PRESENCE OF FORMALDEHYDE IN LEATHER. COMPARATIVE OF METHODS OF ANALYSIS AND INFLUENCE OF DIFFERENT TREATMENTS APPLIED

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Abstract.

Formaldehyde has a wide application in the tanning sector, mainly in the retanning operation, as it forms part of two large groups of organic retanning products: synthans and resins. Resins can be partially hydrolyzed to release formaldehyde. Consequently, formaldehyde detected in leather may be free or derived from the partial hydrolysis of applied resins.

Currently, due to the recently confirmed carcinogenic character of formaldehyde and other health problems, there is a growing demand for formaldehyde-free leather goods or leathers with formaldehyde content under permitted legislative and market limits.

The main objective of this work is the search for different formulation options in the retannage process that guarantee the elimination or reduction of formaldehyde in leather to the permitted limits. Resins of different type and origin are studied, and how they affect the formaldehyde content in leather. The aim is to reduce the presence of formaldehyde in the leather by adding different vegetal compounds (mimosa, quebracho and tara) in the retanning process, and to check the effect of some specific colorants applied in the dyeing operation.

The EN ISO 17226 Standard, which consists of three parts, is the official method for the determination of formaldehyde content in leather. In this paper, the results of formaldehyde in leather obtained by applying parts 1 "Quantification by HPLC" and 2; "Quantification by colorimetric analysis" are compared. These two methods have a common initial extraction step and differ in the subsequent reaction of the extracted formaldehyde and the way of quantifying it.

Keywords: Formaldehyde, retanning, resins.

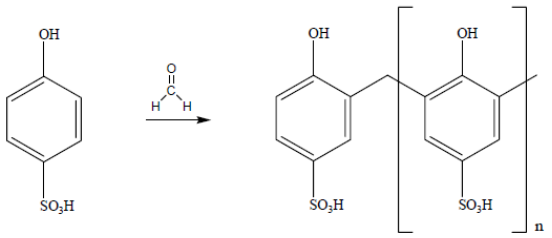
1. Introduction

Formaldehyde is a colorless, flammable, strong odor chemical that is used in building materials and to produce numerous household products. It is used in pressed wood products, such as particle board, plywood, fiber boards; glues and adhesives; coatings of paper products and some insulation materials, etc. It is also commonly used as an industrial fungicide, germicide and disinfectant, and as a preservative in hospitals and medical laboratories. Formaldehyde also occurs naturally in the environment, in small amounts, as part of the normal metabolic processes of most living organisms (1,2).
One of the main uses of formaldehyde is the production of resins for different applications and as an intermediary in the synthesis of different chemical products. (3)
In tannery, formaldehyde has the most

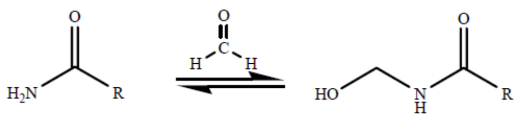
important application in the retanning operation since it takes part of two large groups of synthetic organic retanning agents:

I) Syntans; Chemicals prepared through the condensation of aromatic compounds like phenols or naphthols with formaldehyde

II) Resins; Condensation products between formaldehyde and cyanamide, melamine, urea, amino acids, etc., which are susceptible to partial hydrolysis and to release formaldehyde.



Syntans, irreversible reaction



Resins, reversible reaction (4)

Therefore, the origin of formaldehyde detected in leather by the currently available analysis methods may be: free formaldehyde and formaldehyde from the partial hydrolysis of the retanning resins.

In the case of free formaldehyde, the main causes of its presence in leather at present are: impurity of syntans and resins (very frequent in products of Asian origin); residue from the fixing operation of protein finishes such as casein (infrequent); residue from the ironing operation of fur wool (frequent) and residue as a preservative in chemicals for the final wet phase (rare).

Despite the listed applications, formaldehyde (FM) has a high toxicity in humans. The inhalation of formaldehyde can produce breathing problems, irritation of the eyes, nose and throat. Also, by skin direct contact, it can cause dermatitis. Studies in humans have related exposure to formaldehyde and lung and nasopharyngeal cancer. Animal inhalation studies have shown an increase in nasal squamous cell cancer. It is for this reason that the EPA (Environmental Protection Agency) considers formaldehyde as a probable human carcinogen (group B1). (3,8)

Based on sufficient animal and human studies. (9,10), in 2011 the HHS (Department of Health and Human Services) attributed to formaldehyde a carcinogenic character to humans.

