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REDUCTION OF THE FORMALDEHYDE CONTENT IN LEATHERS TREATED WITH FORMALDEHYDE RESINS BY MEANS OF PLANT POLYPHENOLS

Agustí Marsal[a*], Sara Cuadros[a], Albert Mª Manich[a]; Francina Izquierdo[b], Joaquim Font[c]

[a]Instituto de Química Avanzada de Cataluña, IQAC-CSIC, C/ Jordi Girona 18-26, Barcelona, Spain

[b]Asociación Química Española de la Industria del Cuero, Avda. Pla de la Massa 8, Igualada, Spain

[c]Cátedra A[3], Escola d'Enginyeria Igualada, Avda Pla de la Massa 8, Igualada, Spain

Abstract

Formaldehyde has applications in many industrial processes, including synthesis of resins and syntans to be used in the retanning process of leather. When resins are employed, they can hydrolyse, releasing formaldehyde. Due to the carcinogenicity of formaldehyde, its presence in leather should be avoided or kept below allowable limits.

The aim of this study is to determine the effect of polyphenols contained in vegetable compounds (mimosa, quebracho and tara) in the reduction of the formaldehyde content in leathers treated with resins synthesized with formaldehyde (melamine-formaldehyde and dicyandiamide-formaldehyde). The formaldehyde content in leathers treated only with resin increases with time while the formaldehyde content in leathers treated additionally with vegetable compounds is reduced. The lower the formaldehyde content in the leather, the higher the ability of vegetable compounds to reduce such content. Mimosa shows the strongest ability to reduce the formaldehyde content, and this capacity increases with ageing. The addition of 4% (on shaved wet-blue weight) of mimosa gives rise to an 85% reduction in the formaldehyde content 140 days after leather processing of split hides treated with a formaldehyde resin of low formaldehyde content. However, this reduction is 68% in splits hides treated with a resin of high formaldehyde content. This is of great importance in baby's leather articles, in which the formaldehyde content is low; therefore, the addition of a small amount (3%) of vegetable compounds (especially mimosa) guarantees that the formaldehyde content is below the allowed limits (16 mg/kg in the most restrictive regulation). Reducing the formaldehyde content using the polyphenols contained in vegetable compounds constitutes a good alternative not only in the leather sector but also in other industrial sectors (wood, textile, etc.) that use formaldehyde resins.

Keywords: clean technology; plant polyphenols; condensed/hydrolysable tannins; leather; formaldehyde resins; formaldehyde content

*Corresponding author. Fax: +34 93 204 59 04

E-mail address: agusti.marsal@iqac.csic.es (A. Marsal)

1. Introduction

The main current application of formaldehyde in tannery is in the retanning operation since it is a component of two groups of synthetic tanning agents: syntans and resins.

However, the carcinogenic character attributed to formaldehyde (IARC, 2012 and Dixit et al., 2015) makes that measures should be taken to guarantee that formaldehyde contents in leather are below the allowable limits or that it is completely excluded.

Formaldehyde in leather can be avoided by using, for example, protein or acrylic syntans that confer optimum properties to leather. The higher the concentration of protein or acrylic syntans, the smoother the leather (Thanikaivelan et al., 2007). The affinity of dyes to leather retanned with short chain acrylic syntans is higher than that to leather retanned with other anionic retanning agents of higher molecular weight. This can be attributed to the enhanced penetration ability of acrylic syntans of low molecular weight (Heidemann, 1993). It has also been observed that protein or acrylic syntans do not appreciably reduce the tensile strength (Mohan et al., 2008). The development of a new tanning system consisting of compounds of aluminium, silicon and natural polycarboxylic acids that allows the production of "wet bright" leather, free from aldehydes and aldehyde precursors, has also been suggested (Bacardit et al., 2014).

Some authors have replaced formaldehyde as a condensing agent by a natural product (derived from periodate oxidation of sodium alginate) and sodium metabisulphite for preparing melamine resins (Kanth et al., 2012).

Nevertheless, the use of formaldehyde condensed with compounds such as melamine, dicyandiamide or urea (resins) is sometimes required. Resins can hydrolyse, under certain conditions, with the consequent release of formaldehyde (Barret, 1993). If that happens, it is recommended that measures be adopted so that the formaldehyde present in the leather is undetectable by the current analytical methods or remains below the allowable limits. Literature refers to some formaldehyde scavengers that can be used to achieve this objective. Boran et al. (2011) studied the effect of adding different amine compounds to urea-formaldehyde resin to reduce the formaldehyde emitted by medium density fibreboard. Likewise, sodium metabisulphite proved to be an excellent scavenger for formaldehyde during wood-based panel production (Costa et al., 2013).

The aim of this work is to determine the possible effect of the polyphenols (tannins and non-tannins) contained in some vegetable compounds (mimosa, quebracho and tara), normally used in tanning/retanning processes, on the reduction of formaldehyde content in leathers treated with resins synthesized with formaldehyde. The variation of formaldehyde content with time and its reduction with respect to the control samples (with only resin) is also considered.

The authors believe that the reaction between the polyphenols of the vegetables compounds and formaldehyde may decrease the formaldehyde content in leather. The reaction of polyphenol with formaldehyde has been described in the bibliography (Hillis and Urbach, 1959; Vázquez et al., 1987; Pizzi, 2008).

Few publications on this subject have been found. Bayramoglu et al. (2008) attribute the ability of plant extracts (Vinca Rosea and Camellia Sinensis), mainly of the Camellia Sinensis (Green Tea), in reducing the formaldehyde content in leather to the presence of antioxidants. In other work, the proanthocyanidins of the grape seed structure are responsible for reducing the formaldehyde content in leather (Bayramoglu, 2013). For wood substrates, Boran et al., (2012) studied the effect of adding tannins extracted from the white oak bark to urea-formaldehyde resins on the reduction of formaldehyde emitted by panels of medium density fibreboard and found that the higher the content of tannins, the lower the free formaldehyde in the urea-formaldehyde resin.

Taking advantage of the ability of polyphenols from vegetables to reduce the formaldehyde content of leathers treated with formaldehyde resins is an excellent example of clean technology in the tannery sector, especially given the known harmful nature of formaldehyde. Such measures help to achieve a more sustainable leather industry.

2. Materials and methods

2.1 Materials

2.1.1 Starting material: split leather

Butts of wet-blue splits of German origin shaved to a thickness of 1.5 mm supplied by Despell S.A were the starting material. This format of hide was selected because it has the greatest possible homogeneity in the leather substrate. This minimizes the influence of the hide zone (belly, butt or neck) on the absorption of chemicals in the different tests to be performed. Splits of 1.5 mm thickness facilitate penetration of chemicals in the different treatments to be compared.

2.1.2 Formaldehyde-based resins

These resins are synthesized by condensation of formaldehyde with compounds such as melamine, urea, and dicyandiamide and are normally employed in the retanning process of chrome leather to impart certain properties to the final article (Naviglio et al., 2006). The reaction between melamine and formaldehyde occurs in two steps. The first step results in the formation of N-methylol groups (methylolation reaction). The second step leads to the formation of large number of different oligomers containing methylene and methylene ether bridges (condensation reaction) (Merline et al., 2013). The formaldehyde-based resins are susceptible to hydrolysis with consequent release of formaldehyde (Barret, 1993).

Resins of melamine-formaldehyde (MF) and dicyandiamide-formaldehyde (DCDF) were used in this work. Both low formaldehyde content (termed A), which were of European origin, and high formaldehyde content (termed B), which were manufactured in Asia, versions of each resin were evaluated. Analyses of the resins carried out in accordance with the method described in section 2.2.3 resulted in the following formaldehyde contents ± 95% confidence interval: MF (A): 4514±326 mg/kg; DCDF (A): 6428±466 mg/kg; MF (B): 23481±369 mg/kg and DCDF (B): 21216±1000 mg/kg. The experimental results are the mean value of five replicates.

2.1.3 Vegetable compounds

Two different vegetable extracts (mimosa and quebracho) and one vegetable powder (tara) were considered in this work. These vegetable compounds contain tannins and non-tannins, which are of polyphenolic nature. Mimosa extract comes from the bark of specially planted black wattle (*Acacia mearnsii*), most of them certified by the Forest Stewardship Council. Quebracho extract is obtained from the quebracho tree (*Schinopsis balansae and Schinopsis lorentzii*) hearthwood that grows in South America (Haslan, 1989). To obtain the extracts, the raw material (bark: mimosa; wood: quebracho) is subjected to a milling process. Then, the material is extracted with hot water followed by concentration of the liquors and spray-drying.

