

Influence of naphthalenesulfonic acid derivatives on the dyeing properties of the leather. Part II

Olga Ballús¹, Toñy Catalan², Ramón Palop¹, Ricardo Micó¹

¹Laboratorio de Curtidos. Cromogenia Units S.A, Phone: (+34) 932643462, e-mail:

oballus@cromogenia.com

²Laboratorio de Curtidos. Quimipiel S.L, Phone: (+34) 934329402, e-mail: tcatalan@quimipiel.com

Abstract.

The first part of this paper studied the influence of the composition of different types of naphthalenesulfonic acid derivatives, used in the neutralization phase, on certain characteristics of the leather when two dyes (Acid Black 210 and Acid Brown 83) were used separately.

This second part assessed the influence of these products on the same leather characteristics when equal parts of the same dyes were used together and an amphoteric dyeing auxiliary was added.

The results confirm that the greater the molecular weight of the naphthalenesulfonic derivative, the better the penetration of the dye mixture, and that this mixture behaves uniformly in terms of penetration and levelness. The addition of an amphoteric dyeing auxiliary led to outcome maximization.

Keywords: auxiliary, amphoteric, naphthalenesulfonic, neutralization, dyeing

1. Introduction

After tanning the hide has an (approximately 4) acid pH and also a strong positive charge on account of chromium complex cationicity (Morera 2003; Soler 2000). During the neutralization process and by means of alkaline neutralizing agents, hide pH is increased to values close to 5-5.5. This operation, however, is insufficient by itself to facilitate the penetration and distribution of retanning agents, fatliquoring agents, and

dyes (Heidemann 1993; Portabella 1962).

A change of charge in the hide, both on the surface and inside, is thus required through the addition of anionic auxiliary products, such as naphthalenesulfonic acid salts, to allow good penetration and distribution of further added products and consequently good physical and organoleptic properties (Palop et al. 2008; Ballús et al. 2014).

Anionic auxiliaries are naphthalenesulfonic acid derivatives with a relatively small molecular weight. On the one hand, they decrease the isoelectric point and thus facilitate the penetration of further added products; on the other hand, they may act as dyeing auxiliaries. When applied as dyeing auxiliaries they compete with the dye for fixation to the chrome tanned leather by decreasing substrate-dye interaction, and provide better levelness and usually decreased dyeing intensity (Covington 2009).

Non-ionic auxiliaries are also used to achieve good dyeing penetration. Because acid dyes are highly reactive in chrome tanned leathers, their penetration and levelness can be improved by adding this type of auxiliaries. Non-ionic auxiliaries form complexes with the dye, block its reactive points and decrease its reactivity. These compounds contain high quantities of oxygen atoms as well as a nitrogen group that provides them with weak cationicity. Occasionally, they may also increase dyeing intensity (Portabella 1962; Covington 2009). The penetrating power of a dye depends on molecular weight, particle size, sulfonation, and solubility. Given the wide range of currently available dyes, its choice in this study was mainly based on its molecular weight. Two acid dyes with different molecular weights were selected. The dye

with a higher molecular weight is expected to penetrate less than the dye with a lower molecular weight. This will allow assessing the influence provided by each auxiliary used.

In this study, the physical and chemical properties (molecular weight, number of sulfonic groups, and chain length) of several naphthalenesulfonic acid salts were related to the properties they provide to the leather, measured by anionicity penetration and dyeing properties (penetration, levelness and intensity) when a mixture of two acid dyes was added. The influence of an amphoteric auxiliary on dyeing properties was also assessed by measuring the above described parameters using a non-ionic amine.

Therefore, characterizing naphthalenesulfonic acids is essential. Reversed-phase high-performance liquid chromatography (RP-HPLC) allows to qualitatively determine the degree of condensation of each product, and gel permeation chromatography (GPC) allows determining the relative molecular weights of each product.