This is why there are a number of guidelines for exposure to this product. Different organizations propose FM limits in different sectors; as in drinking water; In the exposure of workers to formaldehyde or standards for FM emissions in buildings, among others (9).

The presence of formaldehyde in leather (free or from the partial hydrolysis of formaldehyde-derived products) should be avoided or its presence below the allowable limits. Different countries have formaldehyde limits in products of daily use and major brands present their own limits for formaldehyde according to the "Restricted Substances Lists" (RSL).

Some authors have investigated how to replace or reduce formaldehyde present in leather through natural extracts of plants, or of grape seeds (11,12). Another study suggests replacing the resins used by others free of formaldehyde for avoiding the presence of formaldehyde in leather (13,14).

Currently, the International Organization for Standardization (ISO) has as the official Standard for the determination of formaldehyde in leather, the ISO 17226 Standard, which includes three parts; ISO 17226-1 "Quantification by HPLC" (5); ISO 17226-2 "Quantification by colorimetric analysis" (6) and ISO 17226-3 "Formaldehyde emissions from leather" (7).

2. OBJECTIVES

Two main objectives are considered in this paper: i)To study the influence that different chemicals applied (formaldehyde retanning resins of different origin, vegetable compounds and dyes) exert on the formaldehyde content, ii) the comparison between the results of formaldehyde content obtained by applying two different methods; chromatographic (EN ISO 17226, part 1) and colorimetric (EN ISO 17226, part 2).

3. MATERIAL AND METHODS

Starting material. Applied formulation

Butts of wet-blue splits shaved to a thickness of 1.5 mm of "Germany" origin supplied by Despell S.A were the starting material. This format of hide has been selected to have the greatest possible homogeneity in the leather substrate and to minimize the influence of hide area (belly-butt-neck) on the absorption of chemicals in the different tests to be performed. Working with 1.5 mm splits will facilitate penetration of chemicals in the different treatments to be compared.

Once received from tannery, the leather was checked by chromatographic analysis to confirm that it is free from formaldehyde, then the splits were subjected to the general recipe shown in Table 1. All tests carried out had a common process up to retanning.

TABLE 1

Process	%	g	Chemical	ºC	Time	pH/remarks
Wetting	300		Water	35		
	0,3		Formic Acid (1:10)			
	0,5		Nonionic degreasing agent		60'	Drain, wash good
Rechroming	100		Water	35		
	0,4		Formic Acid (1:10)		10'	pH 3.5
	4		Basic Chrome sulphate 33%			
	1		Sodium-aluminium silicate		60'	pH 4.0/4.2, drain, wash
Neutralization	150		Water	35		
	2		Sodium formate		20'	
	1		Sodium bicarbonate (1:10)		90'	pH 5.2/5.4, check cut drain, wash
Retanning	50		Water	30		
	y		Acrylic Resin		60'	
	5		Resin based on formaldehyde		60'	
	x		Vegetable compound		60'	
Dyeing	4		Dye		60'	
Fatliquoring	100		Water	50		
	8		Synthetic sulphated oil			
	4		Phosphoric ester based oil		60'	
	1		Formic Acid (1:10)	cold	20'	
	1		Formic Acid (1:10)	cold	20'	
	1		Formic Acid (1:10)	cold	20'	
Washing	150		Water		3'	
Horse up (24 hours), setting out (by hand)						
Air dry (toggle)						
Stake						
Analytical determinations						
						**All quantities are calculated on shaved wet blue weight*

The formaldehyde-based resins studied were;

- Melamine formaldehyde (MF)
  - MF.A (low formaldehyde content) MF.B (high formaldehyde content)
- Dicyandiamide formaldehyde (DCDF)
  - DCDF.A (low formaldehyde content) DCDF B (high formaldehyde content)

Three types of vegetable retanning were applied;

- Mimosa M (at concentrations 2-4%) (Clarotan supplied by Tanac)
- Quebracho Q (at concentrations 2-4%) (Indusol ATO, supplied by Silva)
- Tara T (Tara Powder, supplied by Silva)

The dyes chosen for the study were supplied by Trumpler Española, S.A.;

- Acid Black 234 (AB), black dye
- Acid Red 337 (AR), red dye

Once processed, leathers were stored and formaldehyde content was determined at different periods after leather processing. The results of formaldehyde content shown in this study were determined at 90 days after treatment.