Tannins of mimosa and quebracho belong to the group of condensed tannins, which have the structure of polyflavonoids. The main monomer (flavonoid) of condensed tannins is repeated in mimosa and quebracho tannins several times (2-11) (Pizzi, 2008). The most abundant polyphenolic pattern in mimosa condensed tannins consists of resorcinol A-rings and pyrogallol B-rings and to a less extent, of resorcinol A-rings and catechol B-rings (Pizzi, 1980). Pasch et al., (2001) employed the Maldi-Tof mass spectrometry technique to study the characteristics and the structural differences of mimosa and quebracho tannins. They found that mimosa tannin is predominantly composed of prorobinetinidins (resorcinol A-rings, pyrogallol B-rings) while quebracho is predominantly composed of profisetinidins (resorcinol A-rings and catechol B-rings). The isolation of the flavonol quercitrin and myricitrin from mimosa immature bark demonstrated the presence of phloroglucinol-type monomeric flavonoids (Roux, 1992). Additionally, it has been reported (Özacar et al., 2006) that 20% of the flavonoid units in mimosa tannin consist of phloroglucinol A-rings – pyrogallol B-rings and phloroglucinol A-rings – pyrocatechol B-rings. Similar patterns exist in quebracho extract but, probably without the phloroglucinol A-ring pattern or at a much lower quantity (King et al., 1961; Roux et al., 1975; Clark-Lewis and Roux, 1959).

Tara (*Caesalpinia spinosa*) is a tree that grows wild in South America, especially in Perú. The tara powder is obtained from its fruits (pods) (Haslan, 1989). The tara pods are threshed, and the seeds are separated. Tara powder is obtained by mechanical milling and sieving.

Tannins contained in the tara powder, called gallotannins, belong to the group of hydrolysable tannins and are mixtures of gallic and ellagic acids, esters of glucose with gallic and digallic acids, and more complex structures containing ellagic acid (Pizzi, 2008).

Table 1 shows the commercial name, chemical supplier, tannin, non-tannin and total polyphenols contents (in %) of the two vegetable extracts (mimosa and quebracho) and the tara powder considered in this work. All these compounds were applied at offers of 2% (on shaved wet-blue weight) along with the mimosa and quebracho at offers of 4%.

(Table 1)

2.2 Methods

2.2.1 Processing of leathers. Experiments carried out

Once received from the tannery, the splits were subjected to the general recipe shown in Table 2. All tests carried out had a common process up to retanning, where 3% of a commercial acrylic resin and 5% of formaldehyde resins were applied in all the trials. As a function of the formaldehyde resin used, two series of experiments were carried out: a) The splits were treated with resins of low formaldehyde content ((MF (A) and DCDF (A)). Initially, the effect of 2% of each of the vegetable compounds considered (mimosa, quebracho and tara) was studied. Afterwards, the offer was increased to 4% but only for mimosa and quebracho since the differences between the regression lines of quebracho and tara at 2% were not significant (Mead et al., 2003). b) The splits were treated with resins of high formaldehyde content ((MF (B) and DCDF (B)). Only the effect of the highest offer of vegetable compound (4%) was considered. After retanning, a fatliquoring operation was performed with chemicals of common use in a tannery, supplied by Pulcra Chemical S.L. All of the offers refer to the shaved wet-blue weight. Once dried, leathers were analysed at different times after leather processing to determine the formaldehyde content. During this storage period, the samples for analysis were kept in airtight plastic bags in the dark. The plastic bags were maintained in a standard atmosphere at 23°C and 50% relative humidity (EN ISO 2419 Standard, 2012) so that each portion of the sample taken for analysis was always at the same conditions.

(**Table 2**)

2.2.2 Analysis of formaldehyde content in leather

The EN ISO 17226 Standard "Determination of formaldehyde content in leather. Part 2: Quantification by colorimetric analysis" (EN ISO 17226-2 Standard, 2008) was used to determine the formaldehyde content in splits treated in accordance with the formulation shown in Table 2.

Initially, the formaldehyde present in leather is extracted by gently shaken in a reciprocal linear shaker (Selecta, Unitronic) with a 0.1% solution of sodium dodecyl sulphate. We used this surfactant instead of sodium dodecyl sulphonate (as specified in the Standard) because similar results of formaldehyde content in leather were obtained with both chemicals (Cuadros et al., 2016). The method used for the extraction of formaldehyde from leather has a paramount influence on the formaldehyde content results as will be explained in a future work. After filtration of the extract, an aliquot of the filtrate is reacted with acetylacetone solution in ammonium acetate and glacial acetic acid medium and, afterwards, the absorbance is measured spectrophotometrically at 412 nm.

Two samples from each treatment were analysed and three replicates for each sample were performed. The experimental result of formaldehyde content for each treatment is the mean value of six measurements.

2.2.3 Analysis of formaldehyde content in formaldehyde resins

An adaptation of the EN ISO 17226 Standard “Determination of formaldehyde content in leather. Part 1: Quantification by HPLC” (EN ISO 17226-1 Standard, 2008) was employed to determine the formaldehyde content in the formaldehyde resins. In summary, the method consists of the extraction of the formaldehyde resins with 0.1% sodium dodecyl sulphate solution during 30±2 minutes at 40ºC. After filtration of the extract solution through a glass fibre filter, an aliquot of the filtrate is reacted with dinitrophenylhydrazine during 60 minutes. Then, the content of formaldehyde is determined by HPLC. Five replicates of the analysis of formaldehyde content in the resins were performed.

2.2.4 Analysis of tannins, non-tannins and total polyphenols in vegetable compounds

Tannin and non-tannin content determination was carried out in accordance with the EN ISO 14088 Standard “Quantitative analysis of tanning contents by filter method” (EN ISO 14088 Standard, 2012).

The concentration of total polyphenols in the vegetable compounds was determined after the redox reaction with Folin-Ciocalteau’s reagent, a mixture of phospho-tungstenic and phospho-molybdenic acids. This led to the formation of a coloured W_8O_{23} and Mo_8O_{23} oxide complex, which has a maximum absorbance at 750 nm. Concentrations were determined by means of a calibration curve using gallic acid at different concentrations (Spagna et al., 1996). Five replicates of the analysis of tannins, non-tannins and polyphenols in vegetable compounds were carried out.

2.2.5 Regression analysis

For comparative purposes, a linear regression analysis was used to estimate the evolution of formaldehyde content **[FC]** as a function of the number of days elapsed after treatment, ND. The results of the initial formaldehyde content, $\mathbf{[FC]_0}$, and the rate of change of the content, $\mathbf{[FC]_{rate}}$, as a function of the number of days elapsed after treatment, together with the correlation coefficient, **r,** of the linear regression equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$, are shown in Table 3 (for resins of low formaldehyde content) and Table 4 (for resins of high formaldehyde content). Table 3 and 4 also include the 95% confidence interval of the coefficients of the regression lines. For each point of the regression lines, the formaldehyde content is the average of six measurements.

3. Results

The variability of each experimental result used to fit the regression equations is measured by the coefficient of variation that relates the standard deviation with the mean value in %. For all the analyses carried out, the coefficients of variation ranged from 0 to 2.23% with a mean value of 0.44%.

3.1 Treatments with resins of low formaldehyde content

Figure 1 shows the formaldehyde content as a function of the number of days elapsed after treatments of splits retanned with only MF (A) resin and with the addition of 2% or 4% of vegetable compounds.

(Figure 1)

The two splits retanned with only MF (A) resin (used as reference) were grouped to enable a more precise determination of the variation of formaldehyde content [FC] with the number of days ND elapsed after treatment. Table 3 shows the linear regression analysis of the formaldehyde content versus time, providing the initial formaldehyde content ($[FC]_0$), the slope ($[FC]_{rate}$) and the correlation coefficient (r)**.**

(Table 3)

For the two splits used as reference ((only MF (A)), the variation of formaldehyde content with time resulted in a growth of +0.16±0.02 mg/kg of formaldehyde per day elapsed after treatment. The increase in formaldehyde content with time could indicate that, besides free formaldehyde due to an excess in the resin preparation process, the resin is progressively hydrolysed.

