Influence of syntan retanning on leather dyeing

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Abstract

The main purpose of syntan retanning is to provide stuffing and compactness to the emptiest parts of the hide. Also, this technique has a major influence on dye penetration, intensity and leveling.
In this study, eleven different syntan types were used. The penetration power of two types of dye –a brown-colored type of medium molecular weight, and a black-colored type of high molecular weight– was assessed in terms of anionicity. Depending on the constitutions of the dye and the syntan, there is a synergy that determines the penetration power of each dye.
Moreover, color intensity (L*) of these dyes was assessed colorimetrically on the grain side, and their distribution (leveling) was measured by (total color) ΔE scattering (vs. the untanned reference.
All syntan retanning products used were shown to improve the penetration and leveling power of dyes vs. the untanned reference.

Keywords: Retanning, syntans, penetration, leveling, dye.

1. Introduction

The chemical structures of all syntans share sulfonic groups. These groups act as solubilizing agents in the sulfonic and phenolic acid derivatives, or as part of the binding between contiguous benzene groups in the so-called sulfones (see Structures). The visualization of these groups in the hide, on both the inner and outer surfaces, provides valuable information of syntan penetration and distribution in the hide. In this study, dye penetration and dye distribution in the grain side will be assessed.

2- Experimental part

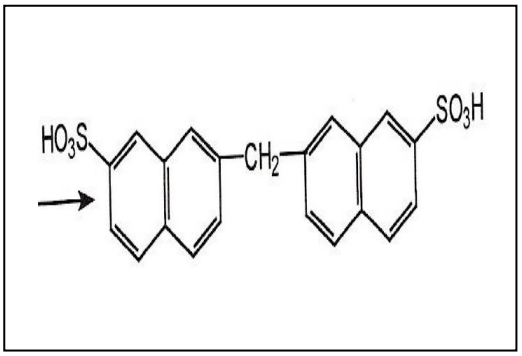
2.1. Products used

2.1.1 Syntans

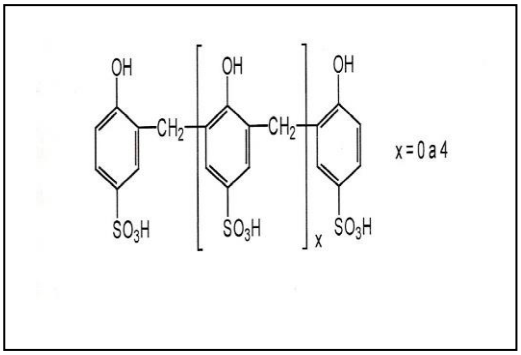
SYNTAN	NATURE	ACIDITY (mg KOH)	DEGREE OF CONDENSATION
1	Phenolsulfonic	5-10	HIGH
2	Phenolic	9-15	HIGH
3	Naphthalenesulfonic (90-10)	25-30	MEDIUM
4	Phenolic	35-40	LOW
5	Phenol-Protein	1-5	HIGH
6	Phenolsulfonic	60*65	MEDIUM
7	Naphthalenesulfonic (70-30)	85-90	MEDIUM
8	Phenolic	80-85	HIGH
9	Phenol-Polymer	65-70	MEDIUM
10	Diphenylsulfonic	13*15	MEDIUM
11	Naphthalenesulfonic	1-5	LOW

Table 1- Three chemically differentiated groups can be distinguished within the complexity of each syntan applied.

a) Sulfonic acid salts:



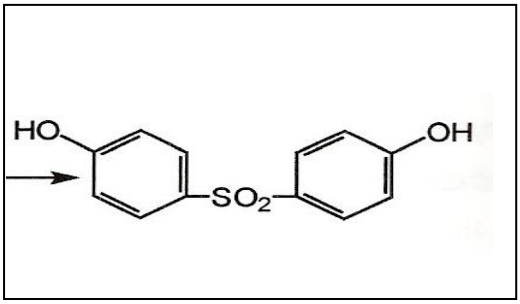
Naphthalenesulfone structure (Syntan 11)



Phenolsulfone structure (Syntan 6)

Their strong anionicity results from the binding of each aromatic ring of condensate to a sulfonic group.

