Characteristics of Full Chrome Cow Leathers Dyed with Sulfur Dye

The fastness of the colored leather such as its rub fastness, light fastness, wash fastness, perspiration fastness, fastness to color stain, migration into PVC was evaluated by using standard protocols, and these results are presented in Table III. Their fastness characteristics are generally good with a rating of 4 and above except in the case of Maroon TBB, the perspiration resistance has been found to be relatively inferior with the rating of 3-4. Fastness to migration into PVC for all the dyes was found to be excellent.

Light fastness for all the dyes on leather were moderately good with a rating of 4-5, and on the blue scale of 1-8 in all the cases except for chocolate brown LFP (rating of 4).

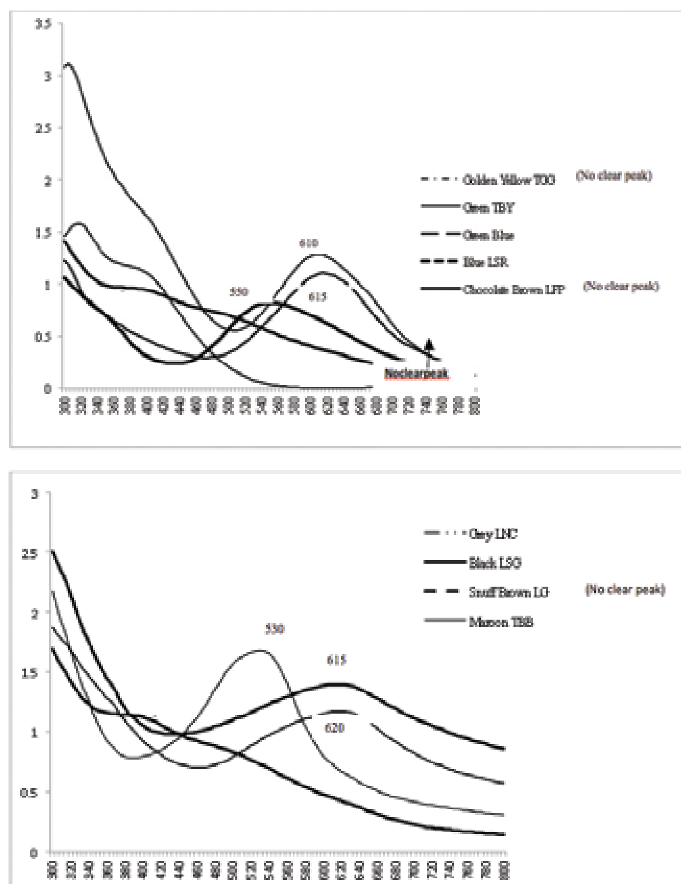

Figure 1 (a&b). Absorption Spectra of the sulfur dyes.

TABLE I
Results of the solution studies with sulfur dyes.

Parameters	Assessment Grade									
	Maroon TBB	**Green Blue LVC**	**Snuff Brown LG**	**Black LSG**	**Blue LSR**	**Green TBY**	**Golden Yellow TGG**	**Choco-late Brown LFP**	**Grey LNC**	**Brown LVR**
Solubility (SLF 201) g/l	70	80	70	60	80	55	50	60	55	70
Fastness of dye solution to acid (SLF 202) Formic Acid Sulfuric Acid	4-5 4-5	4 3	4-5 4-5	4-5 4	4-5 4	4-5 2-3	3-4 1-2	4-5 4	4-5 4	4-5 4
Stability of dye solution on acid addition** (SLF 203)	5	2	5	5	3	2	3	5	2	5
Stability of dye solution on alkali addition	4-5	4	3	4	4	4	4	4-5	4	4
Stability of dye solution to hard water***(SLF 205)	5	5	5	5	5	5	5	5	5	5

*TEST METHOD SLF – 450/1965

**The rating was done according to the following scheme

Rating 5	No precipitation with either acid
Rating 4	No precipitation with Formic acid Incipient precipitation with Sulfuric acid
Rating 3	No precipitation with Formic acid Marked precipitation with Sulfuric acid
Rating 2	Incipient precipitation with Formic acid
Rating 1	Marked precipitation with Formic acid

*** The rating was done according to the following scheme

Rating 5	No precipitation with hard water
Rating 4	No precipitation with hardness equivalent to 200 mg CaO/litre. Incipient precipitation with 400 mg. CaO/litre
Rating 3	No precipitation with hardness equivalent to 200 mg. CaO/litre, marked precipitation with 400 mg. CaO/litre
Rating 2	Incipient precipitation with hardness equivalent to 200 mg CaO/litre.
Rating 1	Marked precipitation with hardness equivalent to 200 mg CaO/litre.