The addition of vegetable compounds in the retanning process modified the variation of formaldehyde content with time. When 2% of mimosa (on shaved wet-blue weight) was added, the formaldehyde content was reduced at a rate of -0.17±0.07 mg/kg per day elapsed after treatment. This reduction suggests that the sequestering capacity of mimosa towards formaldehyde is increased with time. When mimosa was added in a higher offer (4%), the reduction rate increased to -0.23±0.17 mg/kg per day elapsed after treatment. This suggests that the sequestering capacity towards formaldehyde increases with increasing concentration of mimosa.

For quebracho, the addition of 2% caused a slight reduction in the rate of increase of formaldehyde content with time (+0.08±0.05 mg/kg). A higher offer (4%) of quebracho caused a reduction of the formaldehyde content at a rate of -0.08±0.06 mg/kg.

The effect of 2% of tara led to some sequestering capacity for formaldehyde, similar to that shown by quebracho (4%). No significant differences between regression equations for 2% of tara and 4% of quebracho were observed (Mead et al., 2003).

The sequestering capacity of mimosa towards formaldehyde was higher than that of quebracho. As expected, the higher the vegetable compound offer, the greater the formaldehyde content decreased with time after treatment.

By comparing the results of formaldehyde content for each different vegetable compound with those of its reference (only with resins), it was possible to determine the reductions in formaldehyde content (in %) by applying the following equation at each time of the analysis:

$$\text{Reduction in formaldehyde content (\%)} = \frac{([FC]_{resin} - [FC]_{resin+veg.extr.})}{[FC]_{resin}} \text{ x } 100$$

Figure 2 shows the variation of the reduction of formaldehyde content with time

(**Figure 2**)

This reduction increased for higher vegetable compound offers and for longer times after treatments. The effect was clear for mimosa since the formaldehyde content reduction varied from 64% to 85% for offers of 2% and 4%, respectively, in the analyses carried out at 140 days after treatments. Given that $[FC]_{resin}$ increased with time and $[FC]_{resin+mim}$ decreased over time, the reduction in formaldehyde content, which is the difference between the two values at a given time, increased progressively. For quebracho and tara, an offer of 2% was not sufficient to totally compensate for the increase in formaldehyde content in splits treated with MF (A) resin only. For quebracho, the effect on formaldehyde reduction was more evident for an offer of 4%. A reduction of 43% was observed in the analysis carried out at 140 days after treatments.

When DCDF (A) resin was applied, similar effects as those for MF (A) resin were observed. The results are shown in Figure 3.

(Figure 3)

As observed in Table 3, the initial content of formaldehyde was lower than that of leathers treated with MF (A) resin (+36.12±2.61 vs +51.94±1.22 mg/kg) and the growth rate of formaldehyde content per day elapsed after treatment was reduced by half (+0.07±0.03 vs +0.16±0.02 mg/kg). This confirms that the DCDF (A) resin is hydrolysed with time but at a lower rate than that of the MF (A) resin.

The effect of adding vegetable compounds on the reduction of formaldehyde content was more evident. Here, again, the addition of mimosa reduced the initial formaldehyde content the most (22.04±2.34 mg/kg and 14.91±3.48 mg/kg for offers of 2% and 4%, respectively). The effects of adding 2% of quebracho and tara on the reduction were not significantly different (Mead et al., 2003). By comparing the regression analyses for Figure 3 of Table 3, it can be said that the higher the offer of vegetable compound, the lower the initial formaldehyde content. The formaldehyde content decreased with time at a similar rate regardless of which vegetable compound or concentration was used.

Figure 4 shows the effect of adding vegetable compounds on the reduction of formaldehyde content of splits treated with DCDF (A). Most likely, due to the lower formaldehyde content in splits retanned with DCDF (A) (Figure 3) than those with MF (A) (Figure 1), the effect of adding vegetable compound was accentuated. Higher reductions were observed at longer times after treatment.

(**Figure 4**)

The addition of 2% of quebracho, which had a very low effect with MF (A) resin, caused a reduction of approximately 15% of the formaldehyde content in leathers treated with DCDF (A) resin, when the analysis was performed at only seven days after treatments. This reduction reached 60% at 140 days after treatments, whereas reductions of 84.8% and 81.7% for an offer of 4% of mimosa and quebracho, respectively, were observed after this period. The effects of adding 2% of quebracho or tara were similar.

Figure 4 clearly shows that the effect of adding vegetable compound in reducing the formaldehyde content was more pronounced when the formaldehyde content in the leather was lower, as in leathers treated with dicyandiamide-formaldehyde (A) resins.

3.2 Treatments with resins of high formaldehyde content

Trials following the general recipe shown in Table 2 for an offer of vegetable compound of 4% applied on splits treated with formaldehyde resins of high formaldehyde content were carried out. Figure 5 shows that the formaldehyde contents in splits treated with MF (B) resin were higher than those treated with MF (A) resin (as seen in Figure 1).

(**Figure 5**)

The results of the regression analysis are shown in Table 4. As observed, the initial formaldehyde content ($[FC]_0$) of reference leather treated with MF (B) resin was almost four times (192.00±24.23 mg/kg) that of the leather treated with MF (A) resin (51.94±1.22 mg/kg, Table 3). The rate of increase in formaldehyde content ($[FC]_{rate}$) was between two and three times greater than that observed for MF (A) resin.

(**Table 4**)

The addition of 4% of vegetable compounds modified the formaldehyde content when compared with the reference leather. For leathers treated with quebracho and tara, the initial formaldehyde contents were similar to that of the reference and the quebracho does not significantly modify the formaldehyde content with time, with a regression coefficient of -0.05±0.21 mg/kg per day elapsed. However, the tara caused a significant reduction in formaldehyde content (-0.24±0.20 mg/kg per day elapsed) showing a sequestering capacity towards formaldehyde. Mimosa showed the highest sequestering capacity towards formaldehyde yielding a significant decrease in the initial formaldehyde content (141.76±17.64 mg/kg) and the highest reduction rate of the formaldehyde content (-0.30±0.16 mg/kg per elapsed day).

Figure 6 shows the reduction caused by the addition of 4% of vegetable compounds in leathers treated with MF (B) resin. Mimosa had a higher capacity than quebracho and tara in reducing the formaldehyde content of leathers treated only with resin and this reduction grew more pronounced with greater elapsed time from the production process. For an offer of 4% of mimosa, the reduction varied from 13.7% (analysis performed at 7 days after treatment) to 63.5% (analysis carried out at 202 days after treatment). However, this reduction was less than when an MF resin of lower formaldehyde content was used (Figure 2).

(**Figure 6**)

When results of formaldehyde content in leathers treated with DCDF (B) resin of high formaldehyde content with and without 4% of vegetable compound are examined, the same trends as seen for the MF (B) resin were obtained (Figure 7).

(Figure 7)

Results of the regression analysis are included in Table 4. For splits treated only with DCDF (B) resin, the variation of the formaldehyde content (FC) with time showed that the initial content ($[FC]_0$) was nearly four times higher (137.73±17.55

mg/kg) than the initial content of leather treated with DCDF (A) resin (36.12±2.61 mg/kg, Table 3), and the increase with time ($[FC]_{rate}$) was between two and three times greater than that observed with the DCDF (A) resin.

The addition of 4% of vegetable compounds showed very similar results for quebracho and tara. Their regression equations are not significantly different (Mead et al., 2003). They reduced the initial formaldehyde content of leather from ~138 to ~93 mg/kg and reduced the formaldehyde content at a rate of~ -0.18 mg/kg per day elapsed, showing a sequestering capacity towards formaldehyde. Mimosa caused the highest reduction in the initial formaldehyde content from 137.73±17.55 to 58.18±5.49 mg/kg while the reduction rate was not significantly different from zero (-0.06±0.07 mg/kg per day elapsed).

Figure 8 shows the results of adding 4% of the vegetable compounds to leather treated with the DCDF (B) resin.

(**Figure 8**)

The highest reduction in formaldehyde content with respect to leathers treated only with resin was achieved by adding 4% of mimosa. This reduction varied from 51.7% (analyses carried out at 10 days after treatments) to 67.6% (analyses carried out at 90 days after treatments). However, this reduction was lower than that achieved with leathers treated with the DCDF (A) resin with a lower formaldehyde content. In that case, the reduction of formaldehyde content in the analyses carried out at 90 days after treatments due to the addition of 4% mimosa was 82.1% (Figure 4). As shown in Figure 8, only slight differences in the reduction of formaldehyde content were observed when 4% of quebracho or tara were added in the retanning process performed with the DCDF (B) resin.