3. Material and methods

Naphthalenesulfonics characterization

Six different products derived from naphthalenesulfonic acid were selected. RP-HPLC was first used for qualitative determination. Jasco HPLC model PU-2089J equipment was used, with a 5 μ m 25x0.46 Tracer Extrasil ODS2 column. A Jasco UV-2075 plus detector at a wavelength of 285nm was used. Pressure and mobile phase flow were set at 110-130Mpa and 1ml/min, respectively. A mixture of two solvents was used as the eluent solution: 0.01M of 99% TBAB in water and 1% in glacial acetic acid

as solvent A; and 0.01M TBAB in 99% acetonitrile as solvent B. These solvents were used in different percentages in an elution program. At first 120 minutes a mixture of 80% of solvent A and 20% of solvent B were used, followed by 100% of solvent B during 40 minutes. Finally applied a mixture of 80% of solvent A and 20% of solvent B for 10 minutes.

Quantitative determination was performed by GPC with the same equipment, with a Shodex KS 803 column and a Jasco UV-

2075 plus detector at a wavelength of 227nm, flow rate 0.8 ml/min, temperature 30°C, using a Jasco CO-2065 plus oven. The eluent solution was prepared with acetonitrile and a Na₂SO₄ 0,05M (80/20) solution. A polystyrene sulfonate standard was used for the calibration curve.

Raw material

Wet blue Spanish cattle hide shaved at 2.2 mm was used for this study. The but was cut in pieces of 10 x 15 cm. Hides were treated in a 300 mm-diameter, 150-mm wide laboratory drum, model Simplex-4 (Inoxvic), set at a rotation rate of 24 rpm. The test was performed in triplicate.

pH control and anionization

Bromocresol green indicators and universal indicator were used to control leather pH, and a cationic dye methylene blue solution was used to determine the degree of anionization. Bath pH was determined with a GLP 21 pH meter.

Products used

Two variables were used in this test: variable 1 for tests performed without amphoteric auxiliary, and variable 2 for tests performed with amphoteric auxiliary during the dyeing process. In variable 1, naphthalenesulfonic-free tests were used as a reference. In variable 2, an amine ethoxylated at 35% of active matter was used as amphoteric auxiliary (amine E), with amine-free tests used as a reference.

Dyes

Dyes Acid Brown 83 and Acid Black 210 were selected (see characteristics in Table I). The formula is shown in Table II (with % based on wet blue weight). Except for the dyes, the products were weighed in a 0.01 g precision laboratory scale. The products used in this process were commercially available products.

Evaluation of dyeing properties

In order to assess the dyeing properties of the different products used, dyeing intensity and levelness were measured with a Color Data Spectraflash SF-30 colorimeter. The same colorimeter was used to measure

color levelness (ΔE^* values: variation in total color) on ten points of the grain surface versus a reference point located in the center of the sample.

In order to control bath exhaustion, filter paper strips were impregnated with the different residual baths and allowed to dry.

Colorimetric measurement of L^* values was then performed.

$L^*=100$ value indicates maximum luminosity, more white. $L^*=0$ indicates minimum luminosity, more dark or more fixed dyestuff.

Table I
Characteristics of the dyes and the amine used

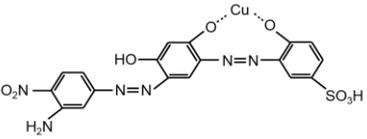
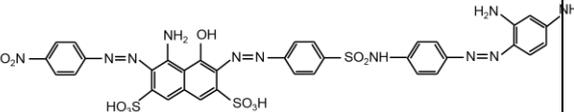
Name	Description	Structure	MW
Acid Brown 83	Cu-metallized diazo acid		557.5
Acid black 210	Triazo acid		861

Table II.
Procedure for the application of dyeing auxiliaries

PROCESS	OPERATION	OBSERVATION
Washing	200% Water at 35°C, 0.2% Acetic acid, run 10 min. 0.2% Non-ionic surfactant, run 10 min, pH =3.2. Drain bath and wash 20 min.	
Neutralization Anionization	150% Water at 35°C, 2% formate, run 30 min 0.2% Sodium bicarbonate, run 60 min, pH=4.4 5% Naphthalenesulfonic , run 120 min, pH= 4.5-5.2. Drain bath and wash 10 min.	Control of pH and degree of anionization in the leather.
Dyeing Fatliquoring	100% Water at 45°C - 2% amine E , run 20 min 1.5% Acid Brown 83, 1.5% Acid Black 210 , run 60 5% Sulfated neatsfoot oil 5% Sulfochlorinated fatty oil, run 60 min 1% Formic acid, run 60 min, pH= 3.8-4 Drain and wash 10 min.	Control of penetration and bath exhaustion.