Methods. Determination of formaldehyde in leather

The EN ISO 17226 Standard "Determination of formaldehyde content in leather" in parts 1 "Quantification by HPLC" and 2 "Quantification by colorimetric analysis" were used to determine the formaldehyde content in leathers treated in accordance with the formulation shown in Table 1.

In both methods, the initial phase of extraction of formaldehyde present in leather is common. A given amount of leather is gently shaken with 0.1 % sodium dodecyl sulphonate solution for 60 minutes at 40 ºC. The warm extract solution is immediately filtered through a glass fiber filter into a flask. The filtrate is cooled down to room temperature. The quantification of formaldehyde depends on the method:

EN ISO 17226 Standard. Part 1. "Quantification by HPLC"

An aliquot of the filtrate is allowed to react at least 60 minutes up to 180 minutes with 0.3 % solution of dinitrophenylhydrazine in o-phosphoric acid and formaldehyde is quantified by HPLC after filtration through a nylon syringe filter (5).

EN ISO 17226 Standard. Part 2. "Quantification by colorimetric analysis"

An aliquot of the filtrate is reacted with acetylacetone solution in ammonium acetate and glacial acetic acid for 30 minutes at 40 ºC. After cooling (in the dark), the absorbance is measured spectrophotometrically at 412 nm.

4. RESULTS AND DISCUSSION

The experimental results of formaldehyde content at 90 days after treatment are shown next:

Test Code	Resin applied	Vegetable Code		Dye code	Formaldehyde content (ppmFM)	
		Vegetable type	%		COL.	CHROM.
710	MF.A	--	--	--	69,6	71,1
711	MF.A	M	2	--	59,2	76,4
712	MF.A	M	4	--	30,5	65,8
814	MF.A	--	--	--	69,3	65,3
815	MF.A	Q	2	--	74,4	77,6
816	MF.A	Q	4	--	62,3	78,9
902	DCDF.A	--	--	--	50,0	85,7
903	DCDF.A	M	2	--	22,2	63,4

904	DCDF.A	M	4	--	12,5	61,4
1006	DCDF.A	--	--	--	53,7	89,1
1007	DCDF.A	Q	2	--	28,3	72,0
1008	DCDF.A	Q	4	--	15,6	64,3
1109	MF.A	--	--	--	87,0	75,7
1110	MF.A	--	--	AB	18,7	42,4
1111	MF.A	M	2	--	30,3	69,9
1112	MF.A	M	2	AB	5,13	36,6
1213	MF.A	Q	2	--	74,4	92,8
1214	MF.A	Q	2	AB	8,07	42,0
1215	MF.A	T	2	--	73,3	90,5
1216	MF.A	T	2	AB	8,68	45,5
1301	DCDF.A	--	--	--	53,3	93,8
1302	DCDF.A	--	--	AB	7,55	48,0
1303	DCDF.A	M	2	--	15,1	61,7
1304	DCDF.A	M	2	AB	5,15	51,8
1405	DCDF.A	Q	2	--	25,6	62,5
1406	DCDF.A	Q	2	AB	4,69	40,7
1407	DCDF.A	T	2	--	26,3	65,5
1408	DCDF.A	T	2	AB	5,51	40,5
1509	MF.A	--	--	--	96,7	90,2
1510	MF.A	--	--	AR	85,1	75,4
1511	MF.A	M	2	AR	22,7	56,3
1512	MF.A	Q	2	AR	69,2	73,2
1613	DCDF.A	--	--	--	58,3	77,3
1314	DCDF.A	--	--	AR	43,9	62,0
1615	DCDF.A	M	2	AR	11,3	38,2
1616	DCDF.A	Q	2	AR	18,2	48,1
1701	MF.A	--	--	--	101	96,9
1702	MF.A	T	2	AR	69,0	72,3
1703	DCDF.A	--	--	--	58,9	84,6
1704	DCDF.A	T	2	AR	19,0	44,6
1805	MF.B	--	--	--	305	494
1806	MF.B	M	4	--	126	388
1807	MF.B	Q	4	--	221	516
1808	MF.B	T	4	--	227	473
1909	MF.B	--	--	--	269	522
1910	MF.B	--	--	AB	228	453
1911	MF.B	M	2	AB	152	370
1912	MF.B	Q	2	AB	194	443
2013	DCDF.B	--	--	--	187	274
2014	DCDF.B	M	4	--	64,6	165
2015	DCDF.B	Q	4	--	101	204
2016	DCDF.B	T	4	--	88,0	194
2101	DCDF.B	--	--	--	199	259
2102	DCDF.B	--	--	AB	160	223
2103	DCDF.B	M	2	AB	85,8	170
2104	DCDF.B	Q	2	AB	119	218