4. Discussion

4.1. Influence of plant polyphenols on formaldehyde content of splits retanned with formaldehyde resins

Mimosa showed the highest sequestering capacity of formaldehyde in splits retanned with formaldehyde resins. This may be probably attributed to the reactivity of formaldehyde with the phloroglucinol A-rings (Özacar et al., 2006) and with resorcinol A-rings (Pizzi, 2008) whose presence in mimosa tannins was reported by Pizzi (1980) and Pasch et al., (2001). The reaction of formaldehyde with mimosa polyphenols could justify the lower formaldehyde content found in the analysis.

The lower sequestering capacity of quebracho towards formaldehyde, can be probably explained by the lower reactivity of quebracho polyphenols, due to the almost complete absence of phloroglucinol A-rings (King et al., 1961; Roux et al., 1975; Clark-Lewis and Roux, 1959). As in the case of quebracho, the addition of 2% of tara powder is not enough to reduce the formaldehyde content. As stated in the bibliography (Garro – Gálvez and Riedl, 1997; Özacar et al., 2006), hydrolysable tannins such as tara, are less reactive towards formaldehyde than phloroglucinol and resorcinol flavonoid units in the condensed tannins.

In leathers treated with formaldehyde resins of lower formaldehyde content, the effect of vegetable polyphenols, mainly from mimosa, on the reduction of formaldehyde content was very relevant. The capacity of vegetable compounds to reduce the formaldehyde content in leathers treated with formaldehyde resins was more pronounced for higher concentrations of polyphenols in the treated leathers (i.e., for a higher offer of vegetable compounds in the leather production process). This would agree with the results found by Boran et al., (2012) when studying the effect of adding the tannin extracted from the white oak bark to urea-formaldehyde resins. They found that the content of free formaldehyde decreased with increasing tannin content in the urea-formaldehyde resin.

4.2. Influence of plant polyphenols on the variation with time of formaldehyde content in leathers retanned with formaldehyde resins

The content of formaldehyde in leather retanned with formaldehyde resins progressively increases with time at a rate which depends on the formaldehyde content of the resin. The conditions of the treated leather (slightly acidic pH, a certain level of humidity) facilitate the gradual hydrolysis of the resins, releasing formaldehyde. This agrees with Barret (1993) who reported the reversibility of the reaction between melamine and formaldehyde for resin preparation.

As a general rule, the addition of plant polyphenols in leathers retanned with formaldehyde resins makes the formaldehyde content decrease with time at a rate that depends on the amount of polyphenols in leathers (i.e., the offer of vegetable compounds in the leather production process) and the type of vegetable polyphenols. Leathers containing mimosa extract show the highest rate of formaldehyde content reduction which can be attributed to the high reactivity of mimosa polyphenols (resorcinol and phloroglucinol) (Pizzi, 2008; Özacar et al., 2006). The polyphenols react with free formaldehyde coming from an excess of formaldehyde in the resin preparation process and/or with formaldehyde produced from the hydrolysis of the resin. The extent of the reaction between formaldehyde and polyphenols depends on the amount of polyphenols in the retanned leather. This reacted formaldehyde (free and that coming from the resin hydrolysis) is not quantified in the analytical method.

Given that the resin is progressively hydrolysed with time, less cross-linked resin can be extracted in the extraction step of the analytical method with time. The extracted resin, due to the analytical method conditions, is hydrolysed releasing formaldehyde, which is quantitatively determined in the analytical method. Consequently, if the amount of resin extracted decreases with time, the quantified formaldehyde will be lower. All of this will depend on i) if there is a sufficient amount of polyphenols in the leather and ii) the reactivity of the polyphenols. The reactivity of the other vegetable polyphenols considered was not as significant as mimosa. Quebracho has a lower content of phloroglucinol than mimosa (King et al., 1961; Roux et al., 1975; Clark-Lewis and Roux, 1959) and tara consists of polyphenols derived from gallic acid which are recognized to have less reactivity than condensed polyphenols (Garro – Gálvez and Riedl, 1997; Özacar et al., 2006). Consequently, these vegetable polyphenols produce intermediate situations between those observed for leathers treated only with resins and leathers treated with resin and mimosa extract.

5. Conclusions

The results obtained in this work enable us to confirm that the formaldehyde content of leathers treated only with resin (melamine-formaldehyde or dicyandiamide-formaldehyde) increased with ageing when determined by colorimetric quantification. This could indicate that the retanning resins are partially hydrolysed with time with the result that more formaldehyde is released. Among the three vegetable compounds considered (mimosa, quebracho and tara), mimosa showed the highest capacity to reduce the formaldehyde content of the resin-treated leathers. This can be explained by the high reactivity of the polyphenols of the mimosa extract towards formaldehyde. This capacity is accentuated with ageing. Therefore, due to the influence of ageing, the formaldehyde content in leather will depend on when the quantitative determination is carried out. The lower the formaldehyde content in leathers, the higher the capacity of vegetable compounds to reduce formaldehyde content. This is of great importance in baby's leather articles, in which the formaldehyde content is low, and therefore, the addition of a small amount (3%) of vegetable compounds (especially mimosa) in the leather production process guarantees that the formaldehyde content is maintained below the allowable limits (16 mg/kg in the most restrictive regulation). Reducing the formaldehyde content using the polyphenols contained in vegetable compounds constitutes a good alternative not only in the leather sector but also in other industrial sectors (wood, textile, etc.) that use formaldehyde resins.

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FIGURE CAPTIONS

Figure 1. Influence of the addition of vegetable compounds on the formaldehyde content of leather treated with Melamine-Formol (A) resin

Figure 2. Reduction of formaldehyde content (%) as a function of the vegetable compound added. Resin: Melamine-Formol (A)

Figure 3. Influence of the addition of vegetable compounds on the formaldehyde content of leather treated with Dicyandiamide-Formol (A) resin

Figure 4. Reduction of formaldehyde content (%) as a function of the vegetable compound added. Resin: Dicyandiamide-Formol (A)

Figure 5. Influence of the addition of vegetable compounds on the formaldehyde content of leather treated with Melamine-Formol (B) resin

Figure 6. Reduction of formaldehyde content (%) as a function of the vegetable compound added. Resin: Melamine-Formol (B)

Figure 7. Influence of the addition of vegetable compounds on the formaldehyde content of leather treated with Dicyandiamide-Formol (B) resin

Figure 8. Reduction of formaldehyde content (%) as a function of the vegetable compound added. Resin: Dicyandiamide-Formol (B)

Figure 1 revised
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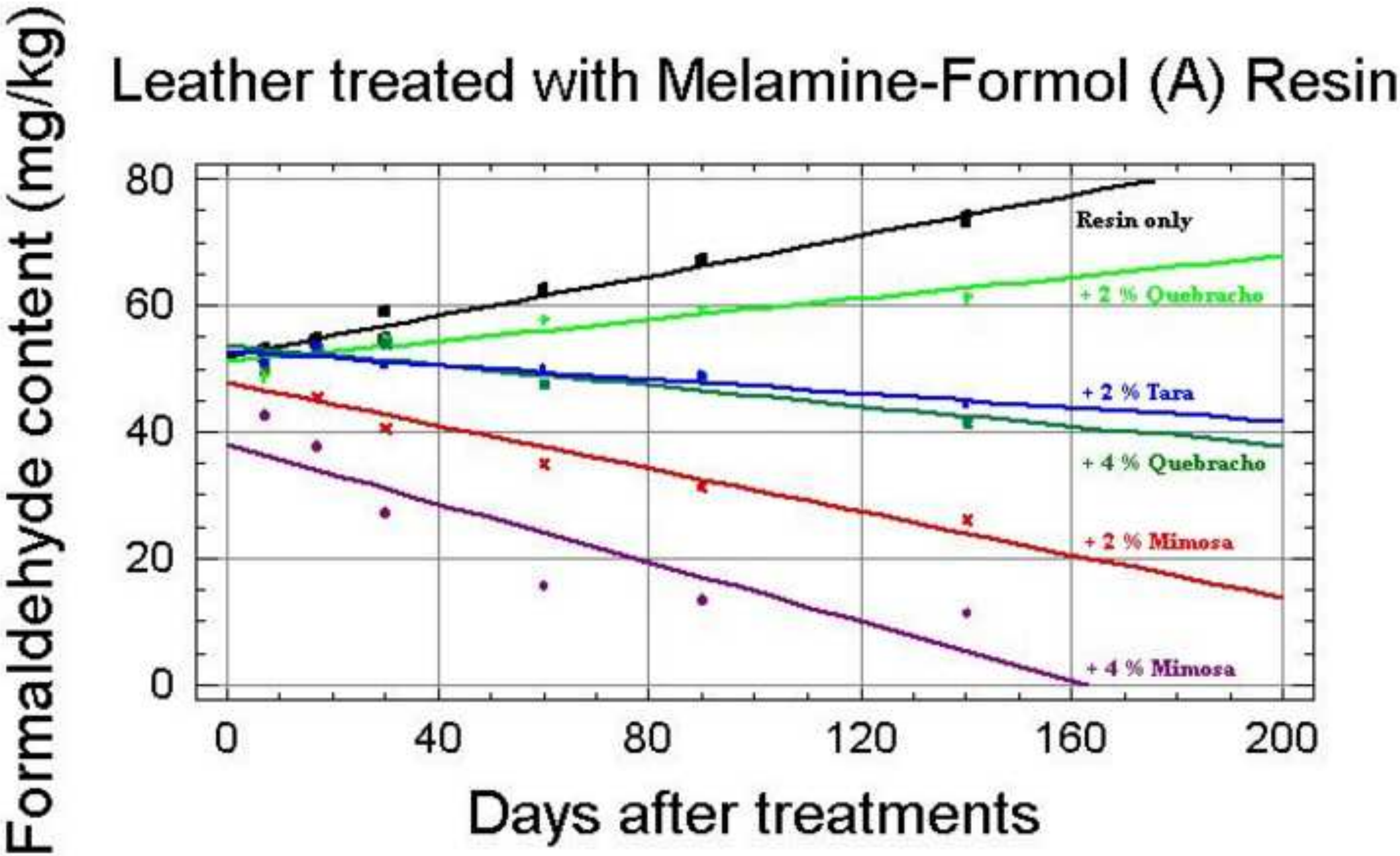