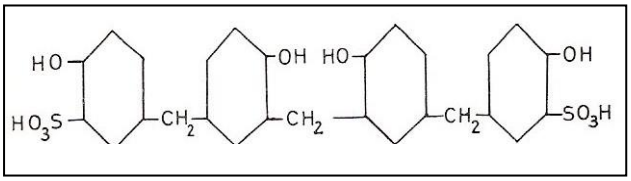
b) Diphenylsulfone Derivatives



Diphenylsulfone Structure (Syntan 10)

Low anionicity and good tanning power.

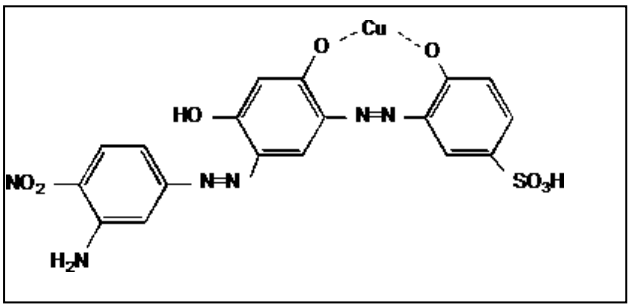
c) *Phenol Derivatives*



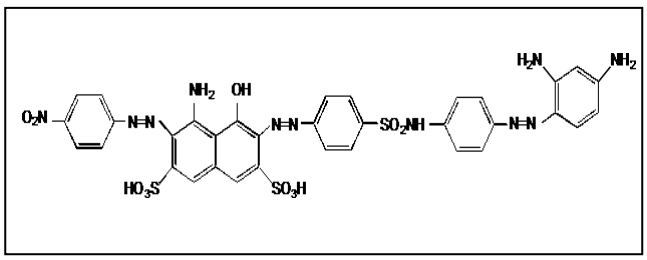
General Phenol Structure

Medium anionicity and variable tanning power –depending on the degree of condensation.

2.1.2. DYES



Acid Brown 83 (C18 H11 Cu N6 O8 S Na), Cu-metalized diazo acid type and molecular weight 557.5.



Acid Black 210 (C34 H27 N11 O11 S3), triazo acid type and molecular weight 861.

2.2. LEATHER SUBSTRATE

Chrome-tanned cowhide shaved at 2 mm was rounded and split in 15 x 15 cm pieces.
Three pieces were used in each test –one for anionicity, one for Acid Brown 83, and one for Acid Black 210.

2.3 PROCESS USED

Dose on wet blue weight shaved at 2 mm

WASHING	
200% water at 30º C	
0.2% oxalic acid	
0.2% non-ionic tensioactive	Run for 30 min. Run off and wash for 10 min.
RETANNING	
100% water at 35º C	
2% sodium formate	Run for 30 min. pH=4.4
5 % SYNTAN (active matter)	Run for 60 min
X% sodium bicarbonate	Run for 60 min. Adjust pH=5.5. (uniform throughout the cut)
	Run off and wash for 10 min.
(DRY ONE PIECE TO ASSESS METHYLENE BLUE ANIONIZATION)	
DYE-FATLIQUORING	
60% water at 30ºC	
3% Acid Brown 83 (ONE PIECE)	Run for 30 min
3% Acid Black 210 (ONE PIECE)	Run for 30 min
50% water at 60ºC	
10% synthetic fatliquor	Run for 60 min
1% formic acid	Run for 60 min
Run off and wash for 10 min	
MECHANICAL OPERATIONS	
Rest for 24 hours	
-Dry toggling with air at 45º C.-Condition and stake.	

Process 1

2.3.1. Anionicity

One of the pieces is removed before dyeing and fatliquoring, and dyed with a 2g/L solution of methylene blue (cationic dye). Syntan penetration (Figure 1) and surface distribution (Figure 2) are assessed.