Influence of the offer of the vegetable compound. Previous note:

From the analysis of the variance of the experimental results obtained in splits treated with MF.A resin and retanned with M and Q at offers of 2 and 4% (test codes: 711, 712, 1111 and 815, 816, 1213) and of those of splits treated with DCDF.A resin and retanned with M and Q at offers of 2 and 4% (test codes: 903, 904, 1303 and 1007, 1008 and 1405), it has been observed that there are no significant differences between the formaldehyde content determined by any of the two methods that can be attributed to the offer of the vegetable compound. Therefore, the analysis of experimental results will only consider the effect of the type of the vegetable compound applied regardless of its concentration.

1. Results obtained of splits treated with Melamine Formol A resin

Experimental results: 20

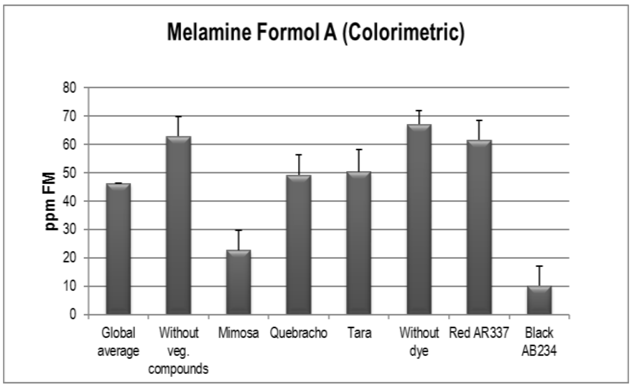
Effect of the vegetable compound: it is obtained by comparing the results obtained of the 7 samples without vegetable compound, with those of 5 samples treated with mimosa, 5 samples treated with quebracho and 3 samples treated with tara.

Effect of the dye: it is obtained by comparing the results obtained of 12 non-dyed samples, with those of 4 samples dyed with the AR337 red dye and 4 samples dyed with AB234 black dye.

Test Code	Resin applied	Vegetable Code		Dye code	Formaldehyde content (ppmFM)	
		Vegetable type	%		COL.	CHROM.
710	MF.A	--	--	--	69,6	71,1
711	MF.A	M	2	--	59,2	76,4
712	MF.A	M	4	--	30,5	65,8
814	MF.A	--	--	--	69,3	65,3
815	MF.A	Q	2	--	74,4	77,6
816	MF.A	Q	4	--	62,3	78,9
1109	MF.A	--	--	--	87,0	75,7
1110	MF.A	--	--	AB	18,7	42,4
1111	MF.A	M	2	--	30,3	69,9
1112	MF.A	M	2	AB	5,13	36,6
1213	MF.A	Q	2	--	74,4	92,8
1214	MF.A	Q	2	AB	8,07	42,0
1215	MF.A	T	2	--	73,3	90,5
1216	MF.A	T	2	AB	8,68	45,5
1509	MF.A	--	--	--	96,7	90,2
1510	MF.A	--	--	AR	85,1	75,4
1511	MF.A	M	2	AR	22,7	56,3
1512	MF.A	Q	2	AR	69,2	73,2
1701	MF.A	--	--	--	101	96,9
1702	MF.A	T	2	AR	69,0	72,3

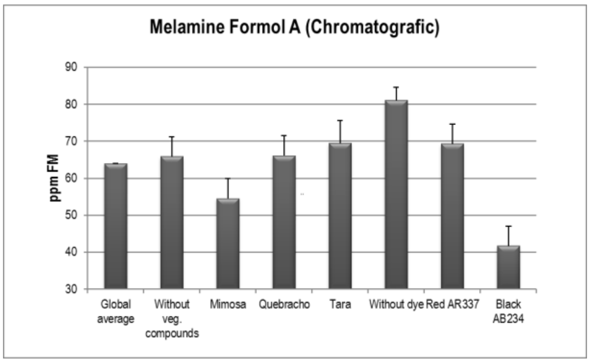
1.1 Colorimetric Method

The analysis of the variance pointed out a slightly significant effect (6.97%) of the vegetable retanning agent and a very significant effect (0.98%) of the AB234 dye on the formaldehyde content determined by this method, while the interaction between these factors is non-significant at all, so that they influence formaldehyde content independently.



