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## DYESTUFFS AND FORMALDEHYDE CONTENT IN SPLIT LEATHER TREATED WITH FORMALDEHYDE RESINS

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### Abstract

Formaldehyde resins are present in textile, leather and wood industries. Due to the harmful character of formaldehyde, different alternatives have been found to exclude or reduce its content on processed goods. However, the effect of dyestuffs on the formaldehyde content of goods containing formaldehyde-synthesized resins has not been studied up to date. The aim of this work is to check if the presence of free amino groups in the structure of dyestuffs exerts an influence on the formaldehyde content on leathers treated with formaldehyde-synthesized resins. Six dyes, belonging to three different families (acid dyes, direct dyes and basic dyes), have been taken as examples to evaluate how their structures affect the reaction with formaldehyde present in leather. The variation of the formaldehyde content in dyed leathers with respect to control samples (treated with resin only) and its evolution with time have been also considered.

It has been found that the ability of dyes in reducing the formaldehyde content in leather depends on the amount of amino groups amenable to reaction with formaldehyde. Those amino groups that in their vicinity have other functionalities, with which to form relatively stable structures, have a reduced reactivity with formaldehyde.

The reduction ability of dyes also depends on the formaldehyde content in leather. The lower the formaldehyde content is in the leather, the higher this reduction ability. Acid Black 234 dye caused a formaldehyde content reduction of approximately 84% in leathers treated with melamine-formaldehyde resin of low formaldehyde content in the analysis carried out after 90 days of leather processing whereas the reduction was approximately 20% when the resin was of high formaldehyde content.

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62 The highest reduction ability of basic dyes corresponded to the dye that has the greatest  
63 amount of amino residues amenable to reaction with formaldehyde (Basic Orange 2).  
64 Basic Orange 2 dye exhibited higher reduction ability (90% of reduction in leathers  
65 treated with resin of high formaldehyde content after 90 days of leather processing) than  
66 the Acid Black 234 dye (approximately 20%), both containing similar amount of free  
67 amino residues. Thin layer chromatography analysis revealed that the Basic Orange 2  
68 dye is mainly a single major component, while the Acid Black dye 234 is a mixture of  
69 components that can have a reduced reactivity with formaldehyde. Further experiments  
70 are required to investigate if the surface leather dyeing (Basic Orange 2 dye) have a  
71 higher influence on formaldehyde content reduction than the through-dyeing (Acid  
72 Black 234 dye).  
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81 *Keywords:* dyes-formaldehyde interaction; acid/basic dyes; formaldehyde resins;  
82 formaldehyde content reduction; leather, textile, wood industries.  
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121 **1. Introduction**  
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123 Many international organizations encourage the implementation of cleaner technologies  
124 in leather and textile processing [1, 2, 3]. These cleaner technologies must be  
125 developed to prevent the presence of some restricted chemicals, which take part in the  
126 formulation of commercial products used at various stages of the tannery processes.  
127 Due to its carcinogenic character [4, 5], formaldehyde is one of these chemicals  
128 included in the “restricted substances list” of major brands.  
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130 Different alternatives have been proposed to exclude the presence of formaldehyde in  
131 leather: use of protein or acrylic syntans [6, 7], or to reduce its content to allowed levels:  
132 application of formaldehyde scavengers for leather substrate [8] or for wood substrate  
133 [9, 10]. In a previous study [11], the ability of four scavengers (ethylene urea,  
134 pyrogallol, gallic acid and hydroxylamine sulphate) on reducing the formaldehyde  
135 content in leathers treated with formaldehyde resins was studied. The authors found  
136 that, although the four chemicals reduce at different extent the formaldehyde content,  
137 some of them have certain disadvantages  
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139 Other authors have proposed the use of plant extracts to reduce the formaldehyde  
140 content in leathers pre-tanned with formaldehyde [12, 13] or the addition of plant  
141 extracts to urea-formaldehyde resins to reduce the emission of formaldehyde from  
142 panels of medium density fibreboard [14]. The effect of the polyphenols (tannins and  
143 non-tannins) contained in some vegetable compounds (mimosa, quebracho and tara),  
144 normally used in tanning/retanning processes, on the reduction of formaldehyde content  
145 in leathers treated with formaldehyde-synthesized resins has been also studied [15]. The  
146 authors found that the high reactivity of the polyphenols of the mimosa extract towards  
147 formaldehyde led to the highest reduction of the formaldehyde content and that this  
148 capacity was accentuated with ageing.  
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150 However, no work has been found in literature dealing with the interaction  
151 formaldehyde- leather dyeing. How dyestuffs can interact with formaldehyde present in  
152 leather has not been studied.  
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154 Leather is dyed to improve its appearance, to make it adaptable for fashion styling and  
155 to increase its value as a commodity. Dyestuffs suitable for leather may be grouped into  
156 anionic and cationic types. Anionic dyes are alkali salts of dye acids; cationic dyes  
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180 (known as basic dyes) are the acid salts of dye bases [16]. Anionic dyes constitute the  
181 greater portion of the dyes used for leather and include acid dyes, direct dyes, mordant  
182 dyes and metal complex dyes.  
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186 The aim of this work is to study the possible effect of the dyeing process on the  
187 formaldehyde content in split leather treated with formaldehyde resins. In particular, the  
188 work is focused to investigate if the presence of free amino groups in the dye structure  
189 causes a reduction in the formaldehyde content of leather treated with formaldehyde-  
190 synthesized resins. The authors believe that the reaction between the amino groups of  
191 the dyes and formaldehyde may decrease the formaldehyde content in leather. The  
192 evolution of formaldehyde content with time and its variation with respect to the  
193 samples treated with resin only (control samples) are also considered.  
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## 199 **2. Materials and methods**

### 200 **2.1 Materials**

#### 201 **2.1.1 Starting material: split leather**

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204 Butts of wet-blue splits shaved to a thickness of 1.5 mm of German origin supplied by  
205 Despell S.A. were used as the starting material. This starting material is characterized  
206 by its homogeneity which minimizes the variation in chemicals absorption, facilitating  
207 their penetration.  
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#### 213 **2.1.2 Formaldehyde-based resins**

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215 The resins used in this study are the same as those employed in previous works [11, 15].  
216 They result from the condensation reaction between formaldehyde with melamine (MF)  
217 and dicyandiamide (DCDF). Resins were selected as a function of their formaldehyde  
218 content: low formaldehyde content (termed A) and high formaldehyde content (termed  
219 B) and were used one or another depending on the experiment. The formaldehyde  
220 content in the resins were analysed in accordance with the method described in Section  
221 2.2.3, providing the following mean values  $\pm$  95% confidence intervals of five  
222 replicates: MF (A): 4514 $\pm$ 326 mg/kg; DCDF (A): 6428 $\pm$ 466 mg/kg and MF (B):  
223 23481 $\pm$ 369 mg/kg.  
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### 2.1.3 Dyes employed

The influence of six dyes belonging to three different families (acid dyes, direct dyes and basic dyes) on the formaldehyde content in split leather treated with formaldehyde resins was studied.