The method is as follows:

REAGENT PREPARATION:
2 g of methylene blue are weighed, covered with 50 ml of water at 20º C, added with 100 ml of isopropylic alcohol, stirred, and finally made up to 1 liter with water at 20ºC.

HIDE DYEING
One 4 x 1 cm sample is cut out.
The sample is immersed in a beaker containing a methylene blue solution that covers the piece. The solution is stirred with a stirring rod for 2-3 minutes and washed with water until clean. The sample is removed and both penetration and surface distribution are assessed.

As shown in Figure 1, the untanned reference is slightly blue on account of dye traces, while retanned pieces have an intense blue area on both grain and flesh sides, with varying penetration. Higher penetrations on the flesh side as compared to the grain side are usually observed, due to the more open fibrous structure of flesh side.

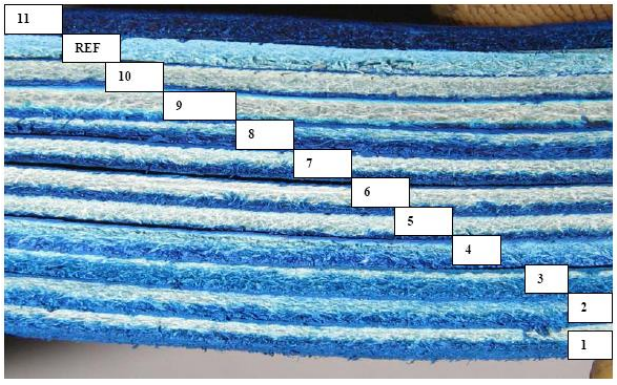


Figure 1. Syntan penetration (methylene blue dye)

Individual photographs of each syntan have been used to assess penetration by microscopic observation and by measurement of the colored part on both flesh and grain sides. Values, total penetration (sum of the two) and color intensity (L*) are shown in Table 2.

SYNTAN #	GRAIN SIDE (%)	FLESH SIDE (%)	TOTAL PENETRATION (%)	COLOR INTENSITY (L*)
1	11	30	41	34.5
2	18	30	48	38.1
3	16	75	91	37.4
4	16	70	86	35.7
5	10	20	30	31.5
6	11	33	44	28.0
7	15	35	50	27.9
8	20	40	60	32.2
9	8	16	24	37.0
10	5	15	20	30.1
REF				53.9
11	15	85	100	29.9

Table 2. Syntan influence on the degree of penetration (%) and intensity (L*) of the anionic part.

Color intensity (L*) in terms of surface distribution on the grain side is shown in Figure 2. Syntan 11 stands out for strong anionicity and total penetration, followed by syntans 3 and 4 –with good penetration but lower anionicity (intensity of blue).

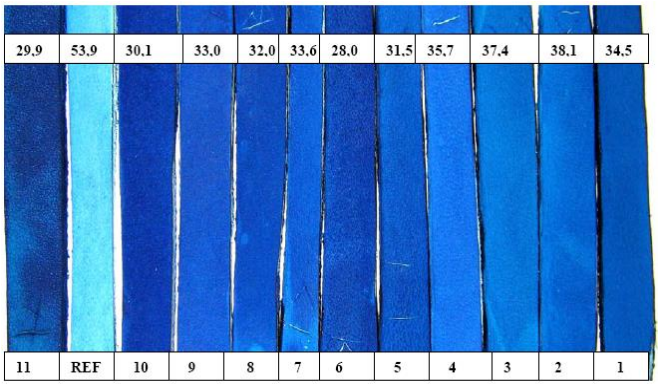


Figure 2. Syntan distribution on the grain side (methylene blue)