1.2 Chromatografic Method

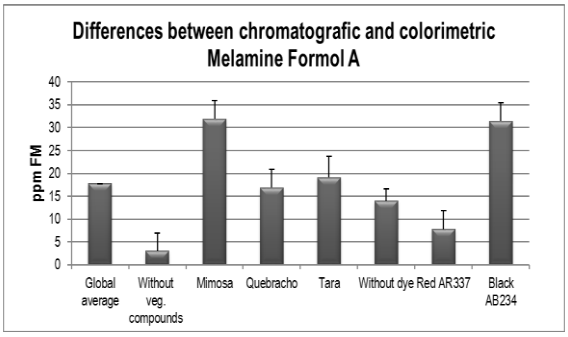
The variance analysis only reveals a very significant influence (0,09%) of the AB234 dye in the formaldehyde content, whereas the effect of the vegetal compound and its interaction with the dye are not significant.



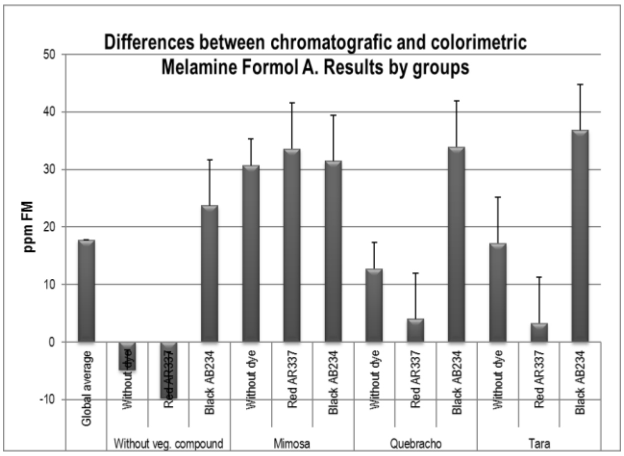
In the colorimetric method, a significant decrease in the free formaldehyde content was observed when mimosa was applied as a vegetable retanning agent, whereas in the chromatographic method, the reduction of the content observed did not reach the level of significance. In both methods, the effect of the AB234 dye on the formaldehyde content diminution was evident.

1.3 Comparison of methods

The same analysis was carried out on the differences between the formaldehyde determinations obtained by the chromatographic method and the colorimetric method. A very significant influence of the vegetable retanning agent and the AB234 dye on this difference was observed, although there is no interaction between these factors, so that it can be affirmed that the retanning and the dye AB234 contribute independently to this difference.



The smallest difference between methods are in splits without retanning with vegetable compounds and in splits dyed with the AR337 dye, while the highest differences would correspond to splits treated with mimosa and dyed with the AB234 dye.



If the results of the different experimental combinations are shown, it can be observed that for splits without retanning with vegetable compound that have not been dyed or dyed with the AR337 dye, the formaldehyde content obtained by the colorimetric method was higher, contrary to what is usual, than the results obtained by the chromatographic method.

2. Results obtained of splits treated with Dicyandiamide Formol A resin

Experimental results: 20

Effect of the vegetable compound: it is obtained by comparing the results obtained of the 7 samples without vegetable compound, with those of 5 samples treated with mimosa, 5 samples treated with quebracho and 3 samples treated with tara.

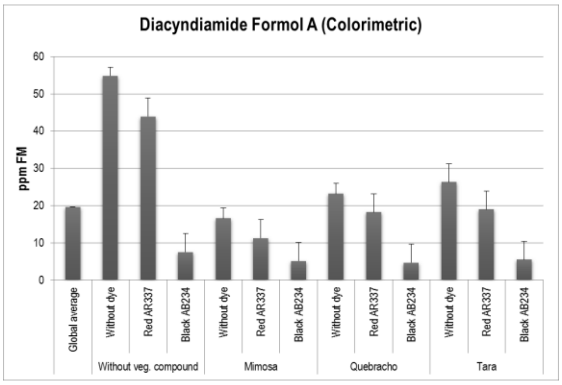
Effect of the dye: it is obtained by comparing the results obtained of 12 non-dyed samples, with those of 4 samples dyed with the AR337 red dye and 4 samples dyed with AB234 black dye