Figure 2 revised
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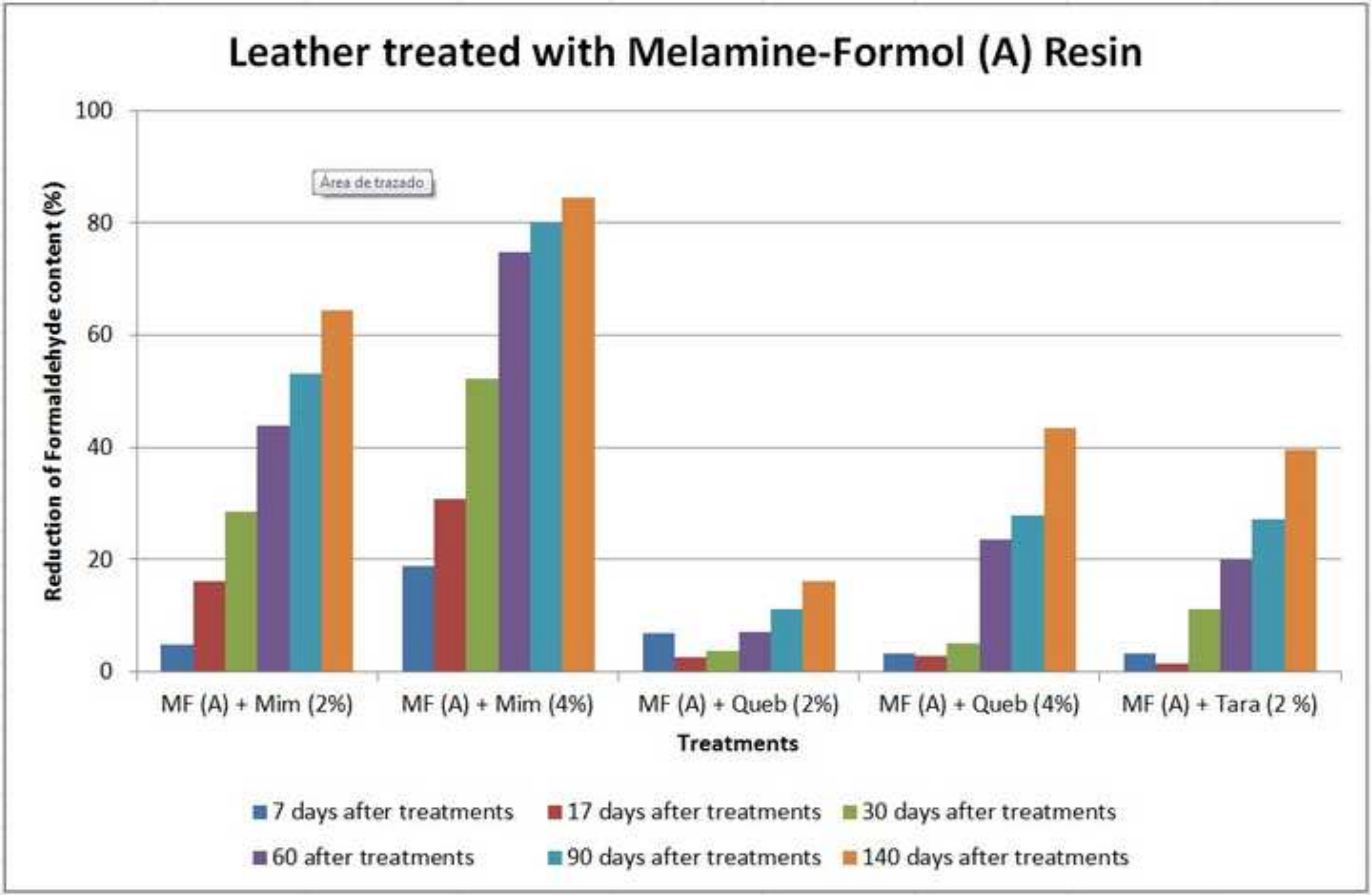

Figure 3 revised
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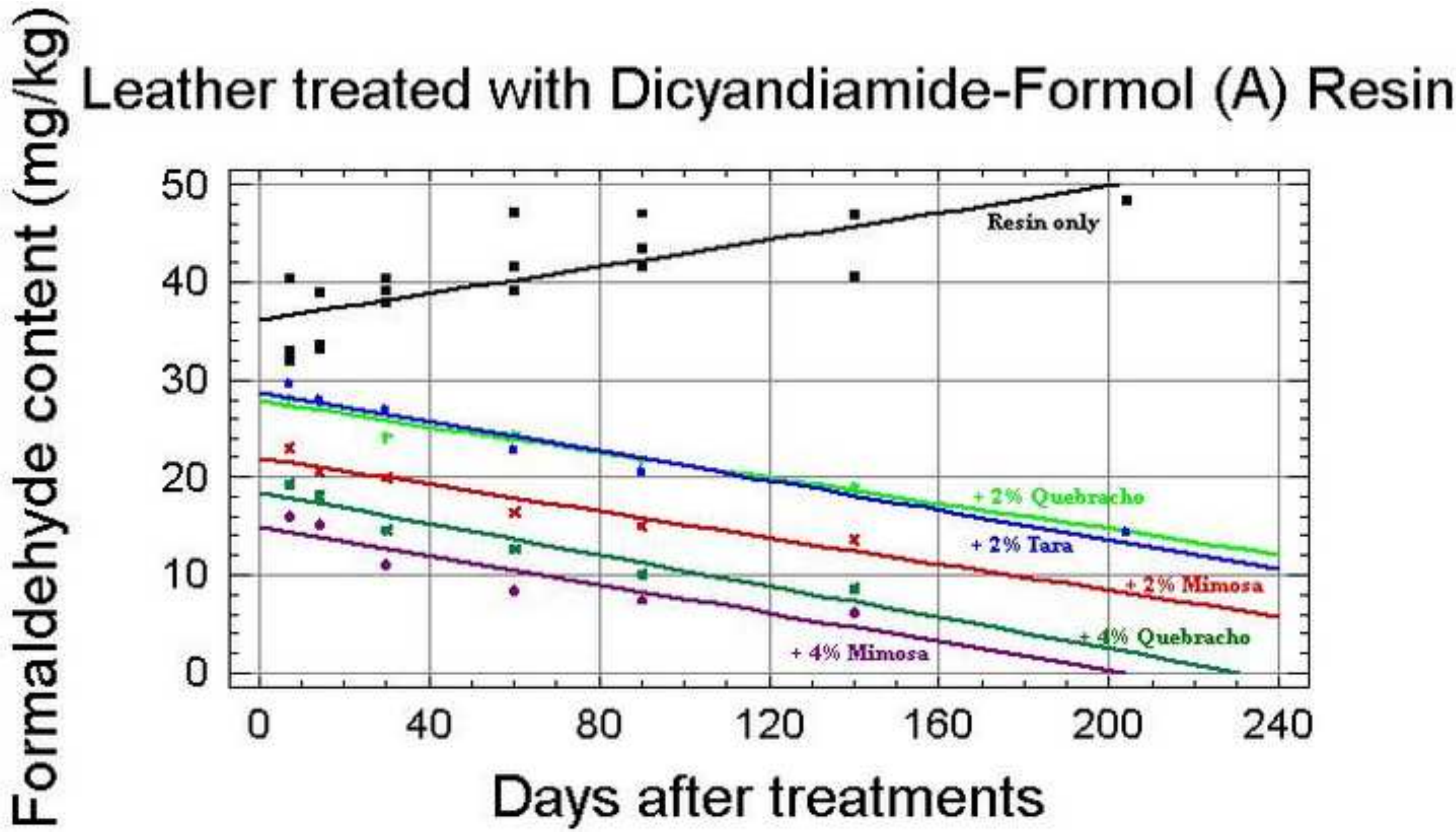