2.3.2. Dyes

The interaction between chemical structures, as well as the molecular weight of syntans and dyes, will define dye behavior in terms of penetration and surface distribution on the grain side.
Acid Brown 83
According to process 1, one of the pieces was dyed with Acid Brown 83, and penetration (Figure 3) and distribution (Figure 4) were assessed as with methylene blue
The **penetration** values on the grain side and the flesh side, as well as total penetration (sum of both), are shown in Table 3. The percentage of penetration has been quantified bearing in mind that some syntans penetrate the different hide areas irregularly –even in the same test tube cut for control. Penetration also depends on the structure of the hide and on the syntan's

ability to retain the dye on the surface or "filter" it). A medium value was selected for syntans 7, 10 and 5.
A "penetration factor" –i.e. the ratio between dye penetration and anionic penetration– was established. Low values suggest equal penetration of both (total penetration with syntans 11, 3 and 4, and partial penetration with syntans 8 and 1). High values suggest a much higher dye penetration than that expected from anionic penetration (syntans 9, 10 and 5).

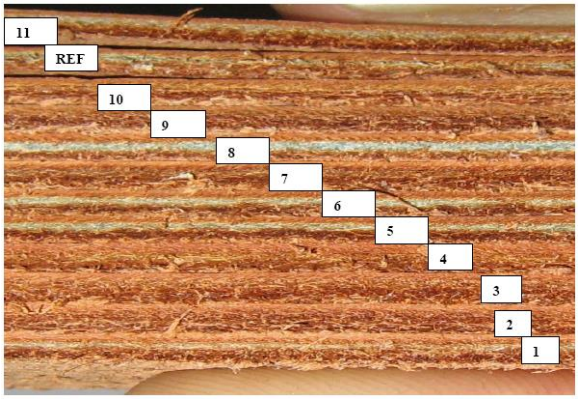


Figure 3. Dye penetration (Acid Brown 83)

SYNTAN #	GRAIN SIDE (%)	FLESH SIDE (%)	TOTAL PENETRATION (%)	PENETRATION FACTOR	COLOR INTENSITY (L*)
1	21	60	81	1.97	57.24
2	30	70	100	2.08	55.30
3	30	70	100	1.09	53.70
4	30	60	90	1.04	49.73
5	25	42	67	2.20	49.92
6	25	40	65	1.40	54.54
7	27	50	77	1.54	60.13
8	20	40	60	1.00	53.41
9	30	70	100	4.16	54.83
10	30	60	90	4.50	57.26
REF	23	40	63		41.13
11	15	85	100	1.00	48.56

Table 3. Syntan influence on the degree of penetration (%) and intensity (L) (Acid Brown 83).*

The penetration of all syntans is equal to or higher than that expected according to their anionic penetration; the penetration of the (untanned) reference is 63%.
Regarding dye surface distribution on the grain side, the highest color intensity (lower value of L*=41.13) is found in the reference (Figure 4). The highest and lowest color intensities of syntans are found in syntans 11 (L*=48.56) and 7 (L*=60.13), respectively. The rest of syntans have similar intensities, with tonalities changing from red to yellow.

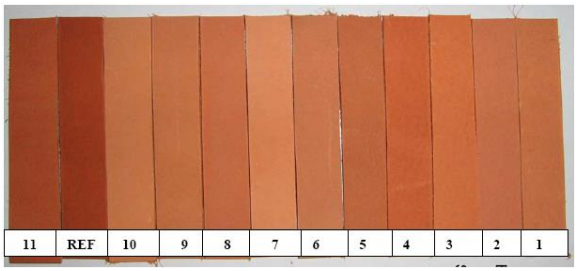
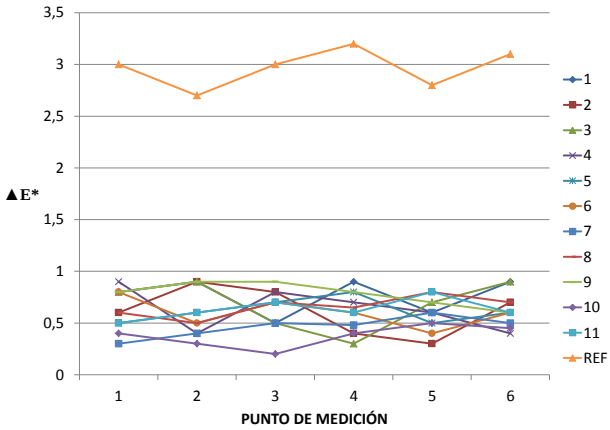