Test Code	Resin applied	Vegetable Code		Dye code	Formaldehyde content (ppmFM)	
		Vegetable type	%		COL.	CHROM.
902	DCDF.A	--	--	--	50	85,7
903	DCDF.A	M	2	--	22,2	63,4
904	DCDF.A	M	4	--	12,5	61,4
1006	DCDF.A	--	--	--	53,7	89,1
1007	DCDF.A	Q	2	--	28,3	72
1008	DCDF.A	Q	4	--	15,6	64,3
1301	DCDF.A	--	--	--	53,3	93,8

1302	DCDF.A	--	--	AB	7,55	48
1303	DCDF.A	M	2	--	15,1	61,7
1304	DCDF.A	M	2	AB	5,15	51,8
1405	DCDF.A	Q	2	--	25,6	62,5
1406	DCDF.A	Q	2	AB	4,69	40,7
1407	DCDF.A	T	2	--	26,3	65,5
1408	DCDF.A	T	2	AB	5,51	40,5
1613	DCDF.A	--	--	--	58,3	77,3
1314	DCDF.A	--	--	AR	43,9	62
1615	DCDF.A	M	2	AR	11,3	38,2
1616	DCDF.A	Q	2	AR	18,2	48,1
1703	DCDF.A	--	--	--	58,9	84,6
1704	DCDF.A	T	2	AR	19	44,6

2.1 Colorimetric method

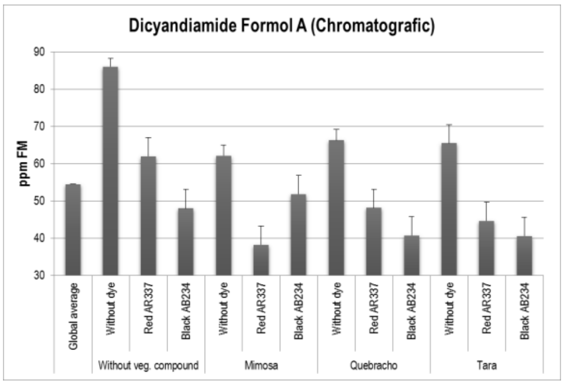
The variance analysis shows a very significant effect (0,05%) of the vegetable retanning process and the dyeing with the AB234 dye (0,01%) on the formaldehyde content. In addition, a significant interaction (3,61%), between both factors was observed so that the influence of the dye will depend on the vegetable compound with which the split was treated.



The vegetable compound-dye interaction in the colorimetric determinations can be observed by the intensity of the decrease of formaldehyde content that took place in the splits without retanning when passing from the red AR337 dye to the black AB234 dye, which was much higher than that observed in this change of dye for the three vegetable retanning agents used. It is observed, how the use of the black AB234 dye led to the diminution of formaldehyde content and that the application of an vegetable compound also decreased this value.

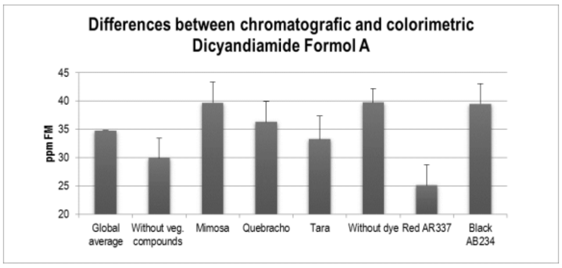
2.2 Chromatographic method

In this case, a very significant influence (0,79%) of both the vegetable retanning agent and the AB234 dye (0,00%) also took place, although the interaction between the two factors is not significant (14,08%).

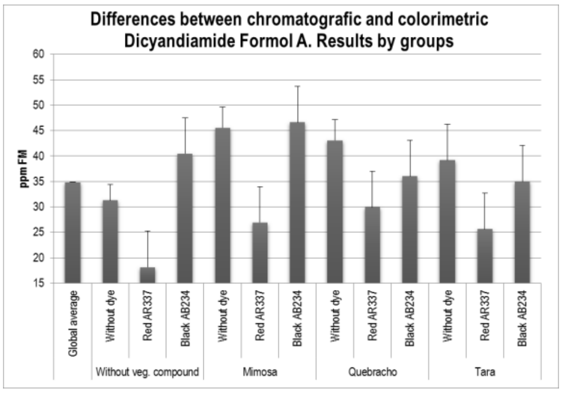


2.3 Comparison of methods

The same analysis on the differences between the FM determinations obtained by the chromatographic method and the colorimetric method was carried out. A significant influence of the black AB234 dye on this difference was observed, whereas the vegetable compound did not present any significant influence on the difference nor the interaction between these factors. The lowest differences between methods would be observed in splits dyed with the red AR337 dye and it seems that the lowest values were obtained for this dye in non-retanned leathers.