Acid Dyes derive their affinity entirely from acid groups within the molecule and behave quite similarly to moderately strong acids. The acid dyes studied in this work are: Acid Red 337 (Colour Index: 17102); Acid Brown 83 (Colour Index: 20250) and Acid Black 234 (Colour Index: 30027).

Direct dyes are also known as cotton dyes. They can be used on cotton fibres without a mordant. The term direct has little significance in chrome leather dyeing. These dyes are generally more of the surface dyeing than acid type. Direct Black 168 (Colour Index: 30420) has been considered in this study.

Basic dyes (called cationic dyes) are applied to substrate with anionic character where electrostatic attractions are formed. They are called cationic dyes because the chromophore in basic dye molecules contains a positive charge. The basic dyes react on the basic side of the isoelectric points. As examples of basic dyes, Basic Brown 1 (Colour Index: 21000:1) and Basic Orange 2 (Colour Index: 11270) have been taken in this study.

All dyes were supplied by Trumpler Española S.A., and they were applied following its recommendations. Figure 1 shows the chemical structure of the dyes considered in this work.

**(Figure 1)**

## 2.2 Methods

### 2.2.1 Processing of leathers. Experiments carried out

Once received from the tannery, all the splits were subjected to a common process of rechroming and neutralization up to pH of 5.2-5.4 as shown in Table 1. Retanning was carried out with a 3% of a commercial acrylic resin and 5% of formaldehyde-synthesized resins. Depending on the formaldehyde content of the resins, two series of experiments were performed: i) Dyeing treatments of splits treated with resins of low

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298 formaldehyde content ((MF (A) and DCDF (A)) and ii) Dyeing treatments of splits  
299 treated with resins of high formaldehyde content ((MF (B) and DCDF (B)). The goal  
300 was to determine the effect that different dyes had on the formaldehyde content in  
301 leathers treated with resins of different formaldehyde content. After dyeing, a  
302 conventional fatliquoring process was carried out with chemicals of common use in the  
303 leather industry, supplied by Pulcra Chemical S.L. Once treated in accordance with the  
304 formulation of Table 1 and after drying, the leathers were analysed for formaldehyde  
305 content in accordance with the EN ISO 17226 Standard. Part 2 [17]. Given that in a  
306 previous work [15], it was found that the formaldehyde content in leathers treated with  
307 formaldehyde resins and retanned with vegetable compounds varied with ageing,  
308 analyses were performed at different times after leather processing. During this period,  
309 the samples for analysis were maintained in the dark, inside airtight plastic bags, in a  
310 standard atmosphere at 23°C and 50% relative humidity [18] to have them always at the  
311 same conditions.  
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321 **(Table 1)**

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323 **2.2.2 Analysis of formaldehyde content in leather**

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326 The formaldehyde content in split leathers was determined in accordance with the EN  
327 ISO 17226 Standard. Part 2 [17]. Given that the method described in the Standard is a  
328 little bit ambiguous, it is very important to clearly define the conditions of the extraction  
329 of formaldehyde from leather. The results of formaldehyde content in leather depend on  
330 the shaking method used in the extraction [19], therefore, this should be clearly  
331 described. The leather was extracted by gently shaken ( $40\pm 1$  rpm) in a reciprocal linear  
332 shaker (Selecta, Unitronic) with a 0.1% solution of sodium dodecyl sulphate. In a  
333 previous work [20], it was found that this surfactant gave similar results to those  
334 obtained with the more expensive sodium dodecyl sulphonate, which is suggested by  
335 the Standard. No variations were made, relative to the Standard, on the quantitative  
336 determination of the extracted formaldehyde through the reaction with acetylacetone.  
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344 The experimental results of formaldehyde content for each treatment, shown in Tables 3  
345 and 4, are the mean value of six measurements corresponding to three replicates for  
346 each of two analysed samples.  
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### 2.2.3 Analysis of formaldehyde content in formaldehyde resins

The determination of the formaldehyde content in the formaldehyde-synthesized resins was performed following an adaptation of the EN ISO 17226 Standard. Part 1 [21]. The quantification of the formaldehyde extracted from the resin with sodium dodecyl sulphate solution was carried out by HPLC after reaction with dinitrophenylhydrazine. Five replicates of the analysis of formaldehyde content in the resins were performed.

### 2.2.4 Determination of the inorganic matter in dyestuffs

Given that there is no official method for the determination of inorganic matter in dyes, this analysis was performed following the EN ISO 4047 Standard [22] with modifications. A given amount of the dyestuff (2 g) was carefully burnt over a low flame (Bunsen) in an open crucible until fumes were no longer visible. Afterwards, the crucibles were placed in a muffle furnace set to 550 °C for 6 hours until complete ashing, cooled in the desiccator and weighed. The mean values  $\pm$  95% confidence intervals of three replicates of the inorganic matter (salts) percentage in the dyes are shown in Table 2.

From the number of NH<sub>2</sub> groups present in the dyes structure, the amount of dye offered and the percentage of inorganic matter in dye formulations, it was possible to estimate the amount of amino residues given for a quantity of leather (100 g) (Table 2).

**(Table 2)**

### 2.2.5 Thin layer chromatography of dyestuffs

In order to check if in the dye manufacturing process a single major component was produced or was a mixture of components, thin layer chromatography (TLC) of several dyes (Acid Black 234, Basic Brown 1 and Basic Orange 2) was carried out by using silica gel 60 F<sub>254</sub> plates (Merck, ref. 1.05554.0001). 50  $\mu$ L of a 1% dye solution were placed at the starting point of the plates and were developed by using the following solvents: n-butanol, 20 mL; glacial acetic acid, 10 mL; distilled water, 50 mL for basic dyes; and n-butanol, 15 mL; acetone, 15 mL; 25 % ammonia, 6 mL; distilled water, 3 mL for acid dyes. The results obtained are shown in Section 4 (Figure 10).