Figure 4. Distribution of Acid Brown 83 on the grain side



Dye levelness was assessed by measuring total color E* at the center of the hide piece and at 6 other sites. The lower the values of ▲E*, the better the levelness.
Legend: Punto de medición = Measuring point
Figure 5. Color levelness of Acid Brown 83

All syntans improve color levelness as compared to the reference. The highest levelness is provided by syntans 7 and 10 (hydroxyphenylsulfone derivatives), followed by syntan 8 (phenol of high molecular weight)
Acid Black 210
According to Process 1, one of the pieces was dyed with Acid Black 210. As with Acid Brown 83, penetration (Figure 6) and distribution (Figure 7), as well as color intensity (L*) on the grain side, were assessed.

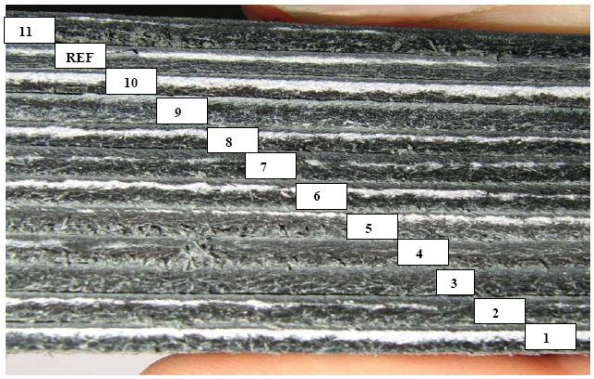


Figure 6. Dye penetration (Acid Black 210)

Syntan penetration is much higher on the flesh side. The highest penetration factor corresponds to syntan 9 (4.1), followed by syntans 5 (2.60) and 10 (2.25). The lowest penetration factors are found in syntans 11 (1.0), 3 (1.09) and 4 (1.04).

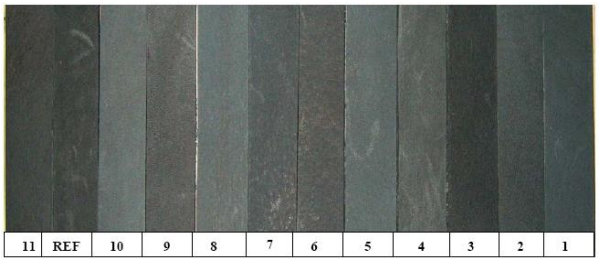


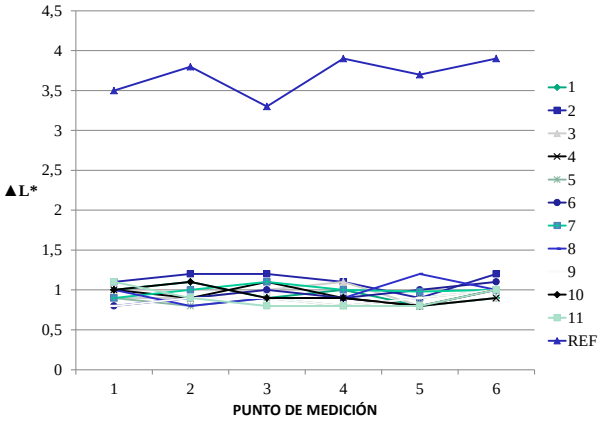
Figure 7. Syntan influence on dye distribution (Acid Black 210)

SINTÁN	LADO FLOR (%)	LADO CARNE (%)	PENETRACIÓN Total (%)	FACTOR DE PENETRACIÓN	COLOR (L*)
1	5	60	65	1,58	36,07
2	10	80	90	1,87	34,53
3	30	70	100	1,09	28,54
4	30	60	90	1,04	34,39
5	8	72	80	2,60	35,08
6	10	50	60	1,36	30,50
7	20	80	90	1,80	30,49
8	15	60	75	1,25	34,78
9	20	80	100	4,1	32,22
10	5	40	45	2,25	35,07
REF	10	50	60		28,14
11	30	68	98	1,0	28,32

Table 3. Syntan influence on degree of penetration (%) and intensity (Acid Black 210)

The highest intensity is found in the reference (L*= 28.14), followed by syntan 11 (L*= 28.32).

