DECOLORIZATION OF CHROMIUM AND DYEING SPOTS ON LEATHER BY BLEACHING AGENTS

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Decolorization was carried out on the leathers with chromium and dyeing spots by different bleaching agents for valorization of defected products. Sodium perborate, sodium percarbonate, hydrogen peroxide, oxalic acid and sodium thiosulfate were used as bleaching agents. Sodium perborate was used by itself and together with other bleaching agents as combined. Color difference on leathers was spectrophotometrically measured by Konica Minolta CM-3600d apparatus. Leathers were re-processed after the bleaching and bleaching process was examined in terms of the strength properties of leather. Sodium perborate provided the best bleach and did not negatively affect the physical properties of leather.

Keywords: leather, defects, bleaching, decolorization, strength.

INTRODUCTION

Chrome stains usually appear as large blue/green spots often in a liquor run mark pattern. Some of the common causes of this type of chrome stains are unneven application of the chrome liquor, patches of uneven pH at the time of tanning and heat damages. Heat degraded collagen will take up more chrome as the breaking of the bonds in the collagen molecule by the heat creates more sites for chrome fixation. Heat damage occurring due to hot liquors or undiluted acids can cause dark run marks to show up after tanning. The most important problem is caused by pooling of chrome liquor. If pools of chrome liquor are allowed to stand on the surface of the skins after unloading from the tanning vessel, the chrome will continue to fix. Wash skins well at the end of tannage and preferably horse up to drain rather than leaving them in skips or tubs for long periods of time. Sometimes chrome stains appear as small spots. This could be due to contamination of the surface with neat chrome powder or contamination with an alkaline powder during tannage causing rapid chrome fixation in the contaminated areas. Occasionally, these intense stains can give rise to the dye resists. Chrome soaps can cause pink stains on wet-blue which can then go on to cause problems in dyeing process. Chrome soaps are caused by the decomposition of natural fats to free fatty acids which react with chrome to give pink stains. Sometimes they can also inhibit the penetration of the tannage and cause raw streaks in the centre of the hide (John, 1996).

Stained appearance in leather products can be also occured because of the defects in dyeing process. Fast fixation, insoluble dyestuffs, inaccurate temperature of the dyeing float and pH adjustment for neutralization can cause the undesirable impurities on leather surface. Thus, homogeneity in color is destroyed. Therefore, bleaching is required for the preparation of fiber based products to remove the colored impurities (Spicka *et al*., 2015; Xu *et al*., 2015).

Oxidative bleaching agents, such as sodium perborate and sodium percarbonate, have been widely used as bleaching components of fabric bleach compositions (Fujiwara *et al*., 1995). Some authors reported that sodium perborate and hydrogen peroxide release oxygen, so their combination should be synergistic and more effective (Valera *et al*., 2009). This study aimed to use different and combined bleaching agents as decolorant for safely reducing of the impurities on wet-blue and dyed leather surfaces.

MATERIALS AND METHODS

Materials

Sheepskins having chromium and dyeing spots on the surface were used as the leather material. Sodium perborate, sodium percarbonate, hydrogen peroxide, oxalic acid and sodium thiosulfate purchased from Sigma-Aldrich were used as bleaching agents.

Methods

Bleaching of Defected Leathers

300% water on the wet leather weight was used at 38^{o}C during 60 min. Sodium perborate and sodium percarbonate with 1% and 3% of solutions were processed by itself at the beginning, and then together with other bleaching agents as combined. All experiments were carried out in triplicate.

Colorimetric Measurements

Konica Minolta spectrophotometer (CM-3600d) was used for measuring the colors of the leather samples which were processed with bleaching agents, and how they bleach and change the leather color was examined compared to the original samples. Spectrophotometric measurements were carried out from five different points on the leather surface and averages were noted. Color differences between the original sample and the leathers processed by bleaching agents were calculated according to CIE Lab-76 color difference formula (CIE, 1976).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

Re-processing of Leathers after Bleaching

Re-processing recipe of wet-blue leathers after decolorizing by bleaching was given in Table 1. It contains neutralization, washing, dyeing, fatliquoring and retanning processes. Dyeing spotted leathers were just re-dyed and washed after bleaching application. Three leather samples were processed without bleaching as control group.

Table 1. Re-processing recipe after bleaching of wet-blue leathers

Process	%	Substance	Temperature (^{o}C)	Time (min)	Remarks
Washing	100	Water	30		
	0.5	Formic acid		45	Drain
Neutralization	100	Water	35		
	1	Sodium formate		10	
	1	Sodium bicarbonate		3x15+45	pH: 5.0-5.2, drain

Process	%	Substance	Temperature (^oC)	Time (min)	Remarks
Washing	300	Water	35	10	Drain
Dyeing-fatliquoring-retanning	100	Water	40		
	5	Dyestuff		60	
	8	Combined natural and synthetic fatliquor		60	
	2	Phenolic syntan		20	
	2	Synthetic tanning agent		20	
	1	Formic acid		3x15+45	Drain
Washing	300	Water	20	10	Drain

Strength Analyses of Final Products

Prior to the analyses all finished leathers were conditioned according to the standard of EN ISO 2419 and sampling was done in accordance with the standard of EN ISO 2418. The final products were subjected to the tests of tensile and tear strength. Shimadzu AG-IS testing device was used for all analyses. Thickness measurement of the samples was performed in accordance with EN ISO 2589, tensile strength with EN ISO 3376 and tear load with EN ISO 3377-2.