3. Results and Discussion

Naphthalenesulfonic derivatives characterization

As previously mentioned, the purpose of this study was to assess the influence of each naphthalenesulfonic on penetration, levelness and intensity at the end of the

dyeing process. The use of two chromatographic techniques allowed classifying naphthalenesulfonics according to their chain length and relative molecular weight.

RP-HPLC allows determining the degree of condensation of the polymers and qualitatively relating this degree to the chain length (n). This being a qualitative

assessment, *n* values are mean and approximate values, and naphthalenesulfonics are classified according to their chromatographic profiles as long chain (*n*=12), medium chain (*n*=6) or short chain (*n*=2) products. Three chromatographic profiles according to time (minutes) and degree of condensation of the polymer are shown in Figure 1. Figures 1A and 1C correspond to the chromatographic profile obtained for the longest chain (NS1) and the shortest chain (NS6) product, respectively. Figure 1B shows the chromatogram of the medium chain products, that is, the remaining naphthalenesulfonics (NS2-NS5). These chromatographic profiles are similar during the first 50 minutes, where the first peak is obtained with the free monomer at a retention time of 20 minutes, followed by the dimer at 40 minutes, etc. These profiles start to differ as of 60 minutes, where the more condensed the polymer, the longer the chain. This is how naphthalenesulfonics are first classified (see Table III).

GPC allows studying the molecular weights of the polymers and the distribution thereof. Quantification is performed from calibration curves using polystyrene sulfonate as standard. Relative molecular weights calculated from time-related polymer concentrations are shown in Table III. These results are consistent with those obtained by RP-HPLC, where the longest chain product (NS1) has the highest molecular weight, the shortest chain product (NS6) has the lowest molecular weight, and the molecular weights of the remaining medium chain products lie between those two.

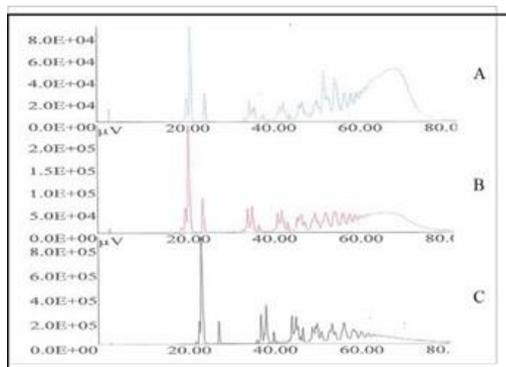


Figure 1. Chromatograms of three naphthalenesulfonics obtained by RP-HPLC. Three degrees of condensation: **A** long chain, **B** medium chain and **C** short chain.

Table III.

Naphthalenesulfonics characterization by RP-HPLC and GPC

Product	<i>n</i>	Relative molecular weight (Da)
NS1	Long	3.000
NS2	Medium	1.200
NS3	Medium	1.400
NS4	Medium	1.200
NS5	Medium	1.300
NS6	Short	600

Assessment of dyeing properties

In order to assess the dyeing properties of the studied products, two control points were marked in the process (Table II). Hide pH and anionization were controlled at the end of the process (after naphthalenesulfonic addition) and the values obtained were compared to the (naphthalenesulfonic- free) standard process. At the end of the dyeing/fatliquoring process (after amine addition), color intensity and degree of penetration of the dye mixture were assessed versus the amine-free reference process.

a) pH and anionization control

At the first control, leather pH was checked with two indicators (bromocresol green and universal indicator) and the degree of anionization and intensity was checked with methylene blue. Leather pH control showed pH values of 4.5-5 with the products and somewhat higher values (5.5-6) with the reference (see Figure 2(a)).