Because black variations are colorimetrically more significant than total color variations (E*) –with total color including the chromatic axis variables– the variation of L* (brightness; black-white axis) was measured to assess **dye levelness**.



Legend: Punto de medición = Measuring point

Figure 8. Color levelness with Acid Black 210

Because reference (syntan-free) ▲L* is higher than the value obtained in retanned hides, syntan retanning improves color levelness.

2.3.3. Summary of dyeing properties

a) Penetration

1- While similar penetration factors are obtained with both dyes, there is a major difference between the two: Acid Brown 83 provides better "diffusion" –even without total penetration it always dyes weakly the center of the hide. With Acid Black 210, a white color is found where penetration ends (please compare Figures 3 and 6).

2- Low penetration factors correspond to naphthalene or phenolsulfone structures (11, 3 and 4; see Figure 9), where methylene blue penetrations match those of both dyes (100% penetration in all).

Figure 9. Relationship between anionicity and dye penetration (Syntan 11)

3- High penetration factors (retanning syntan 9) provide dye penetration much higher than expected on account of the penetration of its anionic part, and corresponds to the phenol-polymer syntan (Figure 10).

Figure 10. Relationship between anionicity and dye penetration (Syntan 9)

With both dyes, the hide cutout shows a clearer color on both grain and flesh sides (corresponding to the anionic part of the syntan) and a more intense color in the center (corresponding to the non-anionized part, accessed by the dye through the interfibrillary network.

4 –There are syntans where a low penetration factor (syntan 8) involves medium penetration in methylene blue and in both dyes.

Figure 11. Relationship between anionicity and dye penetration (Syntan 8)

5 –The levelness of dye penetration is influenced by both the structure of the hide and the compactness of the different fibers in the different areas of the hide. Accordingly, one same syntan may physically stuff larger spaces and facilitate dye penetration in this area. On the other hand, the larger molecular size of Acid Black 210 as compared to Acid Brown 83 makes penetration more difficult under the same syntan and physical structure conditions, so that other syntans such as 6 and 4 have to be added to syntans 10, 7 and 5 –which show irregular penetration with Acid Brown 83– when using Acid Black 210 (Figure 10).

Figure 12. Irregular penetration of Syntan 7

b) Intensity

1- **Syntan 11** shows the highest surface anionicity (L*= 29.9) and the highest surface dye intensity with both dyes, second only to the reference (L*= 48.56 and L*=28.32 for Acid Brown 83 and Acid Black 210, respectively).

2- **Syntan 10** shows strong surface anionicity (L*= 30.1) and very low color intensity with both dyes (L*= 57.26 and L*=35.07 for Acid Brown 83 and Acid Black 210, respectively).

3- In the rest of syntans, an intermediate behavior is found in the ratio between anionicity and color intensity.

c) Levelness

All syntans improve levelness of both dyes as compared to the syntan-free hide.

3- CONCLUSIONS

3.1. If (methylene blue-controlled) total penetration of the anionic part is observed, total dye penetration can be guaranteed.

3.2. On the other hand, non-total anionic penetration and total dye penetration may be observed. This will depend on the molecular weight of the dye and on the structure of the hide.

3.3. The structures of syntan 11 (naphthalenesulfonic acid salt) allow total dye penetration and also maximum color intensity.

3.4. Dye **optimization** will be obtained by selecting syntans that provide good penetration (11), maximum intensity (11) and good levelness (7, 8 and 10).

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NOTE

The products used correspond to the following range of Cromogenia Units S.A.:

Syntan 8 = RETANAL BW

Syntan 10 = RETANAL SUL

Syntan 11 = RETANAL A-4