TLC analysis was carried out by Trumpler Española S.A.

## 2.2.6 Regression Analysis

The variation with time of formaldehyde content in leathers treated with formaldehyde-resins with/without dyeing has been estimated by means of a linear regression analysis. Table 3 (for resins of low formaldehyde content) and Table 4 (for resins of high formaldehyde content) show the results of the initial formaldehyde content,  $[FC]_0$ , and the rate of variation in content,  $[FC]_{rate}$ , as a function of the number of days elapsed after leather treatment **ND**, together with the correlation coefficient, **r**, of the fitted linear regression  $[FC] = [FC]_0 + [FC]_{rate} \times ND$ . Both tables also include the 95% confidence interval of the regression coefficients. For each point of the regression lines, the formaldehyde content is the average of six measurements.

## 3. Results

### 3.1 Treatments with resins of low formaldehyde content

Figure 2 shows the formaldehyde content as a function of the number of days elapsed after treatments in leathers retanned with MF (A) resin and dyed with 4% of Acid Black 234 and Acid Red 337 and without dyeing (control samples).

#### (Figure 2)

To determine with more precision the variation in formaldehyde content  $[FC]$  with the number of days **ND** elapsed after treatment, the two split leather retanned with MF (A) resin without dyeing (control samples) were grouped. Table 3 shows the linear regression analysis of the formaldehyde content versus time (see Section 2.2.6).

#### (Table 3)

For the control samples, the variation of formaldehyde content with time resulted in a growth of  $+0.20 \pm 0.04$  mg/kg of formaldehyde per day elapsed after treatment. As reported in a previous study [15], 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 dyeing process with 4% of Acid Black 234 resulted in a decrease in the initial formaldehyde content from  $51.51 \pm 4.86$  to  $17.77 \pm 4.20$  mg/kg while the reduction rate was not significantly different from zero ( $-0.04 \pm 0.06$  mg/kg per day elapsed). When 4

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475 % of Acid Red 337 was employed in dyeing, a slight reduction in the rate of increase of  
476 formaldehyde content with time ( $+0.10\pm 0.06$  mg/kg) took place. The difference  
477 between the regression equations for undyed leathers (only retanned with MF (A)) and  
478 for those dyed with a 4% of Acid Red 337 was significant at 5% [23]. The Acid Black  
481 234 dye showed a greater ability than the Acid Red 337 dye in reducing the  
482 formaldehyde content in dyed leathers.  
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486 By comparing the results of formaldehyde content for each different dye with those of  
487 its reference (undyed samples), it was possible to determine the reductions in  
488 formaldehyde content (in %) by applying the following equation at each time of the  
489 analysis:  
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$$492 \text{Reduction in formaldehyde content (\%)} = \frac{([\text{FC}]_{\text{resin}} - [\text{FC}]_{\text{resin + dye}})}{[\text{FC}]_{\text{resin}}} \times 100$$

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496 Figure 3 shows the variation of the reduction of formaldehyde content with time. The  
497 formaldehyde content reduction in leathers dyed with Acid Black 234 dye was  
498 important even a few days after leather processing. This is why the reduction rate was  
499 only of  $-0.04\pm 0.06$  mg/kg per day elapsed. The reduction varied from 58 % at 7.5 days  
500 after treatment to 88 % at 203 days elapsed. Given that the formaldehyde content of the  
501 control samples ((only retanned with MF (A)) increased with ageing and that of samples  
502 dyed with Acid Black 234 dye decreased (Figure 2), the reduction in formaldehyde  
503 content, which is the difference between the two values, grew with the time elapsed  
504 after treatments. The Acid Red 337 dye showed a poor capacity for reducing the  
505 formaldehyde content of leathers treated with MF (A) resin. A reduction of the  
506 formaldehyde content of approximately 15% was observed from the analyses performed  
507 at 90 days post treatment. However, this was rather due to the increase in the  
508 formaldehyde content of the control samples than to the reduction ability of the Acid  
509 Red 337 dye.  
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519 **(Figure 3)**

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522 When results of formaldehyde content in leathers retanned with DCDF (A) resin and  
523 dyed with 4% of Acid Black 234 and Acid Red 337 and without dyeing (control  
524 samples) are examined, the same trends as those observed for the MF (A) resin were  
525 obtained (Figure 4).  
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534 **(Figure 4)**  
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536 As in the case of MF (A), the results for the two leathers retanned with DCDF (A) resin  
537 without dyeing (control samples) were grouped to obtain a higher precision in the  
538 determination of formaldehyde content as a function of the number of days elapsed. By  
539 comparing Figures 2 and 4, the formaldehyde content in leather retanned with DCDF  
540 (A) was lower than that of MF (A) treated splits. As observed in Table 3, the initial  
541 formaldehyde content for leathers treated with DCDF (A) resin was  $34.49 \pm 2.51$  mg/kg  
542 while it was  $51.51 \pm 4.86$  when MF (A) resin was used. The growth rate of formaldehyde  
543 content per day elapsed after treatment was reduced between two and three times  
544 ( $+0.07 \pm 0.02$  vs.  $+0.20 \pm 0.04$  mg/kg). This increase of formaldehyde content with time  
545 indicates that the DCDF (A) resin is progressively hydrolysed.  
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553 When the effect of the dyeing process on the formaldehyde content in leathers retanned  
554 with DCDF (A) resin is examined, Table 3 shows that a 4(%) of the Acid Black 234 dye  
555 led to a drastic decrease in the formaldehyde content from the beginning. The initial  
556 formaldehyde content decreased from  $34.49 \pm 2.51$  mg/kg to  $6.67 \pm 1.53$  mg/kg. Given  
557 that the reduction rate ( $-0.02 \pm 0.03$  mg/kg) was not significantly different from zero, it  
558 can be considered that the formaldehyde content was practically constant with time. For  
559 leathers dyed with the Acid Red 337 dye, the initial formaldehyde content was similar  
560 to that of the control samples (retanned with DCDF (A) resin without dyeing) and this  
561 dye did not significantly modify the formaldehyde content with time, with a reduction  
562 rate of  $-0.01 \pm 0.03$  mg/kg per day elapsed.  
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570 Figure 5 shows the reduction in formaldehyde content when samples retanned with  
571 DCDF (A) resin and dyed with Acid Black 234 and Acid Red 337 dyes are compared to  
572 control samples without dyeing. Most likely, due to the lower formaldehyde content in  
573 leathers retanned with DCDF (A) (Figure 4) than those with MF (A) (Figure 2), the  
574 effect of dyeing was a little bit more accentuated. However, the same trends were  
575 observed in the splits retanned with both resins. The effect of dyeing with Acid Black  
576 234 resulted in a reduction of the formaldehyde content that varied from 75 % (analysis  
577 performed at 7 days after treatments) to 92 % (analysis carried out at 204 days after  
578 treatments). The Acid Red 337 dye caused a formaldehyde content reduction that was  
579 much less marked than that of the Acid Black 234 dye. A 31.5 % was the highest  
580 reduction that occurred after 204 days of leather processing. However, given that the  
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591 formaldehyde content of leathers dyed with the Acid Red 337 dye was almost constant  
592 over time (Figure 4), the progressive increase in the reduction of formaldehyde content  
593 up to 31.5% was due to the progressive increase in the formaldehyde content of the  
594 control samples (without dyeing).  
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### 600 **(Figure 5)**

