



Dyeing levelness on full grain leathers

Yun-Tai Yeh, Shiu-Fu Liang, Chih-Hung Yu

Everlight Chemical Industrial Corp., Taoyuan, Taiwan

The levelness of dyeing of aniline and semi-aniline leathers directly affects their use and value within the manufacture of high value leather goods. However, colour variation caused by natural neck growth marks and draw in the belly parts is frequently found and often unavoidable.

An in-depth study has been made using chemicals commonly found in degreasing, chrome retanning, neutralising, retanning, dyeing and fatliquoring that would impact on issues of levelness.

Dyeing is the most important process that impacts the colour performance of these leathers. It involves high production costs because dyes are the most expensive chemicals used in the leather manufacturing process. Moreover, the colour and overall levelness need to be of the highest standards for high value aniline and semi-aniline leathers.

The differences in fibre structure between belly and back, scratches or defects caused by injuries or disease, and natural wrinkles (growth mark and belly draw) all cause uneven dyeing across a leather. In particular, improved levelness of dyeing in wrinkled areas is an imperative issue.

Dyeing research has tended to focus on the structure or characteristics of dyes and their interaction with collagen fibres. There is, however, little information about the interaction between dyestuffs and the chemicals associated with dyeing, and the effects in terms of colour levelness in areas of drawn grain and growth marks.

The investigation

Careful colour comparisons between growth lines in the neck area and the region around these wrinkles when using different permutations of common chemicals in the complete dyeing sequence was investigated. Wet blue steer hides were used in these investigations of thickness 1.4 - 1.6mm in each batch, being processed in stainless steel drums of experimental size. The standard procedure used is outlined in *Panel 1*.

Panel 1: Standard procedure for investigation

```

    Degreasing
    v
  Chrome retannage
    v
  Neutralising
    v
    Retanning
    v
    Dyeing
    v
  Fatliquoring
    v
  Fixation (Formic acid)
    v
    Drying (Toggle)
  
```

Combinations of four different degreasing agents, four rechroming products, four neutralising chemicals, ten retanning agents, four dye penetrating agents, three dyestuffs, and twelve fatliquors were evaluated. These are listed with the

percentage offer used in both the standard process and chemical substitutions in *Panel 2*.

Panel 2: Chemicals used in the investigation (Chemicals and offer used in the standard formulation) (Substitution chemicals and offer)

Process	Chemical	Offer %
Degreasing	Degreasing agent A	1
	Sodium carbonate	1
	Oxalic acid	2
	Formic acid	1
Rechroming	Cr(OH)SO ₄	4
	Chrome tanning A	4
	Chrome tanning B	1.5
	Chrome tanning C	1.5
Neutralising	Sodium formate	3.5
	Sodium bicarbonate	0.5
	Sodium formate	4
	Sodium bicarbonate	3
	Neutralising agent A	4
	Neutralising agent B	4
Retanning	Mimosa	15
	Chestnut	15
	Quebracho	15
	Polymer tanning A	15
	Polymer tanning B	15
	Replacement tanning A	15
	Replacement tanning B	15
	Replacement tanning C	15
	Dispersing tanning A	15
	Resin tanning A	15
Dyeing	Penetrating agent A	1
	Penetrating agent B	2
	Penetrating agent C	2
	Penetrating agent D	1
	Modified Acid Brown 163	3
	Modified Acid Brown 165	3
	Modified Acid Brown 355	3
	Fatliquor A	6
	Fatliquor B	6
	Fatliquor C	6
	Fatliquor D	6
	Fatliquor E	6
	Fatliquor F	6
	Fatliquor G	6
	Fatliquor H	6
	Fatliquor I	6
	Fatliquor J	6
	Fatliquor K	6
	Fatliquor L	6



In addition to these combinations a blank was used at each of the stages to reduce assessment error that might be caused by natural differences between the different hides.

Assessment of dyeing levelness

Assessments were made on the dry crust leather following the chemical substitutions in the standard process by products listed in *Panel 2* where each chemical was applied individually.

The levelness of each of the crust leathers was visually assessed by five experienced colour experts. A gray scale of 1-5 was used with 5 as the best and 1 as the lowest rating. In addition, the overall levelness of the crust was similarly evaluated.