Statistical Analyses

The results were evaluated statistically by using One-Way ANOVA, descriptive statistical and Duncan tests at SPSS 15.0 statistical software package. All data were represented as mean for three independent measurements. Comparison of means was analyzed by Duncan test and differences were considered as significant when $p<0.05$.

RESULTS AND DISCUSSIONS

Bleaching of the defected surfaces was firstly applied with 1% and 3% sodium perborate and percarbonate agents. Four runs were carried out on the dyed leathers to optimize the proportions as beginning. Parameters were 300% water, 38^oC and 60 min for all combinations of the process. Table 2 shows the effectiveness of sodium perborate and percarbonate bleaching with two different percentages.

Table 2. Sodium perborate and percarbonate bleaching effects on dyed surfaces

Runs	Parameters	Bleaching agents	ΔE
R1	300% water 38^oC 60 min	1% sodium perborate	2.39±0.41
R2		3% sodium perborate	5.44±0.52
R3		1% sodium percarbonate	1.52±0.33
R4		3% sodium percarbonate	4.00±0.48

Bleaching effect was increased with the increased proportions of both sodium perborate and percarbonate. The most effective bleaching was carried out with 3% of sodium perborate with R2 as seen in Table 2. Color difference of the bleached surface and control sample was 5.44±0.52.

After determining the better effect of sodium perborate than sodium percarbonate, combined bleaching processes were tried with sodium perborate. Table 3 shows the combined bleaching processes with 3% sodium perborate. Combination agents were hydrogen peroxide, oxalic acid and sodium thiosulfate.

Table 3. Combined bleaching processes with sodium perborate agent

Runs	Bleaching agents	ΔE
R5	3% sodium perborate 1% emulsifier 0.5% hydrogen peroxide	1.90±0.37
R6	3% sodium perborate 1% emulsifier 0.5% oxalic acid	2.15±0.40
R7	3% sodium perborate 1% emulsifier 0.5% sodium thiosulfate	1.93±0.36

Oxalic acid combination provided the better bleaching than hydrogen peroxide and sodium thiosulfate with R6. On the other hand, sodium perborate by itself gave the more effect on the surfaces compared to the all combinations. R2 was selected the optimal parameter for the next processes to be carried out on the chromium defected surfaces of wet-blue leathers. Sodium perborate bleaching and its combinations were also applied on the chromium surfaces, and Table 4 shows all the bleaching process combinations on both dyed and wet-blue sheepskins.

Table 4. Color differences on the wet-blue and dyed surfaces

Runs	Wet-blue sheepskins Bleaching agents			ΔE
R8	3% perborate	-	-	18.61±1.97
R9	3% perborate	1% emulsifier	0.5% hydrogen peroxide	10.74±1.02
R10	3% perborate	1% emulsifier	0.5% oxalic acid	11.02±1.11
R11	3% perborate	1% emulsifier	0.5% sodium thiosulfate	10.91±1.07
Runs	**Dyed sheepskins Bleaching agents**			**ΔE**
R2	3% perborate	-	-	5.44±0.52
R5	3% perborate	1% emulsifier	0.5% hydrogen peroxide	1.90±0.37
R6	3% perborate	1% emulsifier	0.5% oxalic acid	2.15±0.40
R7	3% perborate	1% emulsifier	0.5% sodium thiosulfate	1.93±0.36

Table 4 gives a comparative examination for the bleaching process applied on the wet-blue and dyed surfaces. The most effective bleaching was obtained on the wet-blue leathers by only sodium perborate application. Color difference between the bleached surface and the control sample was 18.61±1.97. Oxalic acid combination was better than the other combinations on both chromium and dyed surfaces. Only sodium perborate application was also more advantage in terms of the economical costs compared to the combined processings.

It is possible for bleaching agents to cause the physical deformation of the materials that they were applied. That's why, mechanical durability of the leathers after bleaching was also examined. The best bleaching effect was obtained on the chromium defected surfaces, thus wet-blue bleached and then finished leathers were subjected to the tensile and tear strength tests. Table 5 gives the test results belong to the final products bleached and re-processed.

Table 5. Strength test results of bleached and re-processed leathers

Process	Tensile strength	Tear strength
Without bleaching	10.24 ± 2.16^{a}	36.02 ± 4.25^{a}
Sodium perborate bleaching	9.87 ± 2.24^{a}	34.98 ± 3.96^{a}
Combined 1	9.13 ± 0.98^{b}	28.54 ± 4.01^{b}
Combined 2	9.81 ± 1.99^{a}	31.15 ± 2.97^{b}
Combined 3	9.21 ± 2.02^{b}	28.65 ± 2.84^{b}

a, b; values in the same column with different superscript letters are significantly different ($p<0.05$).

Sodium perborate bleaching didn't affect the both tensile and tear strength of leathers as seen in Table 5. Oxalic acid combination did not also decrease the tensile strength values statistically as from 10.24±2.16 to 9.81±1.99. Hydrogen peroxide and sodium thiosulfate combinations statistically affected the tensile strength values. All the combined applications reduced the tear loads of bleached leathers with important differences. The highest decreases on the strength values were carried out by hydrogen peroxide bleach. Consequently, the best bleaching effect was obtained by sodium perborate without any physical deformation of leather.

CONCLUSION

Defected leathers having impurities on the surface are poor in terms of the aesthetics and resulted with low prices in sales for the companies. Therefore, such surface defects should be prevented before finishing with the effective ways. Chromium and dyeing spotted surfaces on the leathers were successfully eliminated by this work without any lose of strength properties as the quality indicator of leather. Sodium perborate application gained economical value for the leather products by sustaining the physical composition as safe and gentler bleach.

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