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602 The Acid Black 234 dye showed an ability in reducing the formaldehyde content in  
603 leathers retanned with low formaldehyde content resins ((MF (A) and DCDF (A)) that  
604 was much higher than that of the Acid Red 337 dye. This reduction ability was more  
605 remarkable for lower formaldehyde content in the treated leathers (retanned with DCDF  
606 (A) resin).  
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### 611 **3.2 Treatments with resins of high formaldehyde content**

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613 The formaldehyde content in splits retanned with MF (B) resin and dyed with 4% of  
614 Acid Black 234, Direct Black 168 and Acid Brown 83 and without dyeing (control  
615 samples) as a function of the number of days elapsed after treatments can be observed in  
616 Figure 6. Given that the Acid Red 337 dye showed a much lower ability than the Acid  
617 Black 234 dye in reducing the formaldehyde content in leathers retanned with low  
618 formaldehyde content resins ((MF (A) and DCDF (A)), its study was discarded. As  
619 mentioned in Section 3.1, the same tendencies were observed in the samples retanned  
620 with ((MF (A) and DCDF (A)) and dyed with Acid Black 234 and Acid Red 337 dyes,  
621 therefore, only the use of MF resin with a high formaldehyde content, MF (B), has been  
622 considered.  
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630 The three leathers retanned with MF (B) resin without dyeing (control samples) were  
631 grouped in order to determine with more precision the variation of formaldehyde  
632 content [FC] with the number of days ND elapsed after treatment. Figure 6 shows that  
633 the formaldehyde contents in leathers treated with MF (B) resin were higher than those  
634 treated with MF (A) resin (Figure 2).  
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### 639 **(Figure 6)**

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641 The results of the regression analysis are shown in Table 4. The initial formaldehyde  
642 content ( $[FC]_0$ ) of the control samples retanned with MF (B) resin (without dyeing) was  
643 more than four times ( $218.04 \pm 8.61$  mg/kg) that of samples treated with MF (A) resin  
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652 (51.51±4.86 mg/kg, Table 3). As with the MF (A) resin, the formaldehyde content in  
653 leathers retanned with the MF (B) resin increased progressively with time. The rate of  
654 increase, ( $[FC]_{rate}$ ), was similar for both resins: +0.19±0.08 mg/kg for the MF (B) resin  
655 (Table 4) and +0.20±0.04 mg/kg for the MF (A) resin (Table 3). The dyeing operation  
656 carried out with the Acid Black 234 (4%) led to a decrease in the initial formaldehyde  
657 content of leathers retanned with MF (B) resin from 218.04±8.61 mg/kg to  
658 177.23±13.38 mg/kg. This decrease was much less marked than when MF (A) resin was  
659 used as a retanning agent. Unlike the formaldehyde content in samples retanned with  
660 MF (A) and dyed with Acid Black 234 that remained practically constant over time,  
661 when MF(B) was employed, the formaldehyde content increased as the days elapsed  
662 after treatments ( $[FC]_{rate} = +0.24±0.12$  mg/kg). Most likely, this different behaviour of  
663 the Acid Black 234 dye was due to the higher formaldehyde content of the MF (B)  
664 resin. The effects of dyeing with 4% of Acid Black 234 or Direct Black 168 on the  
665 formaldehyde content of leathers retanned with MF (B) resin were similar so that no  
666 significant differences between their regression equations were observed [23]. The  
667 effect of dyeing with Acid Brown 83 on the reduction of formaldehyde content was less  
668 marked than that of the other two dyes. The initial formaldehyde content decreased from  
669 218.04±8.61 mg/kg (control samples) to 197.28±12.39 mg/kg. Given that the variation  
670 rate (+0.07±0.11 mg/kg) was not significantly different from zero, it can be considered  
671 that the formaldehyde content was practically constant with time.  
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#### 685 (Table 4)

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687 Figure 7 shows the reduction in formaldehyde content when split samples dyed with  
688 Acid Black 234, Direct Black 168 and Acid Brown 83 dyes are compared to control  
689 samples without dyeing. The differences between the three dyes were very small. As  
690 can be seen, in none of the three cases a reduction of the formaldehyde content above  
691 30% was achieved. The fact that the reduction of the formaldehyde content was almost  
692 constant over time was due to that the formaldehyde content of both dyed and non-dyed  
693 samples increased progressively.  
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699 In contrast, the effect of dyeing with Acid Black 234 on the reduction of the  
700 formaldehyde content in leathers retanned with MF (A) (Figure 3) was much higher  
701 (reduction of approximately 84% at 89.5 days after treatments).  
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#### 704 (Figure 7)



### 3.3 Treatments with basic dyes

The influence of two basic dyes (Basic Brown 1 and Basic Orange 2) on the formaldehyde content of splits retanned with MF resin of high formaldehyde content (MF (B)) was determined. Both dyes were applied at an offer of 0.75 % on shaved wet-blue weight. Formulation shown in Table 1 with a modification was followed. Dyeing process was not carried out before fatliquoring as mentioned in Table 1. Dyes were applied after fatliquoring, fixing with formic acid and washing with water. For dye application, dyes were pasted with ethanol, water and acetic acid to increase solubility.

Figure 8 shows the formaldehyde content in leathers retanned with MF (B) resin and dyed with 0.75% of Basic Brown 1 and Basic Orange 2 and without dyeing (control samples) as a function of the number of days elapsed after treatments.