b) Anionization

Penetration control with methylene blue is shown in Figure 2(b). Methylene blue allows observing the degree of penetration of these products. This occurs thanks to the anionic element contained in naphthalenesulfonic acids — the SO₃ reactive group —. This group reacts with

the methylene blue cationic dye to yield a deep blue color. As shown in Table IV, product NS1 has the highest penetration (100%), followed by product NS3 (85%). The product-free reference has a null degree of anionization (0%). Therefore, the higher the molecular weight, the better the penetration of the product. Surface distribution on the grain side when using methylene blue is shown in Figure 2(c), and color intensity (L^*) is shown in Table IV. The lowest L^* value is obtained with NS1 (23.5, highest molecular weight) and the highest L^* value (64.8) is obtained with the product-free reference. The values obtained show that intensity and molecular weight are closely related, that is, the higher the molecular weight, the higher the anionicity.

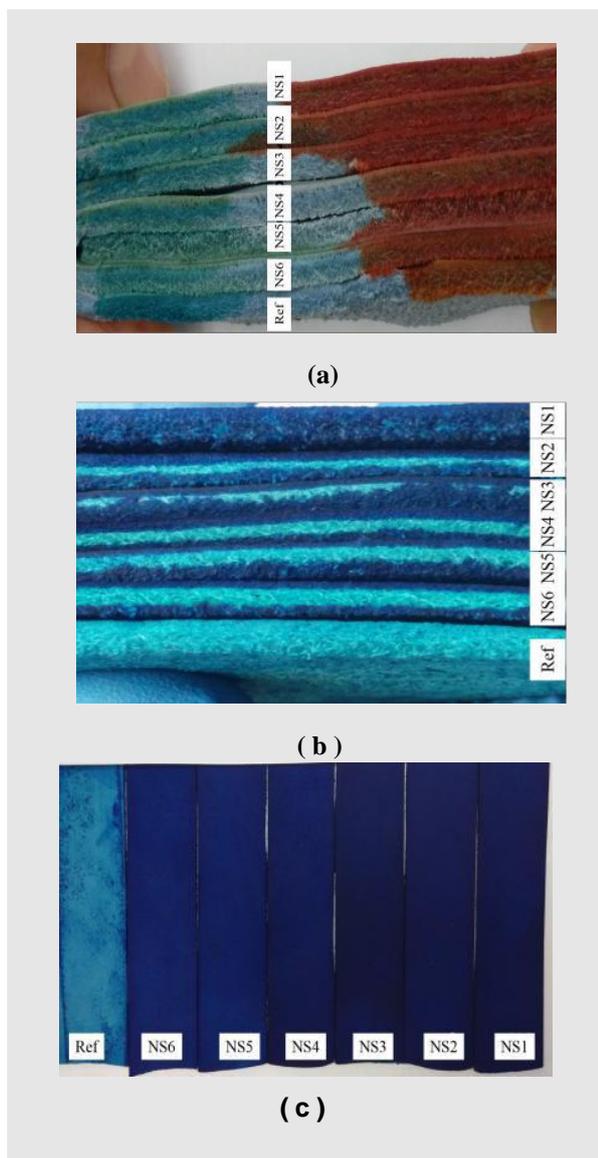


Figure 2. Leather cross sections after naphthalenesulfonic application. (a) Leather pH control with bromocresol green (left) and universal indicator (right). (b) Control of the degree of anionization of the naphthalenesulfonic with methylene blue. (c) Surface distribution on the grain side with methylene blue.

c) Penetration and dyeing intensity control

The second control with the two studied variables was performed upon the completion of the dyeing/fatliquoring process. This included penetration, intensity and levelness control without/with amine E in the substrate, and bath exhaustion control.

Dye penetration without and with amine E after cutting the hide strip is shown in Figure 3(a). The dye mixture shows color levelness in the penetration of both dyes (Acid Brown 83 and Acid Black 210).