In all the cases the results of the chromatographic method exceeded the results of the colorimetric method.



3. Results obtained of splits treated with Melamine Formol B resin

Experimental results: 8

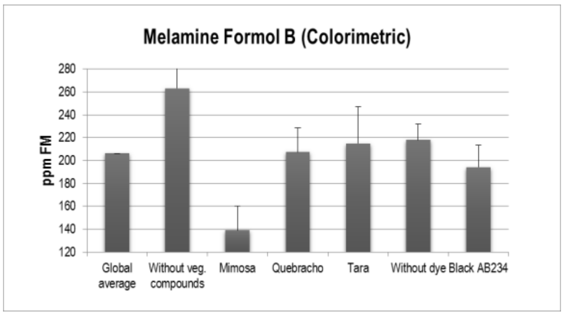
Effect of the vegetable compound: it is obtained by comparing the results obtained of the 3 samples without vegetable compound, with those of 2 samples treated with mimosa, 2 samples treated with quebracho and 1 sample treated with tara.

Effect of the dye: it is obtained by comparing the results obtained of 5 non-dyed samples, with those of 3 samples dyed with the black AB234 dye

Test Code	Resin applied	Vegetable Code		Dye code	Formaldehyde content (ppmFM)	
		Vegetable type	%		COL.	CHROM.
1805	MF.B	--	--	--	305	494
1806	MF.B	M	4	--	126	388
1807	MF.B	Q	4	--	221	516
1808	MF.B	T	4	--	227	473
1909	MF.B	--	--	--	269	522
1910	MF.B	--	--	AB	228	453
1911	MF.B	M	2	AB	152	370
1912	MF.B	Q	2	AB	194	443

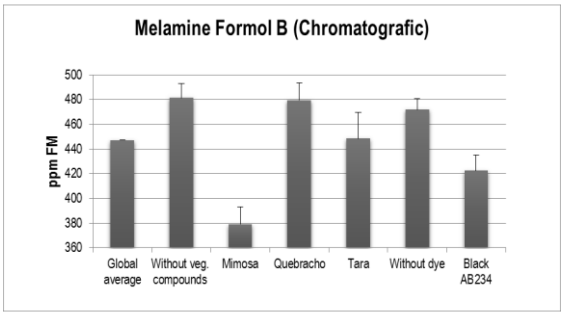
3.1 Colorimetric Method

The variance analysis shows that the influence of the vegetable retanning agent can be slightly significant (7,62%) on the formaldehyde content whereas the. black AB234 dye did not present any significance on the FM content.



3.2 Chromatographic Method

The analysis of the variance, points out that both vegetable retanning agents and the black AB234 dye exerted significant effects on formaldehyde content (3,38 and 4,92%, respectively).



A significant decrease in the free formaldehyde content attributable to the application of mimosa as a vegetable retanning agent was observed in both methods. For the dye, a significant decrease of the FM content attributable to the application of the black AB234 dye was observed in the case of the chromatographic method.

3.3 Comparison of methods

Studying the influence of vegetable retanning agents and the black AB234 dye on the difference between the FM determinations obtained by the chromatographic and the colorimetric methods, the application of the variance analysis does not allow attributing any significant variation of the differences to any of these factors. It can only be stated that the FM content determined by the chromatographic method was 241 ppm higher than that obtained by the colorimetric method.