Degreasing/washing process: The objective of this process is to remove/redistribute surface grease and ensure a fully wetted substrate. Degreasing agent A shows effective colour uniformity between the wrinkles and adjacent areas together with overall colour uniformity. The other agents used show no obvious improvement. The findings are given in *Panel 3*:

Panel 3: The effects of chemicals used in degreasing/washing process on the levelness of dyeing

Chemicals	Blank ^(a)	Wrinkles	Overall levelness
Degreasing agent A	2.5	3.5	3.5
Sodium carbonate	2.0	2.0	1.5
Oxalic acid	2.5	2.0	2.0
Formic acid	2.0	2.0	2.0

(a) Without chemicals in degreasing/washing process.

Chrome retanning process: The purpose of the chrome retanning process is to equalise the surface charge across the whole of the wet blue grain for a more even uptake of anionic chemicals - tannins, dyes and fatliquors - used in subsequent processes. Chrome tanning A produced the best levelness between both the wrinkles and adjacent parts and the overall colour uniformity when compared to the other products. The findings are given in *Panel 4*:

Panel 4: The effects of chemicals used in the rechroming process on the levelness of dyeing

Chemicals	Blank ^(a)	Wrinkles	Overall levelness
Cr(OH)(SO ₄) ₂	3.0	2.5	2.5
Chrome tanning A	1.5	3.0	3.5
Chrome tanning B	3.0	3.0	3.0
Chrome tanning C	1.5	2.0	2.0

(a) Without chemicals in the rechroming process.

Neutralising process: The neutralising process changes the charge of the collagen fibre structure and influences the ability within subsequent processing of chemicals carrying charge to penetrate and combine within the structure. If under a specific pH condition, the collagen fibre has the same charge as a particular chemical then this will readily penetrate the fibre structure. On the other hand, if the charge on the collagen structure is different to the charge of the chemical it can be rapidly fixed to the surface of leather. In these investigations

Neutralising agent A enhances the dyeing levelness to a greater extent than the other products used. The findings are given in *Panel 5*:

Panel 5: The effects of chemicals used in the neutralising process on the levelness of dyeing

Chemicals	Blank ^(a)	Wrinkles	Overall levelness
Neutralising agent A	2.5	3.5	4.0
Neutralising agent B	1.0	2.0	2.0
Sodium bicarbonate	1.0	2.0	2.0
Sodium formate	2.5	2.0	2.0

(a) Without chemicals in the neutralising process.

Retanning process: There are numerous kinds of products used within the retanning process including vegetable tanning extracts, resins, polymers, dispersing and replacement tanning agents. These products influence the characteristics of the final leather, and within these trials the affinity of the dyes and the collagen would be too great without their use. For this reason the samples produced when applying polymer tanning A were taken for the blank sample used for assessment.

Of the three commonly used vegetable tanning agents, chestnut shows the greatest dyeing levelness. However, different manufacturers provide products from different sources, purity, and different manufacturing techniques, so it is difficult to understand the exact factors that impact levelness.

Replacement tanning agents have a similar function to vegetable tanning, and replacement tanning A shows a better improvement to dyeing levelness. Replacement tanning products B and C are amphoteric products and provide less levelness. Both resin tanning A and polymer tanning B provide effective improvement to levelness with both comparisons between growth and adjacent areas and overall levelness. The findings are given in *Panel 6*:

Panel 6: The effects of chemicals used in the retanning process on the levelness of dyeing

Chemicals	Blank ^(a)	Wrinkles	Overall levelness
Mimosa	1.5	2.5	2.0
Chestnut	1.5	3.5	3.5
Quebracho	2.5	3.5	3.0
Dispersing tanning A	2.5	3.5	3.5
Polymer tanning A	3.5	3.0	3.0
Polymer tanning B	3.5	3.5	4.0
Replacement tanning A	2.5	4.0	4.0
Replacement tanning B	3.5	2.5	2.5
Replacement tanning C	3.5	2.0	2.0
Resin tanning A	2.5	4.0	4.5

(a) Using standard formulation (Product Polymer tanning A) during the retanning process.

Levelling/penetrating agents: These products are used to change the surface charge and hence the affinity of the dyestuff with the leather structure. This influences the depth of penetration before fixation and improves the levelness of dyeing. The products used in these investigations show no effective improvement and are given in *Panel 7*:



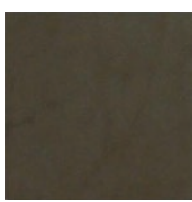
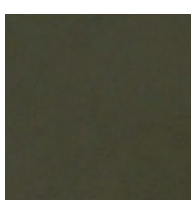
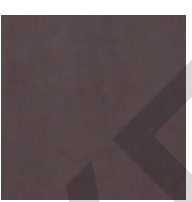
Panel 7: The effects of chemicals used in the dyeing process on the levelness of dyeing

Chemicals	Blank ^(a)	Wrinkles	Overall levelness
Levelling agent A	2.5	2.5	2.5
Levelling agent B	2.5	2.5	3.0
Levelling agent C	4.0	3.5	3.5
Levelling agent D	4.0	3.0	3.5

(a) Without other chemicals except dyestuff.