The (higher relative molecular weight) NS1 product has the highest penetration in the two variables. The (naphthalenesulfonic-free) reference has the lowest penetration. Dye penetration is notably —and uniformly— increased by amine E. The comparison of product penetrations showed that the lower the molecular weight, the higher the influence of amine E. Dye penetration was proportional to anionicity penetration. Contrary to what was expected, the higher the molecular weight and the size of the chain, the better the penetration, both of the anionic part of the naphthalenesulfonic and of the dyes.

The naphthalenesulphonic derivative reduces the cationicity of the leather surface, thus making the product penetrate more easily. The higher the molecular weight, the higher amount of SO₃ groups and cationicity of the leather is reduced to a greater extent. Figure 3(b) shows a schematic representation of this explanation.

Table IV

Control of the penetration and surface distribution of naphthalenesulfonics, and of dye penetration without / with amine E

Products	Control after adding naphthalenesulfonics		Control after adding dyes		
	Degree of anionization (%)	Surface distribution on grain side (L*)	Without amine E (%)	With amine E (%)	% Variation
NS1	100	23.5	100	100	0
NS2	70	31.4	75	80	6
NS3	85	27.0	84	92	10
NS4	60	32.8	75	89	18
NS5	60	37.3	78	90	15
NS6	50	37.4	65	88	35
Reference	0	64.8	45	55	22

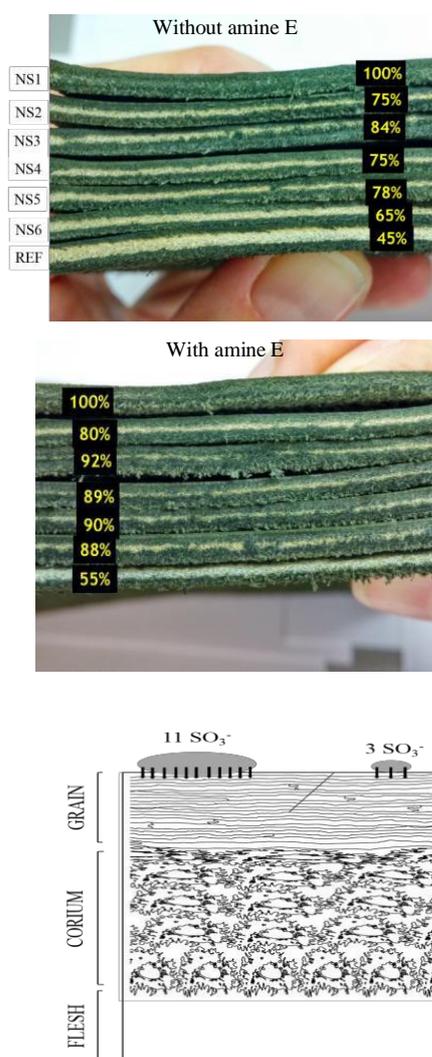


Figure 3. (a) Penetration control of dyes without amine E (left) and with amine E (right). (b) Representation of the physical effect of naphthalenesulfonics on the hide surface.

Color intensity (L*) on the grain surface is shown in Table V. The reference has the highest color intensity (lowest L*),

followed by NS6 (lowest molecular weight), in both variables. Dyeing intensity is increased by adding amine E in the products with higher molecular weights (NS1, NS2, NS3).

d) Color levelness control

Color levelness values were obtained by measurements performed on ten points of each sample. The higher the ΔE^* values, the poorer the levelness. The values obtained for each product in the two variables are shown in Table V. Color levelness gets poorer with decreasing molecular weights in the variable without amine E. In this variable, ΔE^* values show little variation between molecular weights

—from 3.000 (NS1) to 1.200 (NS2 and NS3)— with a sudden fall to molecular weight 600 (NS6) and much lower in the (product-free) reference. The addition of amine E improved the levelness values of all products (variation %), more significantly so with decreasing molecular weights, and to a higher proportion as compared to the product-free variable (reference).