TABLE II
Visual Assessment of the dyeing characteristics of sulphur dyes.

Parameters	Assessment Grade									
	Maroon TBB	**Green blue LCV**	**Snuff brown LG**	**Black LSG**	**Blue LSR**	**Green TBY**	**Golden yellow TGG**	**Chocolate brown LFP**	**Grey LNC**	**Brown LRV**
Penetration										
Conventional process	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Modified process	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4
Levelness for both conventional & modified process	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
Color Intensity										
Conventional process	Moderate	Moderate	Light	Light	Moderate	Moderate	Moderate	Light	Moderate	Light
Modified process	Intense	Intense	Intense	Intense	Intense	Intense	Intense	Intense	Intense	Intense
Exhaustion Rating										
Conventional process	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4
Modified process	4-4.5	4-4.5	4-4.5	4-4.5	4-4.5	4-4.5	4-4.5	4-4.5	4-4.5	4-4.5

These results suggests that this class of sulfur dyes understudy are best suited to color leathers in light and pastel shades and medium shades which require an attendant high degrees of fastness characteristics. They are most suitable for washable leathers as evidenced by good wash fastness characteristics. However, for dark shades, some intervention during wet end processing like changing the process sequence to increase the color intensity may be necessary.

Influence of Process Sequence Variation on Color Strength

An expected improvement in the relative color yield or dye strength resulted when the coloring of leather preceded the retanning and fatliquoring process steps. The visual assessment results (Table II) showed that the dye intensity was remarkably improved by this practice; but without the expected decrease in levelness normally attendant to using conventional dyes. However, there is a drop from 4-5 to 3-4 in the penetration rating for all the dyes.

The relative color strength was measured instrumentally by using the spectrophotometer. Relative Color yield calculated using three different methods, *viz.,* Chromatic color Strength, Apparent color Strength and Integrated wavelength color strength methods are presented in Table IV. As the spectral graphs of some of the sulfur dyes do not have distinct absorption maxima, Apparent color strength and Integrated wavelength color strength methods which are based on calculating K/S values at all wavelengths in the visible range, may be the most appropriate methods to measure the relative color strength. Relative color strength calculated using these two methods are also shown graphically in Fig. 2. The addition

TABLE III
Fastness characteristics of full chrome cow leathers dyed with sulfur dyes.

Parameters	Assessment Grade									
	Maroon TBB	**Green blue LCV**	**Snuff brown LG**	**Black LSG**	**Blue LSR**	**Green TBY**	**Golden yellow TGG**	**Chocolate brown LFP**	**Grey LNC**	**Brown LRV**
Wet Rub Fastness	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Dry Rub Fastness	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Perspiration Fastness	3-4	4	4-5	4	4	4-5	4-5	4	4-5	4-5
Color Staining										
a) Wet Rub	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
b) Dry Rub	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
c) Perspiration	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Light Fastness (Light source – Halogen Tungsten)	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5
Color Fastness to washing	4	4-5	4	4	4	4-5	4	4-5	4-5	4-5
Color staining										
Cotton	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Fastness of leather to PVC Migration	5	5	5	5	5	5	5	5	5	5

of dyes prior to offering the retanning and fatliquoring auxiliaries brought about an impressive gain in the relative color yield along with good penetration, which is normally difficult with classical anionic dyes. Maroon TBB which has exhibited the lowest improvement among the dyes chosen has also registered about 350% increase in color yield. But the most promising results have been recorded for Black LSG and Chocolate Brown LFP with close to 2000% increase in color yield. Such an improvement may be attributed to a higher chance for ion-pair interactions in the absence of competition from anionic retanning and fatliquoring chemicals, when the dye is offered prior to addition of other anionic post tanning auxiliaries. As previously noted, this improvement in color strength is accompanied by a small, but consistent, reduction in penetration.