4. Results obtained of splits treated with Dicyandiamide Formol B resin

Experimental results: 8

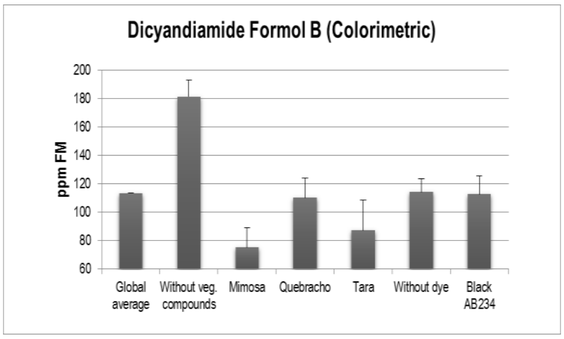
Effect of the vegetable compound: it is obtained by comparing the results obtained of the 3 samples without vegetable compound, with those of 2 samples treated with mimosa, 2 samples treated with quebracho and 1 sample treated with tara.

Effect of the dye: it is obtained by comparing the results obtained of 5 non-dyed samples, with those of 3 samples dyed with the black AB234 dye

Test Code	Resin applied	Vegetable Code		Dye code	Formaldehyde content (ppmFM)	
		Vegetable type	%		COL.	CHROM.
2013	DCDF.B	--	--	--	187	274
2014	DCDF.B	M	4	--	64,6	165
2015	DCDF.B	Q	4	--	101	204
2016	DCDF.B	T	4	--	88	194
2101	DCDF.B	--	--	--	199	259
2102	DCDF.B	--	--	AB	160	223
2103	DCDF.B	M	2	AB	85,8	170
2104	DCDF.B	Q	2	AB	119	218

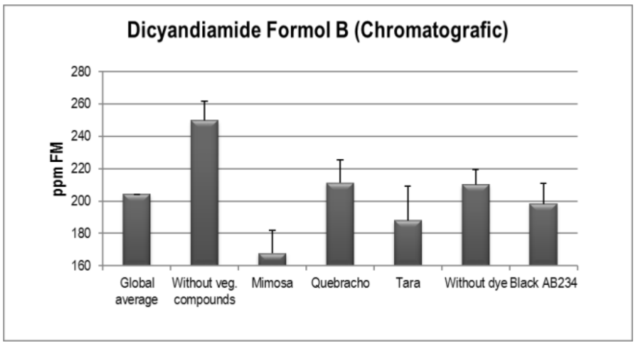
4.1 Colorimetric Method

The analysis of the variance shows that the vegetable compound has a significant influence (2,89%) on the FM content, whereas the dye AB234 has no significance.



4.2 Chromatographic Method

Here, the variance analysis reveals a slight significant influence (7,24%) of the vegetable retanning agents on the formaldehyde content whereas the black AB234 dye did not influence the content of FM.



In both methods, a significant decrease in the free FM content attributable to the application of mimosa as a vegetable retanning agent was observed, whereas for the black AB234 dye none of the methods allows to affirm that its application significantly influences the decrease of FM content.

4.3 Comparison of methods

Also in this case, it is observed that the difference between the FM determinations obtained by the chromatographic method and by the colorimetric method cannot be attributed in a significant way to the retanning agents or the dye. So the only affirmation that can be made is that when dicyandiamide formaldehyde B resin was applied to splits, the chromatographic determinations gave formaldehyde contents that were, on average, 90,7 ppm higher than those provided by the colorimetric method.

5. CONCLUSIONS

From the three vegetable compounds considered (mimosa, quebracho and tara), mimosa caused the greatest decrease in the formaldehyde content of splits treated with resins synthesized with formaldehyde (melanine-formaldehyde and dicyandiamide formaldehyde), both of low and high formaldehyde content when using both the chromatographic and the colorimetric method for the analysis. Only in the case of splits treated with melanine-formaldehyde resin of low formaldehyde content, the chromatographic method did not reveal a significant influence.

The dyeing with the Acid Black 234 dye caused a significant reduction of the formaldehyde content of splits treated with melamime-formol and dicyandiamide-formol of low formaldehyde content when using both the chromatographic and the colorimetric method for the analysis. However, this effect was hardly noticeable with high formaldehyde content resins. Dyeing with the Acid Red 337 dye had no effect on the formaldehyde content.

The chromatographic method of analysis provided results of formaldehyde contents, which were higher than the colorimetric method, mainly in splits treated with resins of high formaldehyde content (241 ppm higher in splits treated with melamine-formaldehyde resin of high formaldehyde content and 90,7 ppm higher in splits treated with dicyandiamide-formaldehyde resin of high formaldehyde content). Most likely, this is because the more acidic conditions in which the chromatographic method of analysis is developed lead to a greater hydrolysis of the resin extracted from the leather.

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