The dyeing process: Three different dyestuffs in the deep brown colour range were used in the investigation. These were modified Acid Brown 163 (used as the standard dyestuff), modified Acid Brown 165 and modified Acid Brown 355. The colour produced by these three dyestuffs is indicated in *Panel 8* being red/brown, green/brown and purple/brown respectively.

Panel 8: Colour/shade of different dyestuffs* used in the investigation

		
Modified Acid Brown 163 (Dyestuff used as standard)	Modified Acid Brown 165	Modified Acid Brown 355

* All dyeing at 3% offer based on wet blue weight

Every dyestuff has a different chemical structure so the affinity to collagen fibres, the ability to cover the defects and the degree of penetration are never alike. It is noted that although not part of this complex investigation, sometimes a top dyeing is used to increase the colour strength. However, it can sometimes reduce the colour difference between wrinkles and adjacent areas and improve the dyeing levelness.

Panel 9: Effect of the fatliquor selected on the levelness of dyeing (and characteristic of fatliquor)

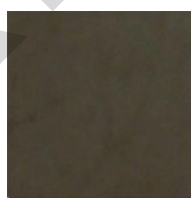
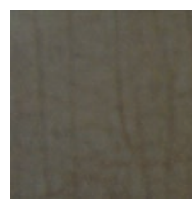
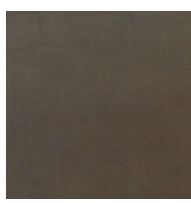
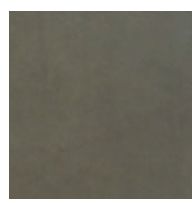
Fatliquor	(Base)	(Charge)	Blank ^(a)	Wrinkles	Overall levelness
A	Lecithin	Anionic/non-ionic	2.0	4.0	4.0
B	Lecithin	Anionic	2.0	1.5	1.5
C	Fish oil/synthetic	Anionic	1.0	2.5	2.5
D	Synthetic	Anionic	1.0	2.0	1.5
E	Copolymer	Anionic	1.0	3.5	3.5
F	Polymeric silicon	Anionic	1.0	2.0	2.0
G	Copolymer	Anionic	1.0	2.0	2.0
H	Fatty amide	Anionic/non-ionic	1.0	4.5	4.5
I	Fatty alcohol	Anionic	2.5	3.0	3.5
J	Phosphated synthetic	Anionic	2.5	2.5	2.5
K	Sulfated synthetic	Anionic	1.5	2.0	2.0
L	Sulfonated neatsfoot	Anionic	1.5	2.0	2.0

(a) Without chemicals in the fatliquoring process.

Fatliquoring process: Fatliquors can be classified according to the source, for example, vegetable, animal, mineral, and synthetic oil. They can also be classified according to charge as anionic, non-ionic, amphoteric and cationic fatliquors, although most are anionic in charge. Normally, fatliquor blends contain different oils to provide different characteristics to the final leathers. The fatliquors used in this investigation together with their base and charge and their effects upon dyeing are given in *Panel 9*.

Fatliquors not only affect the dyeing levelness and change the colour shade and strength of the dyeing, but show the most significant effects among the chemicals used in these investigations. Fatliquors with high affinity to the collagen fibres are rapidly distributed across the surface of leather and enhance the strength of colour, but risk variation to uneven distribution and even grease patches. Different emulsifiers influence the stability of these emulsions, with well emulsified fatliquors forming better dispersed and smaller fatliquor micelles that more readily penetrate the leather fibre structure. The variation in dyeing levelness when using modified Acid Brown 163, being the dyestuff used in the standard formulation, with four different fatliquors is shown in *Panel 10*:

Panel 10: The effect of selected fatliquors (4 of 12 investigated) on the colour/shade of a dyestuff. Dyestuff: Modified Acid Brown 163

	
Fatliquor A	Fatliquor D
	
Fatliquor H	Fatliquor I

Interactions between dyestuffs and fatliquoring agents

Fatliquors are normally applied after the dyeing process, and sometimes in the same bath, so the interactions between dyestuffs and fatliquors on the leather surface are more direct and obvious than other chemicals used in processing.