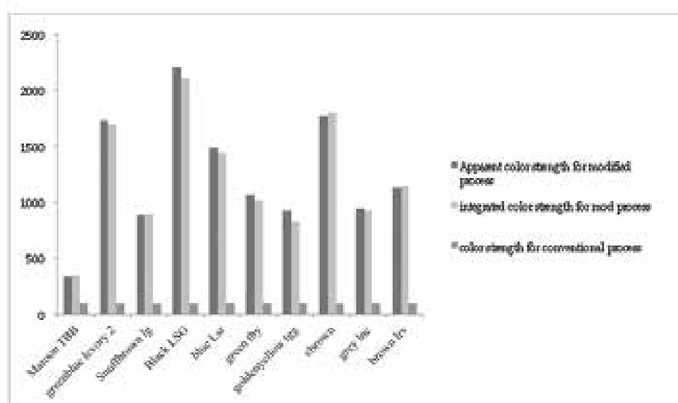

Figure 2. Relative color yield for modified process by apparent color strength and integrated color strength methods.

TABLE IV
Relative Color yield when dyes were added prior to retanning and fatliquoring auxiliaries.

S.No	Name of the Dye	Relative color yield (%)		
		Chromatic	Apparent	Integrated wavelength
1	Maroon TBB	379.0	337.7	341.6
2	Green blue LCV	883.2	1729.2	1692.1
3	Snuff Brown LG	1026.9	884.0	895.8
4	Black LSG	1965.1	2207.6	2115.2
5	Blue LSR	915.7	1487.5	1440.8
6	Green TBY	876.1	1065.3	1015.2
7	Golden yellow TGG	668.6	925.5	831.7
8	Chocolate Brown LFP	1962.1	1768.7	1798.7
9	Grey LNC	801.9	945.2	921.9
10	Brown LRV	1283.5	1126.4	1142.4

CONCLUSION

Soluble sulfur dyes were used in standard application recipes to endow leather with light and pastel shades, and to some extent medium shades with a high degree of cross section penetration, level dyeing of the surfaces and fastness characteristics. A remarkable improvement in color yield was observed when dyeing was done ahead of retanning, and fatliquoring but with a trivial reduction in dye penetration. The modified sulfur dyes are suitable for dying leathers that require a high degree of levelness and fastness characteristics with a good tone-in-tone dyeing.

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Appendix I

Process Details for application of Sulfur dyes

Raw Material:	Wet Blue Cow leather	
	Sam and shave to a thickness of: 1.2-1.3mm	
Acid wash:	200% water	
	0.25% Acetic acid	
	0.5% Tergolix A	- Run for 30’
	Drain	
Rechroming:	100% Water	
	5% Basic chromium sulphate	
	0.5% Cationic fatliquor	- Run for 90’
	+ 0.5% Sodium formate	-Run for 20’
	+ 0.5% Sodium bicarbonate	
	Given in 3 feeds at 10’ interval	- Run for 45’
	Check pH	**pH 4-4.2.**
	Drain wash and pile over night.	
Washing:	200% water	- Run for 15’
	Drain	
Neutralization:	100% water	
	1% Sodium formate	- Run for 20’
	0.5% sodium bicarbonate	
	2 feeds at 15’ intervals	- finally run for 30’
	Check pH with BCG	**pH 5-5.2**

Appendix I continues on following page.

Appendix I continued.

	Drain/Wash/Drain
	Retanning Dyeing & Fatliquoring

Coventional process		**Modified process**	
100% water		100% water	
2% Acrylic syntan	- Run for 20’	2.5% dye	- Run for 30’
+2% synthetic fatliquor	- Run for 15’	Check penetration	
+2% phenolic syntan	- Run for 15’	2% acrylic syntan	- Run for 20’
+2.5% dye	- Run for 30’	+2% synthetic fatliquor	- Run for 15’
Check penetration		+2% phenolic syntan	- Run for 20’
+ 5% synthetic fatliquor		+5% synthetic fatliquor	
2% semi synthetic fatliquor	- Run for 15’	2% semi synthetic fatliquor	-Run for 15’
+0.1% Preservative	-Run for 45’	+0.1% Preservative	- Run for 45’
+4% phenolic syntan		+4% phenolic syntan	
+4% Melamine syntan	-Run for 45’	+4% Melamine syntan	-Run for 45’
Fixing:	2.5% formic acid in 10% water		5 feeds at 5’ interval
	Drain/Wash/Drain		
	Pile overnight		
Next day:	Set, Hook to dry, Set again, stake,		
	Trim, toggle and buff on the flesh side.		