Figure 4 revised

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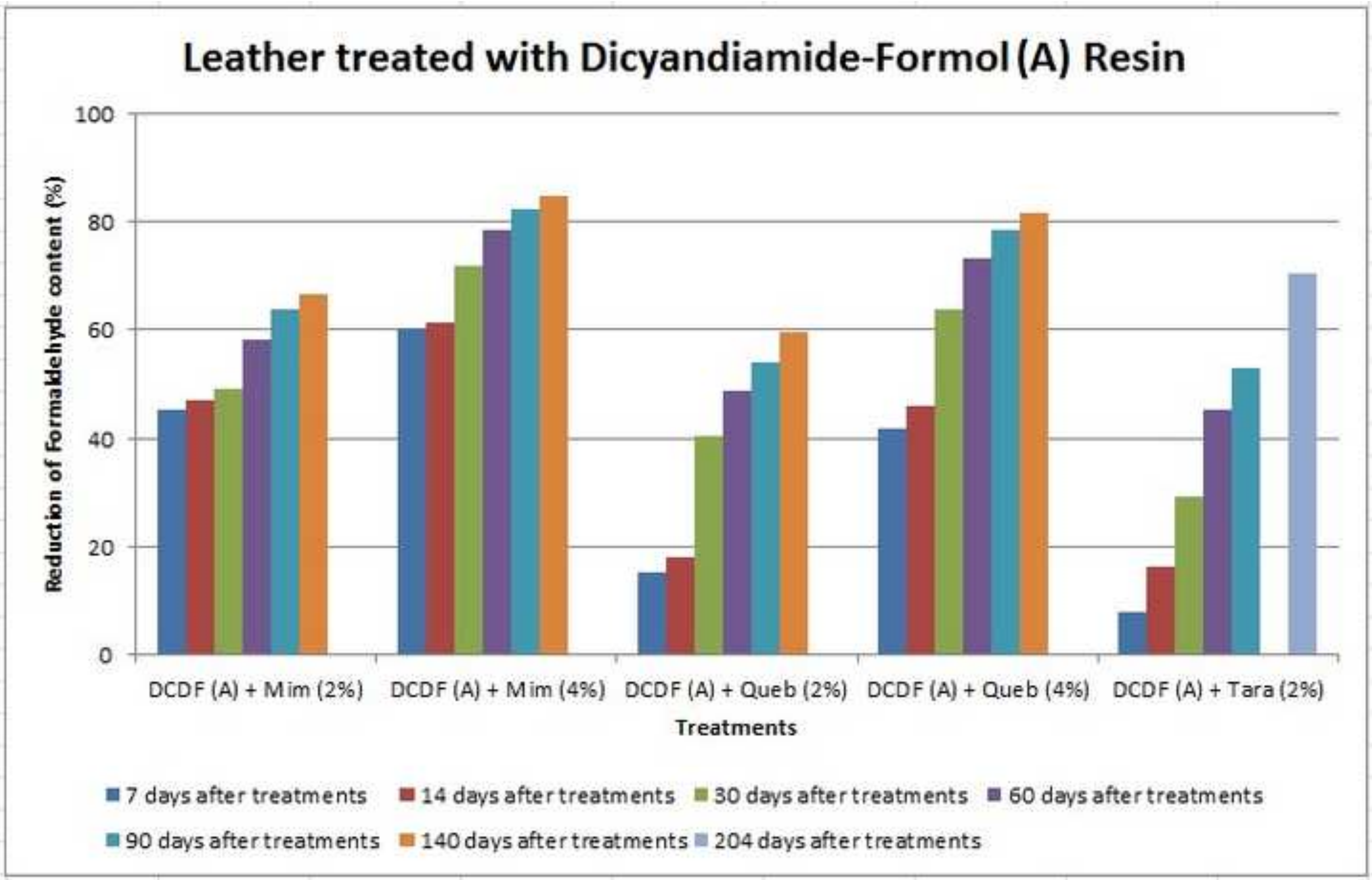

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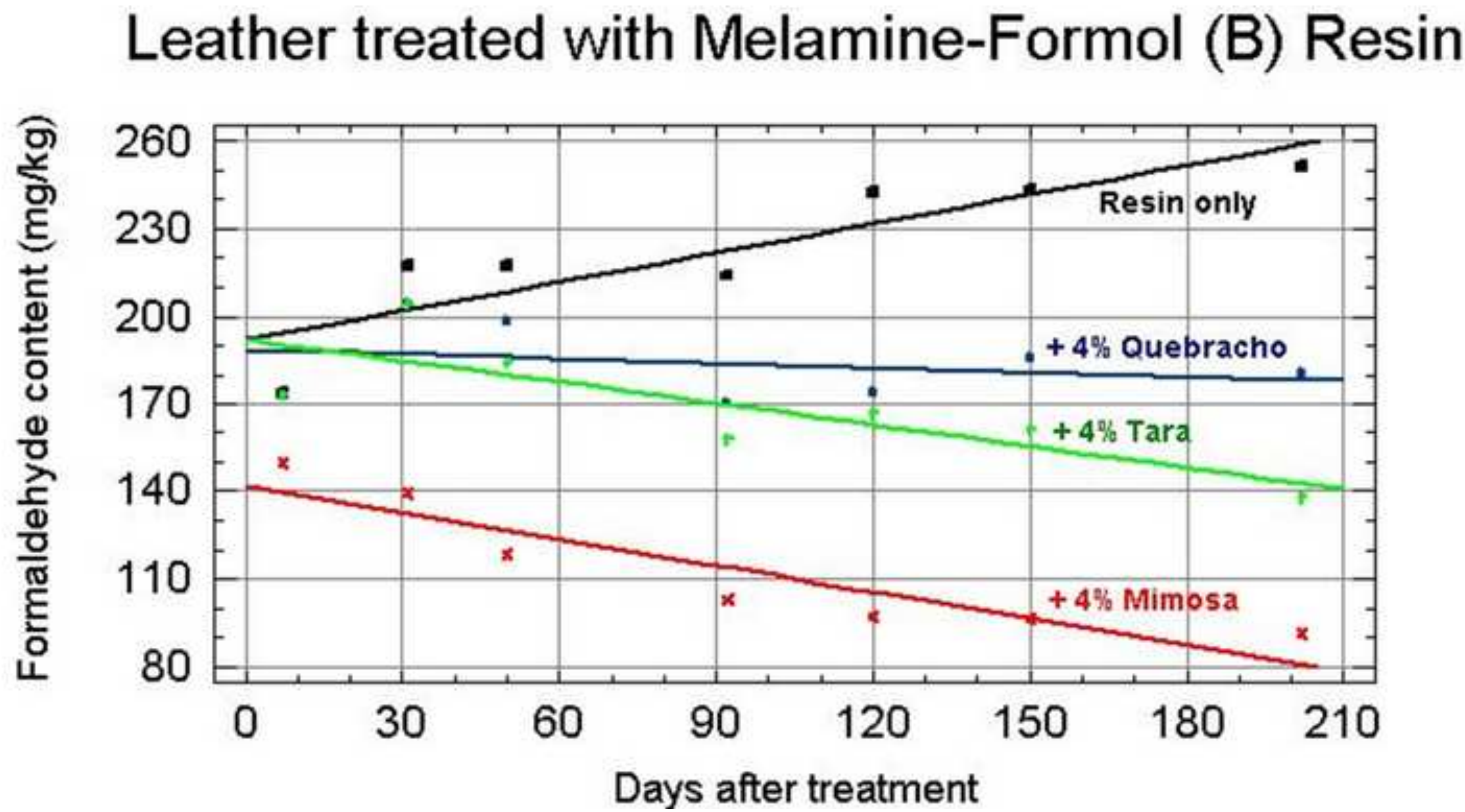