#### (Figure 8)

The results of the regression analysis are shown in Table 4. The initial formaldehyde content ( $[FC]_0$ ) of the control samples retanned with MF (B) resin (without dyeing) was  $211.86 \pm 20.16$  with an increasing rate, ( $[FC]_{rate}$ ), of  $+0.37 \pm 0.17$  mg/kg. Once again the progressive hydrolysis of resins synthesized with formaldehyde is confirmed. The application of 0.75% of Basic Brown 1 resulted in a decrease of the initial formaldehyde content, ( $[FC]_0$ ), from  $211.86 \pm 20.16$  mg/kg (control samples without dyeing) to  $65.09 \pm 7.58$  mg/kg. This highlights the high capacity of the Basic Brown 1 dye in reducing the formaldehyde content in leathers retanned with formaldehyde-synthesized resins. The variation rate, ( $[FC]_{rate}$ ), was  $+0.22 \pm 0.06$  mg/kg, i.e., an increase of formaldehyde content per day elapsed after treatments significantly lower than that of the control samples ( $+0.37 \pm 0.17$  mg/kg). Most likely, this means that the ability of Basic Brown 1 is not sufficient to fully compensate for the increase in formaldehyde content due to the resin hydrolysis. Much more pronounced was the diminution in the initial formaldehyde content due to the application of a 0.75 % of Basic Orange 2 since the ( $[FC]_0$ ) dropped to  $25.51 \pm 9.35$  mg/kg. Although formaldehyde content tended to increase as a function of the time elapsed after treatments, the variation rate ( $+0.09 \pm 0.08$  mg/kg) was not significantly different from zero.

Figure 9 shows the reduction in formaldehyde content when leather samples dyed with Basic Brown 1 and Basic Orange 2 were compared to control samples without dyeing as

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770 a function of the number of days elapsed after treatments. As observed, the ability of the  
771 Basic Orange 2 dye in reducing the formaldehyde content in leather treated with MF (B)  
772 resin was higher than that of the Basic Brown 1. For the Basic Brown 1 dye, the  
773 maximum reduction of formaldehyde content (approx. 70 %) was reached at 30 days  
774 after treatments whereas for the Basic Orange 2 dye the maximum reduction was  
775 approx. 90 % after 90 days. After these periods of time, the reduction of the  
776 formaldehyde content due to both dyes decreased to approximately 62% and 84% for  
777 Basic Brown 1 and Basic Orange 2, respectively at 170 days after the treatments. This  
778 decrease that is observed in the reduction of formaldehyde content after a long time of  
779 the treatments (170 days) is mainly due to the pronounced increase in the formaldehyde  
780 content that occurs due to the hydrolysis of the resin or to certain reversibility of the  
781 reaction between the NH<sub>2</sub> groups of the dyes and the formaldehyde as observed in the  
782 case of hydroxylamine sulfate [11].  
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791 **(Figure 9)**

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794 It should be emphasized that although the application of dyes such as Acid Black 234,  
795 Direct Black 168 and Acid Brown 83 gave rise to a maximum formaldehyde content  
796 reduction of the 30% (Figure 7) in leathers retanned with MF (B) resin, the use of dyes  
797 such as Basic Brown 1 and Basic Orange 2 resulted in reductions of up to 70% and 90%  
798 respectively, as seen in Figure 9.  
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802 **4. Discussion**

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805 The decrease in the formaldehyde content in leather retanned with formaldehyde-  
806 synthesized resins by the dyeing process could be explained by the reaction between  
807 formaldehyde and the amino groups present in the dyes structure. It should be noted that  
808 the extent of this decrease is a function not only of the number of the amino groups  
809 present in the dyes but also of their relative reactivity with formaldehyde. The vicinity  
810 of other functionalities, such as -OH, -N=N- and -NO<sub>2</sub>, to the amino groups can lead to  
811 the formation of relatively stable cyclic structures mediated by hydrogen bonds. When  
812 this occurs, the reactivity of this amino group with formaldehyde can decrease.  
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819 In the treatments carried out with resins of low formaldehyde content ((MF (A) and  
820 DCDF (A)), the Acid Black 234 dye exhibited higher reduction ability of the  
821 formaldehyde content than the ability of the Acid Red 337 dye. This is most likely  
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829 related to the greater amount of amino residues provided by the Acid Black 234 dye for  
830 a certain quantity of leather (see Table 2). The structure of the Acid Black 234 dye has  
831 three NH<sub>2</sub> groups. Two of them may have a reduced reactivity with formaldehyde  
832 because of the proximity of one -OH group, in one case, and one -N=N- group in the  
833 other case. Therefore, the Acid Black 234 dye has one completely free NH<sub>2</sub> group to  
834 react with formaldehyde. The structure of the Acid Red 337 dye has only one NH<sub>2</sub>  
835 group with a -N=N- group very close to it. Therefore, due to the proximity between  
836 both groups, the formation of a relatively stable cyclic structure is possible resulting in a  
837 decreased reactivity with formaldehyde. So, the Acid Red 337 dye has no one free NH<sub>2</sub>  
838 group to react with formaldehyde. Although similar trends were observed, the effect of  
839 both dyes was a little more pronounced when DCDF (A) resin was used due to the  
840 lower formaldehyde content in leathers treated with this resin.  
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849 When a resin with high formaldehyde content (MF (B)) was used, the ability of the  
850 Acid Black 234 was, in percentage, much lower than with the resins with low  
851 formaldehyde content. Most likely, the diminution capacity of the dye is not sufficient  
852 to totally compensate the marked increase in formaldehyde content resulting from resin  
853 hydrolysis. To achieve a reduction in the formaldehyde content in a higher percentage,  
854 the dyeing process should be carried out with a greater offer of dyestuff, which is not  
855 industrially advisable. In the treatments carried out with the other two dyes (Direct  
856 Black 168 and Acid Brown 83), reductions in formaldehyde content greater than 30%  
857 were not obtained. It is important to note that completely free amino groups amenable to  
858 reaction with formaldehyde are not present in both dyes (see Table 2). As observed in  
859 Figure 1, the Direct Black 168 dye has two amino groups that may have a reduced  
860 reactivity with formaldehyde due to the proximity of an -OH group in one case, and one  
861 -N=N- group in the other. The Acid Brown 83 dye has a single amino group, with a  
862 very close -NO<sub>2</sub> group. As mentioned previously, the proximity of other functionalities  
863 to the amino group can lead to the formation of relatively stable structures resulting in a  
864 reduced reactivity of the amino group with formaldehyde. Significant differences  
865 between both dyes (Direct Black 168 y Acid Brown 83) were not observed.  
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877 Referring to the basic dyes (Basic Brown 1 and Basic Orange 2), the Basic Orange 2  
878 showed a greater ability to decrease the formaldehyde content than the Basic Brown 1.  
879 The structure of the Basic Brown 1 dye has four NH<sub>2</sub> groups. Two of them can form  
880 relatively stable cyclic structures with very close -N=N- groups with the result of  
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reduced reactivity with formaldehyde. Therefore, the Basic Brown 1 dye has two completely free NH<sub>2</sub> group to react with formaldehyde, whereas the Basic Orange 2 dye has only one completely free NH<sub>2</sub> group. However, as mentioned above, Basic Orange 2 dye showed a greater ability for formaldehyde content reduction than Basic Brown 1 dye, even having lower number of free NH<sub>2</sub> groups. Most likely, this is because, if the percentage of inorganic matter in dye formulations is considered (Table 2), the Basic Orange 2 dye provides the greatest amount of amino residues amenable to reaction with formaldehyde for a certain quantity of leather.