UNIX S-3



- Synthetic oil
- High light fastness and heat resistance
- Excellent dye levelling

SOFT NESS

CROMOGENIALNITS
YOUR SPECIALIST FOR SPECIALTIES



www.cromogenia.com

Table V
Color intensity and levelness values, with and without amine E

Product	Color intensity			Color levelness		
	Without amine E (L*)	With amine E (L*)	Variation (%)	ΔE^* without amine E	ΔE^* with amine E	Variation (%)
NS1	31.3	26.4	15.6	3.8	3.6	5.2
NS2	31.1	29.4	5.4	4.2	3.8	9.5
NS3	30.8	26.2	14.9	4.3	3.7	13.9
NS4	30.3	30.6	-0.9	4.3	3.6	16.2
NS5	31.0	31.1	-0.3	4.4	3.6	18.2
NS6	27.9	27.4	1.7	7.0	4.0	42.8
Reference	21.3	21.7	-1.8	12.5	6.2	50.4

e) Bath exhaustion

Finally, the values obtained for dyeing exhaustion from baths are shown in Table VI. In the variable without amine E maximum exhaustion was obtained with the reference ($L^*=84.2$) and minimum exhaustion was obtained with NS1 (maximum molecular weight). The rest of products showed similar exhaustions, or exhaustions with minor variations.

In the variable with amine E maximum exhaustion was also obtained with the reference, and exhaustions unrelated to molecular weight were obtained with the rest of products. The addition of amine E increased dye exhaustion in all cases (by 15-17%). Exhaustion variation (influence of amine E) was maximum with NS1 (maximum molecular weight) and minimum with the reference.

Table VI.
Bath exhaustion quantitative assessment

Product	(L*) Exhaustion without amine E	(L*) Exhaustion with amine E	Variation (%)
NS1	44.3	58.6	30.9
NS2	57.1	67.6	18.3
NS3	50.2	58.0	16.7
NS4	53.6	60.7	13.2
NS5	49.8	58.7	17.8
NS6	52.4	64.9	23.8
Reference	84.2	85.0	1,0

4. Conclusion

Six naphthalenesulfonic acid derivatives were characterized with two chromatographic techniques: RP-HPLC and GPC. RP-HPLC allows qualitative

determination of polymer chain length according to their degree of condensation. For its part, GPC is highly suitable to ascertain the distribution of polymer molecular weights. The application of these two

techniques allowed determining the structure of naphthalenesulfonics and thus relating their structure to the physical-chemical properties observed in the application process.

In naphthalenesulfonic derivatives applied as neutralization auxiliaries, the higher the molecular weight and the number of sulfonic products, the better their penetration and the penetration of the dye mixture. While color levelness is increased with increasing molecular weights, bath exhaustion is decreased with increasing molecular weights.

6. References

1. Morera, J M, Química Técnica de Curtición, Escola univ. d'enginyeria, 2003, pp 123.
2. Soler, J, Procesos de curtición, UPC, 2000, pp 177-200.
3. Heidemann, E, Fundamentals of leather manufacturing, Roether, 1993, pp 445.
4. Portabella, M, Tecnología química del cuero, 1962, pp 226.
5. Palop, R, Parareda, J, Ballús, O, Estudio aplicativo de los recurtientes sintéticos. Parte I, AQEIC, 1, 2008.
6. Ballús, O, Palop, R., Influencia de la aplicación de un recurtiente anfótero en las propiedades del cuero, Parte I. 63º Congreso AQEIC, Igualada 2014.
7. Ballús, O, Palop, R., Influencia de la recurtición con sintanes en la tintura del cuero, 62º Congreso AQEIC, Lorca 2013.
8. Covington, A, Tanning Chemistry. The science of leather, RSC Publishing, 2009, pp 385-387.
9. Adzet J M, Química técnica de tenería, Escuela de Tenería de Igualada, 1985, pp 432-433.

Non-ionic amine E is an excellent dyeing auxiliary that improves both the penetration and the levelness of the dyes. Color intensity is notably improved in the products with higher molecular weight. Finally, the addition of non-ionic amine improves exhaustion of all variables.

5. Acknowledgments

The authors would like to thank to the Leather Application Laboratory, Department of Analysis and Department of R&D of Cromogenia Units, S.A.