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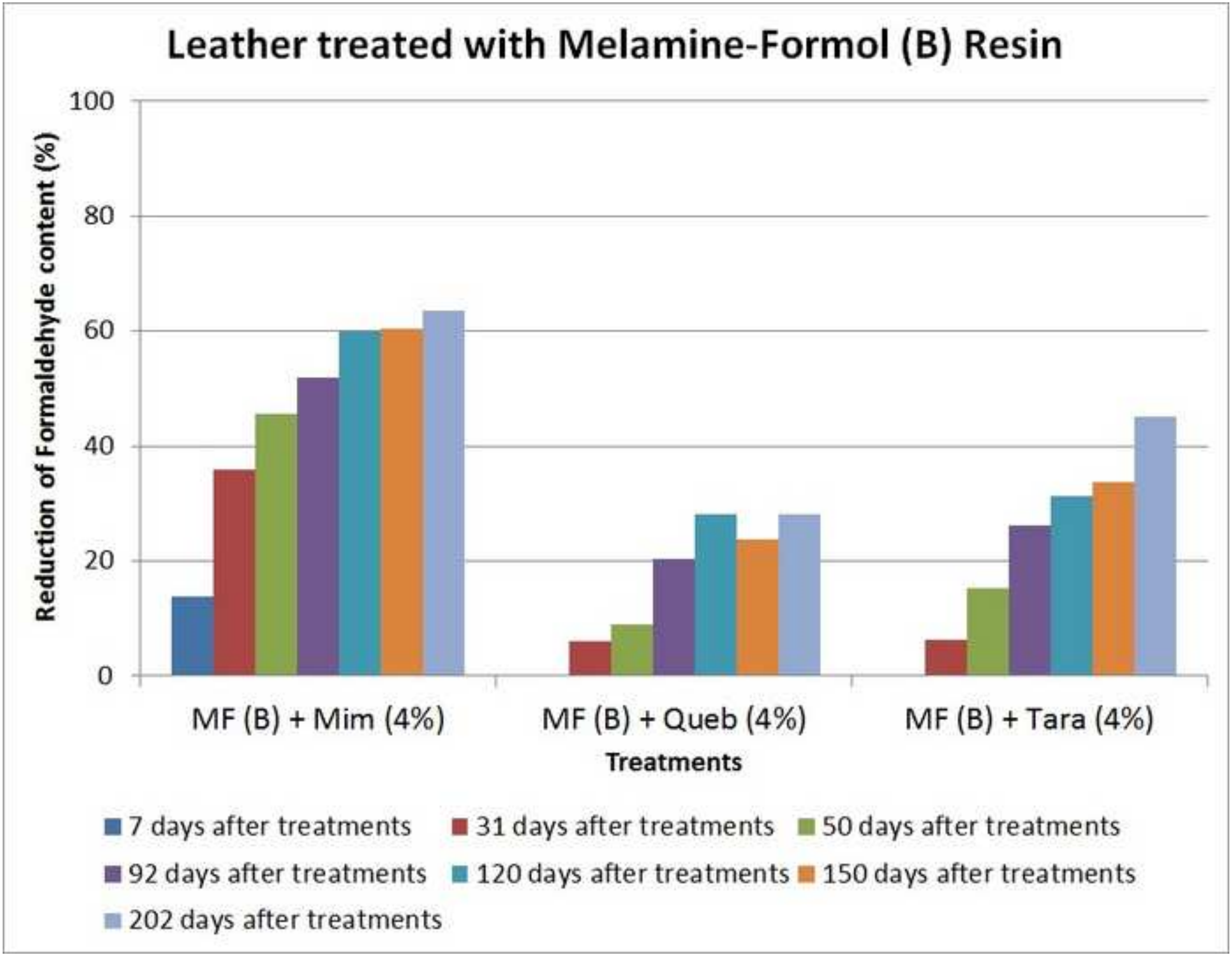

Figure 7 revised

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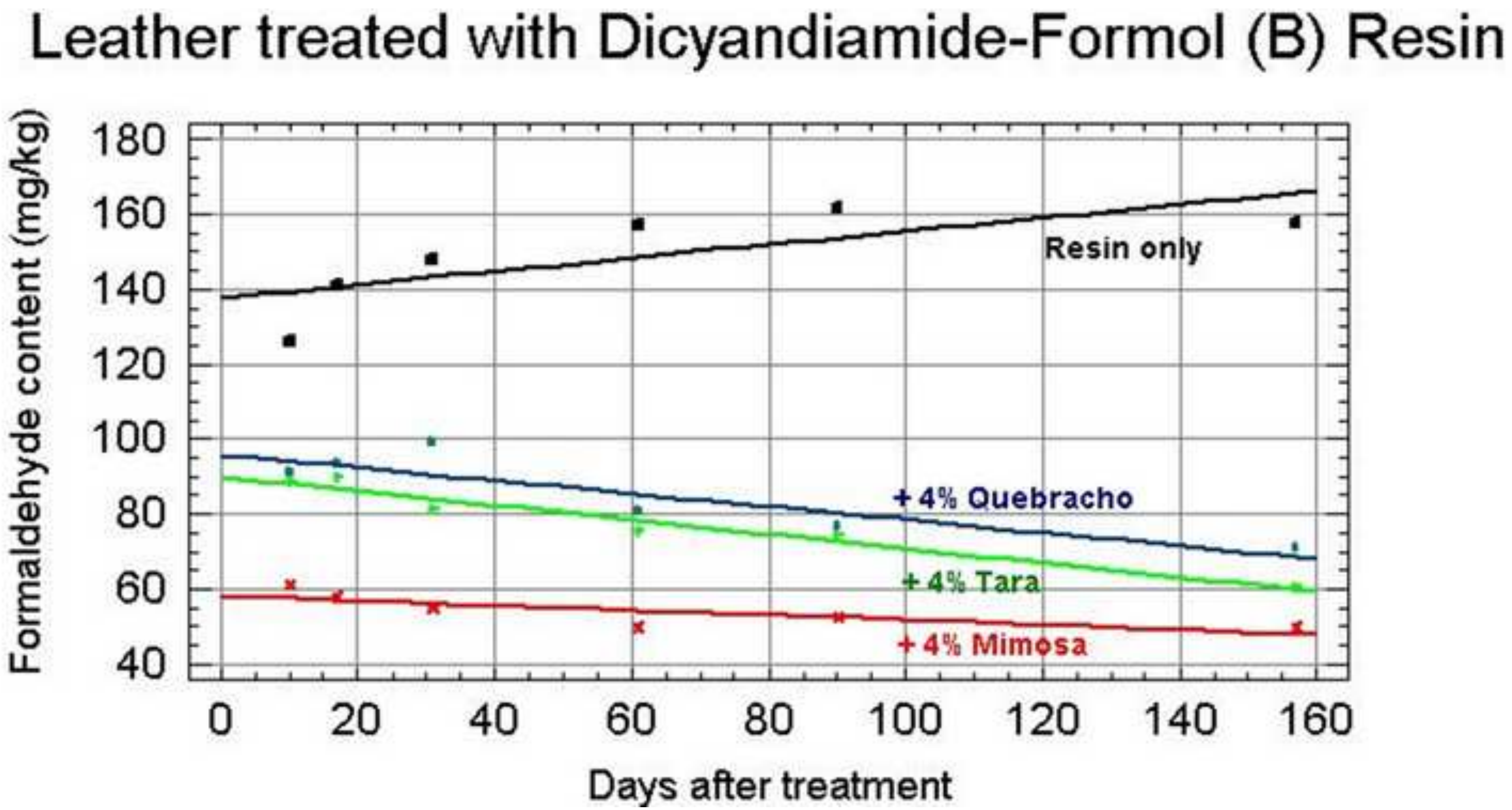