When comparing the ability of Acid Black 234 and Basic Orange 2 dyes (with similar amount of free amino residues, Table 2) in the reduction of formaldehyde content in leathers retanned with resins of high formaldehyde content (MF (B)), the Basic Orange 2 dye showed a higher ability. This could be because, as shown by thin layer chromatography (Figure 10), the Basic Orange 2 dye is mainly a single major component, while the Acid Black dye 234 is a mixture of components that can have a reduced reactivity with formaldehyde. However, further experiments are required to confirm this hypothesis or to investigate if the surface leather dyeing (Basic Orange 2 dye) have a higher influence on formaldehyde reduction than the through-dyeing (Acid Black 234 dye).

**(Figure 10)**

The dyestuffs considered have been taken to illustrate how their structures (presence of free amino groups, relative reactivity of these amino groups) affect the reaction with formaldehyde present in goods.

**5. Conclusions**

The ability of dyes to reduce the formaldehyde content in leather treated with formaldehyde-synthesized resins (melamine-formaldehyde and dicyandiamide-formaldehyde) depends on the amount of amino groups amenable to reaction with formaldehyde. Those amino groups that in their vicinity have other functionalities (groups -OH, -N = N-, -NO<sub>2</sub>) with which to form relatively stable structures, have a reduced reactivity with formaldehyde.

The reduction ability also depends on the formaldehyde content in leather. The lower the formaldehyde content is in leather, the greater the reduction ability. In the specific

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947 case of the Acid Black 234 dye, the reduction was of approximately 84% in leathers  
948 treated with melamine-formaldehyde resin of low formaldehyde content in the analysis  
949 carried out after 90 days of leather processing in front of approximately 20% when the  
950 resin was of high formaldehyde content.  
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954 As regards basic dyes, the highest reduction ability was that of the Basic Orange 2 that  
955 supplied the greatest amount of amino residues amenable to reaction with  
956 formaldehyde. When comparing the reduction ability of Acid Black 234 and Basic  
957 Orange 2 dyes (with similar amount of free amino residues), the Basic Orange 2 showed  
958 a higher ability. Most likely, this was due to that the Basic Orange 2 is mainly a single  
959 major component, while the Acid Black 234 is a mixture of components that can have a  
960 reduced reactivity with formaldehyde.  
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972 interpretation of results.  
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## FIGURE CAPTIONS

**Figure 1.** Structural formulas of the dyes studied in this work.

**Figure 2.** Influence of Acid Red 337 and Acid Black 234 dyes on the formaldehyde content in leathers retanned with MF (A) resin.

**Figure 3.** Reduction of formaldehyde content by the effect of the Acid Red 337 and Acid Black 234 dyes in leathers retanned with MF (A) resin.

**Figure 4.** Influence of Acid Red 337 and Acid Black 234 dyes on the formaldehyde content in leathers retanned with DCDF (A) resin.

**Figure 5.** Reduction of formaldehyde content by the effect of the Acid Red 337 and Acid Black 234 dyes in leathers retanned with DCDF (A) resin.

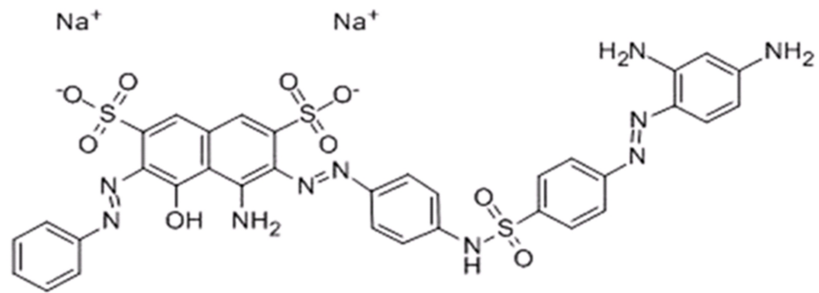
**Figure 6.** Influence of Acid Black 234, Direct Black 168 and Acid Brown 83 dyes on the formaldehyde content in leathers retanned with MF (B) resin.

**Figure 7.** Reduction of formaldehyde content by the effect of Acid Black 234, Direct Black 168 and Acid Brown 83 dyes in leathers retanned with MF (B) resin.

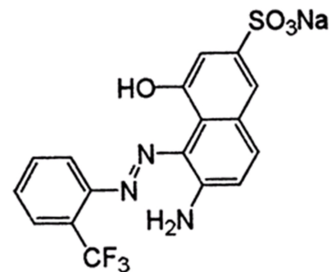
**Figure 8.** Influence of Basic Brown 1 and Basic Orange 2 dyes on the formaldehyde content in leathers retanned with MF (B) resin.

**Figure 9.** Reduction of formaldehyde content by the effect of Basic Brown 1 and Basic Orange 2 dyes in leathers retanned with MF (B) resin.

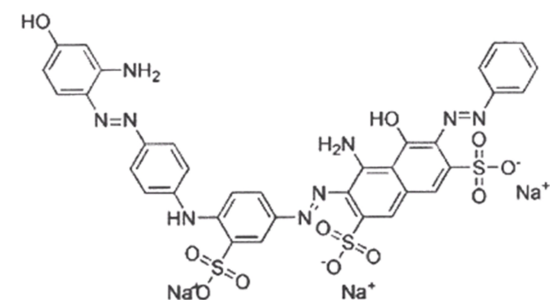
**Figure 10.** Results of the thin layer chromatography analysis for the following dyes: 1. Acid Black 234; 2. Basic Orange 2 and 3. Basic Brown 1, by using the eluents described in Section 2.2.5.