From this study, examples of colour differences produced by the use of two fatliquors (D and H) with the three dyestuffs are shown in *Panel 11*.

In addition to these examples, the dyeing differences between wrinkles and adjacent areas and overall levelness using four fatliquors (A,D,H,I) with each of the three dyestuffs is given in *Panel 12*.

The effect of these interactions is considerable. For example:

- Modified Acid Brown 163 displays dyeing levelness from grade 1.5 to 4.5 with these four fatliquoring agents, and shows different dye behaviour with the other eight fatliquors.



Panel 11: The effects of interactions between dyestuffs and fatliquors upon dyeing behaviour

Fatliquor D			
Fatliquor H			
	Modified Acid Brown 163	Modified Acid Brown 165	Modified Acid Brown 355

Panel 12: Interactions between dyestuffs and fatliquoring agents and their effects upon dyeing levelness

Fatliquor	Modified Acid Brown	Wrinkles	Overall levelness
A	163	4.0	4.0
	165	2.5	2.5
	355	4.0	4.0
D	163	2.0	1.5
	165	4.0	4.0
	355	3.0	3.5
H	163	4.5	4.5
	165	3.0	3.0
	355	4.5	4.5
I	163	3.0	3.5
	165	3.5	3.5
	355	2.5	2.5

- Fatliquoring agent D produces significant differences in dyeing levelness when used with Modified Acid Brown 163, 165 and 355, ranging from 1.5 to 4.0.

Modified Acid Brown 163 and 355 used in combination with fatliquor A and H, and modified Acid Brown 165 used in

combination with fatliquor D, show good dyeing quality; the wrinkles and overall dyeing levelness grade can reach grade 4 to 4.5. Fatliquors A and H, that work well with modified Acid Brown 163 and 355, are classified as anionic/non-ionic, whereas modified Acid Brown 165 is suitable for use with fatliquor D classified as an anionic type of fatliquor.

The type and portion of emulsifier in the fatliquoring agent would also affect the dyeing result, and influence the absorption of other chemicals. However, commercial dyestuffs and fatliquoring agents are complex mixtures and there still remain many difficulties in understanding the exact factors that impact dyeing levelness.

Summary of the investigations

The factors that affect levelness in leather dyeing are not an exact science, but there is a need to improve colour uniformity. In this investigation it was shown that each chemical used in the dyeing sequence affected the overall dyeing result and levelness between wrinkles and adjacent areas.

When the leather was degreased/wet back correctly, the levelness varied with different retanning products, especially vegetable tanning agents. However, among the chemicals investigated dyestuffs and fatliquoring agents play the most important role regarding colour uniformity. Although the precise mechanisms that impact the levelness of dyeing remain unknown, significant improvements can be made by choosing suitable combinations of dyestuff and fatliquoring agent. ☺

Acknowledgments:

- Research financed by Everlight Chemical Ind. Co.
- Tehchang Leather Products Co. for use of drying equipment.

References:

- Ayyasamy, T., Thanikaivelan, P., Rao, J. R. et al., *J. Soc. Leather Technol. Chem.*, 2004, 89, 71.
- Basaran, B., Isik, N. O., *J. Soc. Leather Technol. Chem.*, 2006, 91, 4.
- Covington, A. D., *J. Soc. Leather Technol. Chem.*, 2011, 95, 231.
- Eitel, K., Goebel, H., *Bayer Farben Revue*, 1977, S17, 10.
- Jawahar, M., Venba, R., Jyothi, G. et al., *J. Amer. Leather Chem. Ass.*, 2004, 99, 233.
- Kim, W. J., Heo, J. S., Shin, S. B. et al., *J. Soc. Leather Technol. Chem.*, 2002, 87, 25.
- Zhou, J., He, Q., Liao, X. P. et al., *J. Soc. Leather Technol. Chem.*, 2011, 95, 204.



HIDE PROCESSORS AND EXPORTERS

SYDNEY • MELBOURNE • TASMANIA

Southern Australia's best

Tel +612 9261 4665
Fax +612 9261 0678
Email isb@southernhide.com.au

Wet Blue hides & splits
Salted raw hides
Salted calfskins
www.southernhide.com.au

SOUTHERN HIDE EXPORTS Pty Ltd