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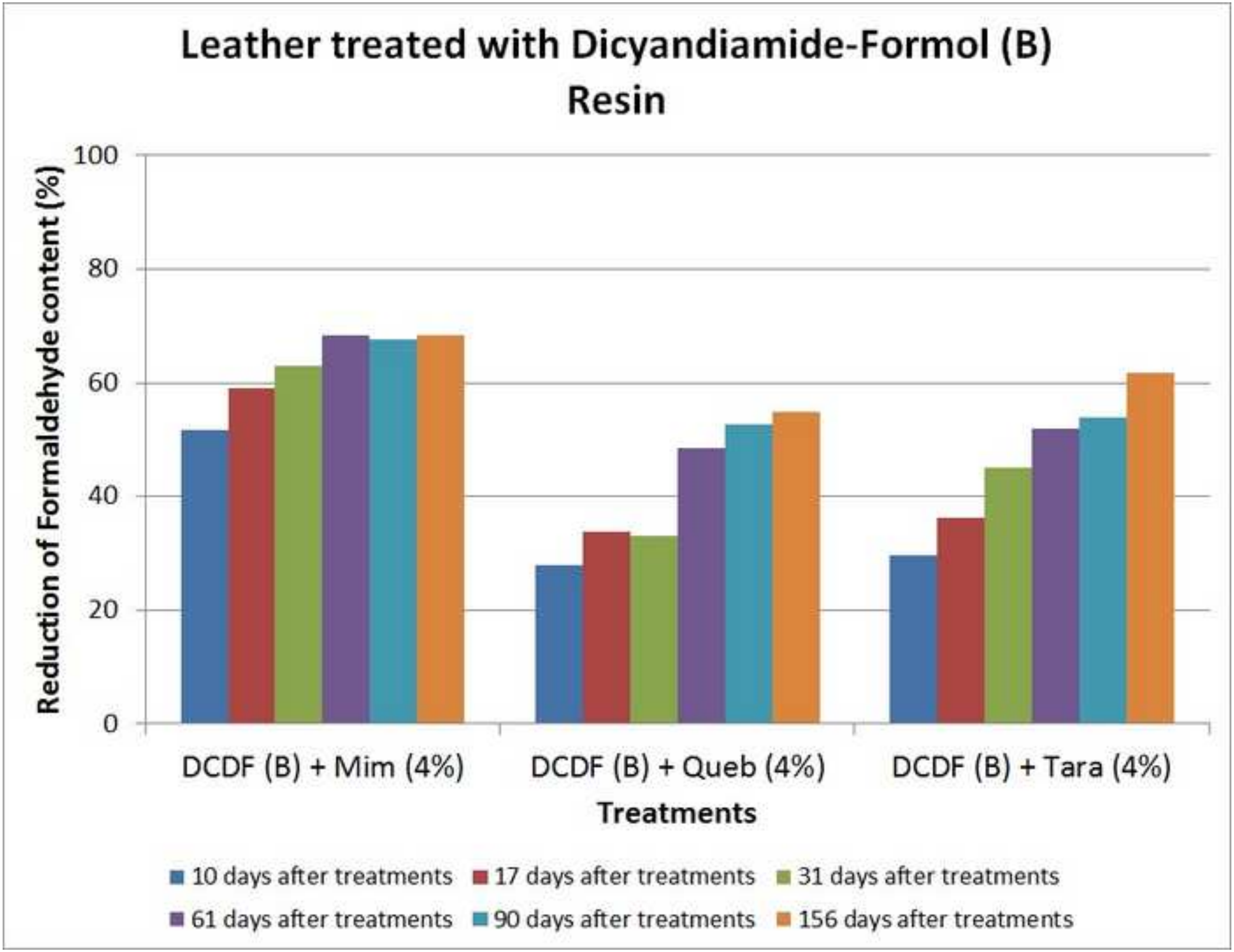

Table 1.
Content of tannins, non-tannins and polyphenols in the vegetable compounds studied, including the 95% Confidence Interval

Vegetable Compound	Chemical Supplier	Commercial Name	Tannins, %	Non-tannins, %	Total polyphenols*, %
Mimosa	Tanac	Clarotan	70.1±1.7	19.8±1.1	81.4±2.7
Quebracho	Silva	Indusol ATO	72.3±1.6	16.3±1.0	90.8±1.3
Tara	Silva	Ormotan T	49.9±1.8	17.0±1.2	67.5±1.6

* Expressed as gallic acid

Table 2

Processing of leathers. Formulation applied

Starting material: Butts of 1.5 mm wet-blue splits

Process	**%**	**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		
	3	Acrylic Resin		60’	
	5	Formaldehyde resins*		60’	
	x**	Vegetable compound		60’	
Fatliquoring	100	Water	50		
	8	Synthetic sulphated oil			
	4	Phosphoric ester based oil		60’	
	1	Formic Acid (1:10)	cold	30’	
	1	Formic Acid (1:10)	cold	30’	
Washing	150	Water		3’	

Horse up (24 hours), setting out (by hand)
Air dry (toggle)
stake
Analytical determinations

***** Depending on the experiment, the formaldehyde resins used were:

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

**x: offer of vegetable compound used depending on the experiment: 2% or 4%

Table 3

Regression equations of formaldehyde content [FC] as a function of the number of days after treatment ND for leathers retanned with formaldehyde resins of low formaldehyde content (A), according to the equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$, including the 95% Confidence Interval for both $[FC]_0$ and $[FC]_{rate}$.

Regression lines	**Retanning Treatments**	**$[FC]_0$ (mg/kg)**	**$[FC]_{rate}$ (mg/kg)**	**r**
Figure 1	MF (A)	51.94±1.22	+0.16±0.02	+0.99
	MF (A) + Mimosa (2%)	47.88±4.82	-0.17±0.07	-0.96
	MF (A) + Mimosa (4%)	38.01±12.22	-0.23±0.17	-0.90
	MF (A) + Quebracho (2%)	51.05±3.55	+0.08±0.05	+0.92
	MF (A) + Quebracho (4%)	53.77±4.05	-0.08±0.06	-0.90
	MF (A) + Tara (2%)	52,78±2.61	-0,06±0.04	-0,91
Figure 3	DCDF (A)	36.12±2.61	+0.07±0.03	+0.75
	DCDF (A) + Mimosa (2%)	22.04±2.34	-0.07±0.03	-0.95
	DCDF (A) + Mimosa (4%)	14.91±3.48	-0.07±0.05	-0.91
	DCDF (A) + Quebracho (2%)	27.92±1.96	-0.07±0.03	-0.96
	DCDF (A) + Quebracho (4%)	18.55±2.75	-0.08±0.04	-0.95
	DCDF (A) + Tara (2%)	28.81±2.10	-0.08±0.02	-0.98

MF: Melamine-Formaldehyde; DCDF: Dicyandiamide-Formaldehyde

$[FC]_0$: the initial formaldehyde content; $[FC]_{rate}$: variation of content vs. ND

r: linear correlation coefficient

Table 4
Regression equations of formaldehyde content [FC] as a function of the number of days after treatment ND for leathers retanned with formaldehyde resins of high formaldehyde content (B), according to the equation $[FC] = [FC]_0 + [FC]_{rate} \times ND$, including the 95% Confidence Interval for both $[FC]_0$ and $[FC]_{rate}$.

Regression lines	**Retanning Treatments**	**$[FC]_0$ (mg/kg)**	**$[FC]_{rate}$ (mg/kg)**	**r**
	MF (B)	192.00±24.23	+0.33±0.21	+0.87
Figure 5	MF (B) + Mimosa (4%)	141.76±17.64	-0.30±0.16	-0.91
	MF (B) + Quebracho (4%)	188.40±23.67	-0.05±0.21	-0.27
	MF (B) + Tara (4%)	192.17±23.04	-0.24±0.20	-0.81
	DCDF (B)	137.73±17.55	+0.18±0.22	+0.75
Figure 7	DCDF (B) + Mimosa (4%)	58.18±5.49	-0.06±0.07	-0.79
	DCDF (B) + Quebracho (4 %)	95.89±9.79	-0.17±0.12	-0.89
	DCDF (B) + Tara (4%)	90.10±5.01	-0.19±0.07	-0.97

MF: Melamine-Formaldehyde; DCDF: Dicyandiamide-Formaldehyde
$[FC]_0$: the initial formaldehyde content; $[FC]_{rate}$: variation of content vs. ND
r: linear correlation coefficient