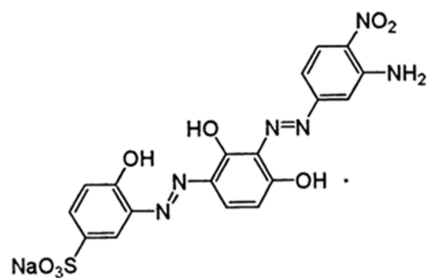
Acid Black 234 (CI: 30027)



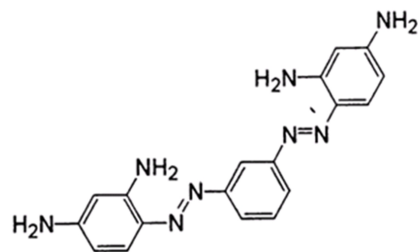
Acid Red 337 (CI: 17102)



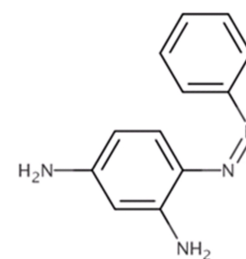
Direct Black 168 (CI: 30420)



Acid Brown 83 (CI: 20250)

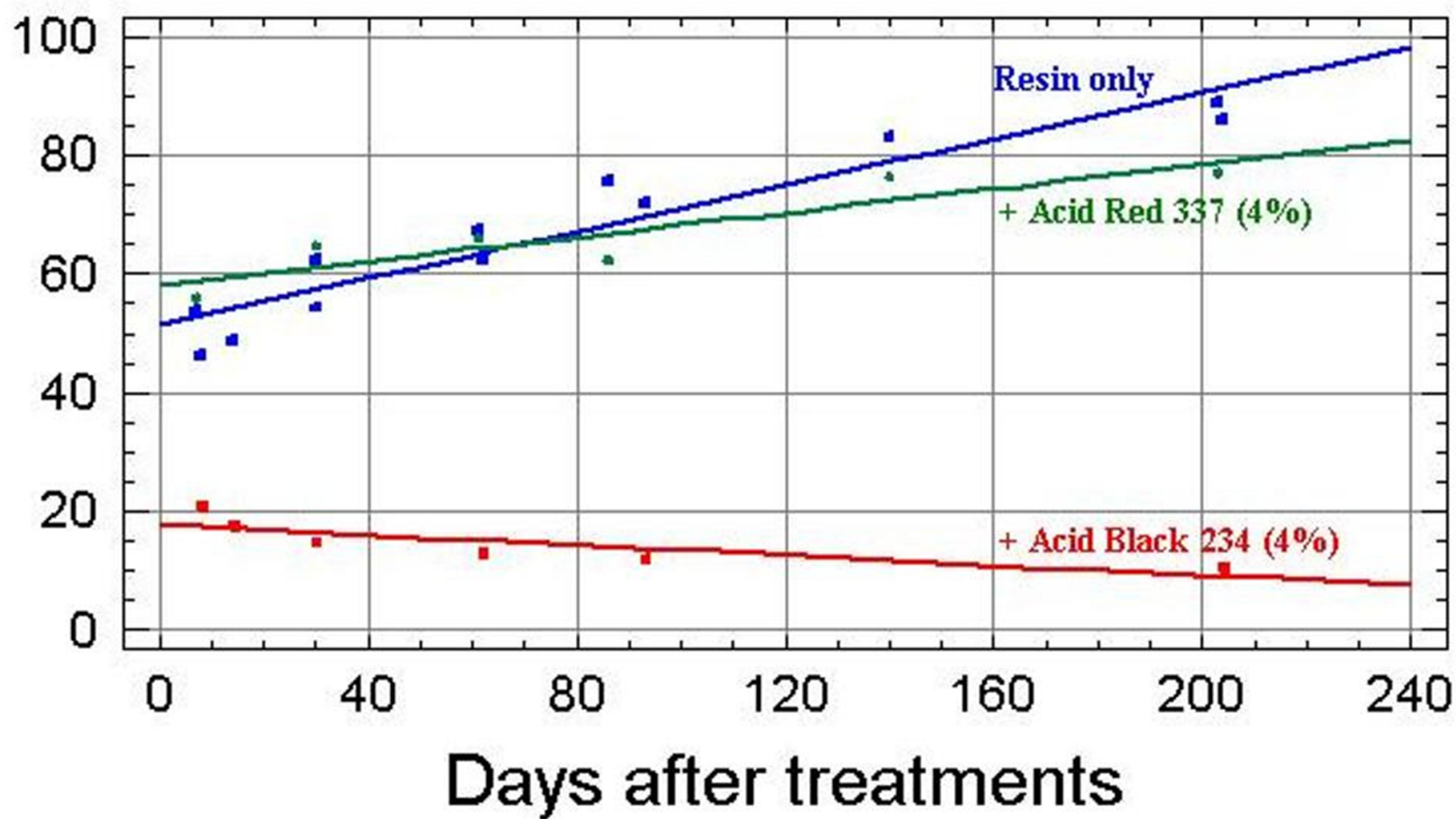


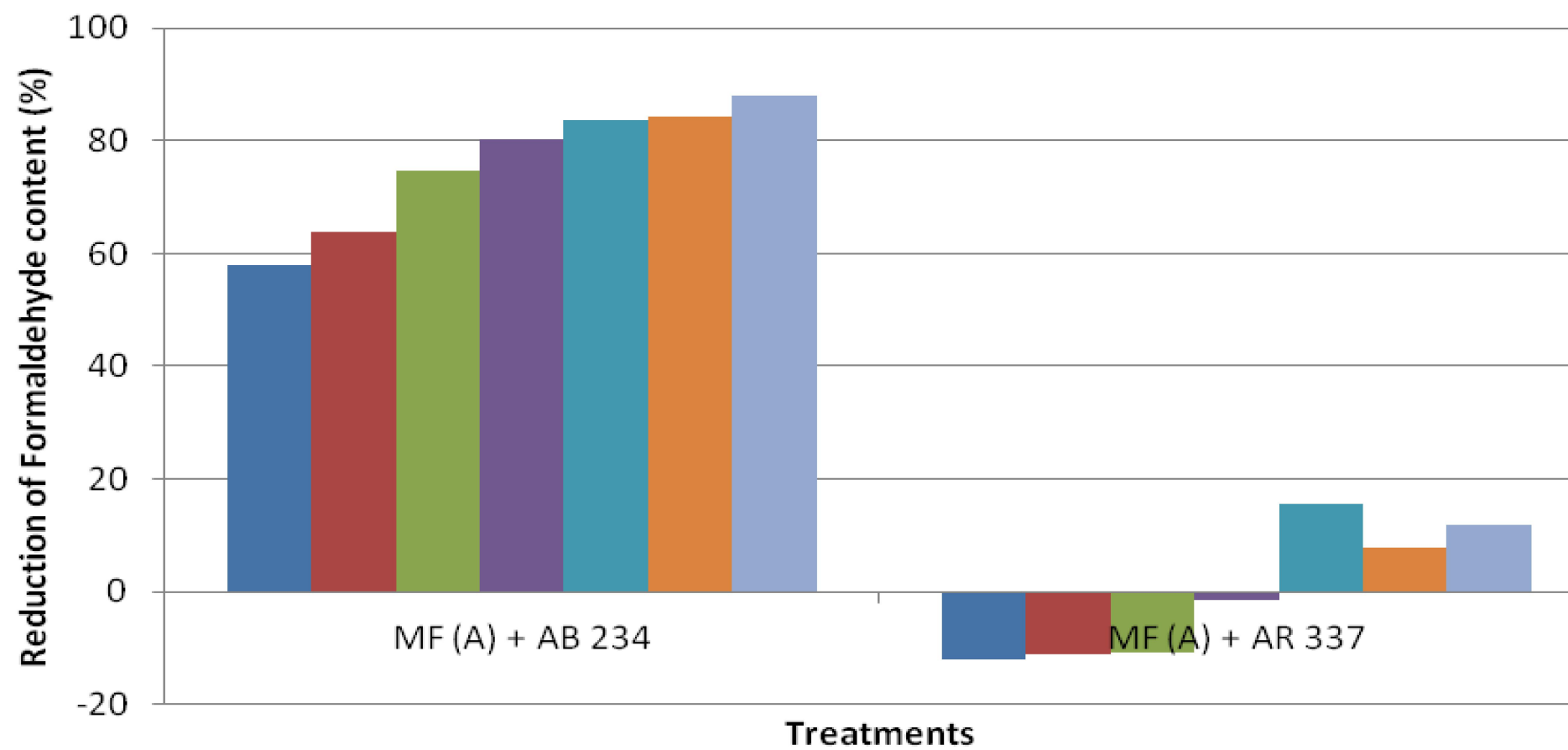
Basic Brown 1 (CI: 21000:1)



Basic Orange 2 (CI: 11270)

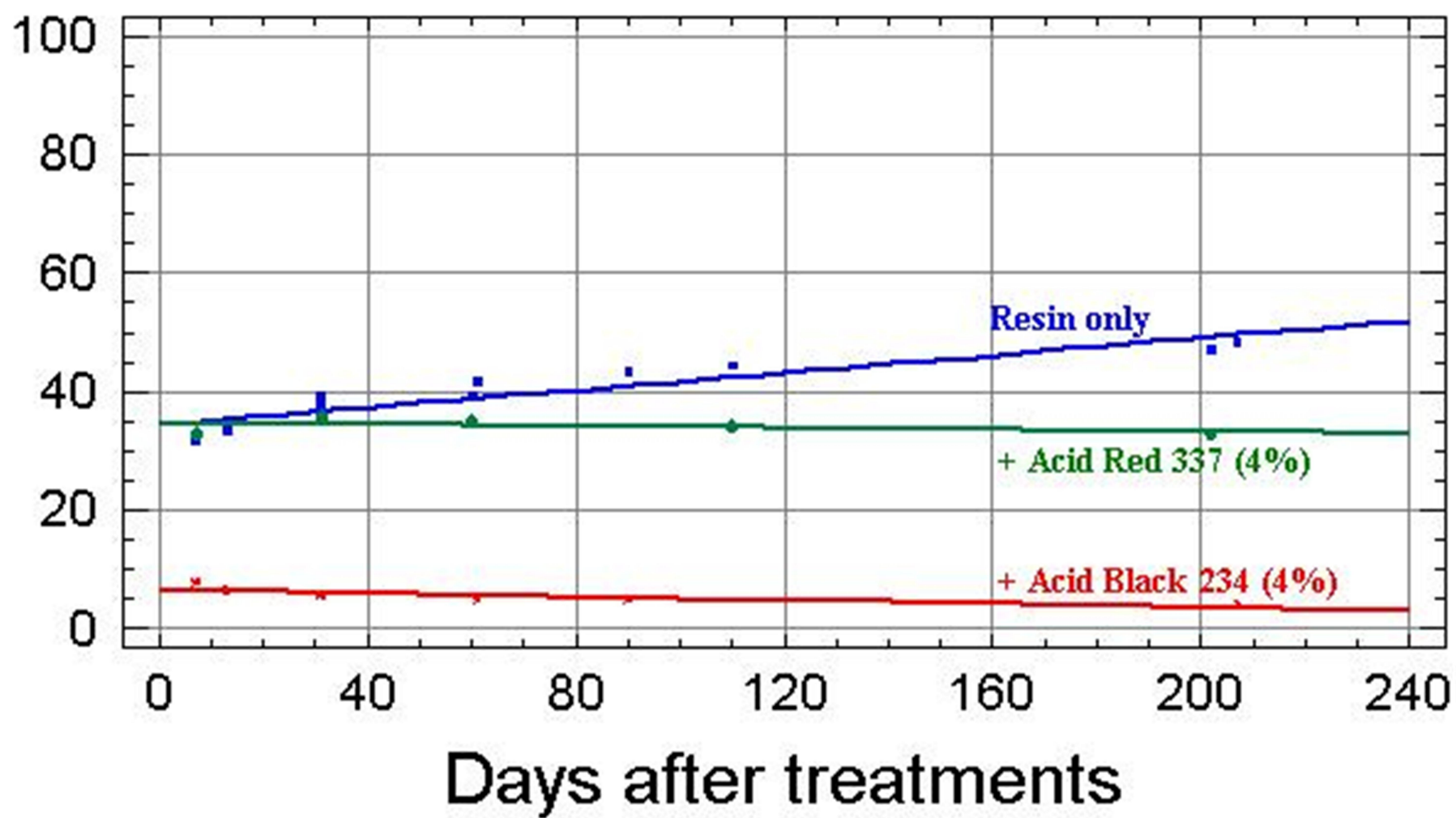
Formaldehyde content (mg/kg)

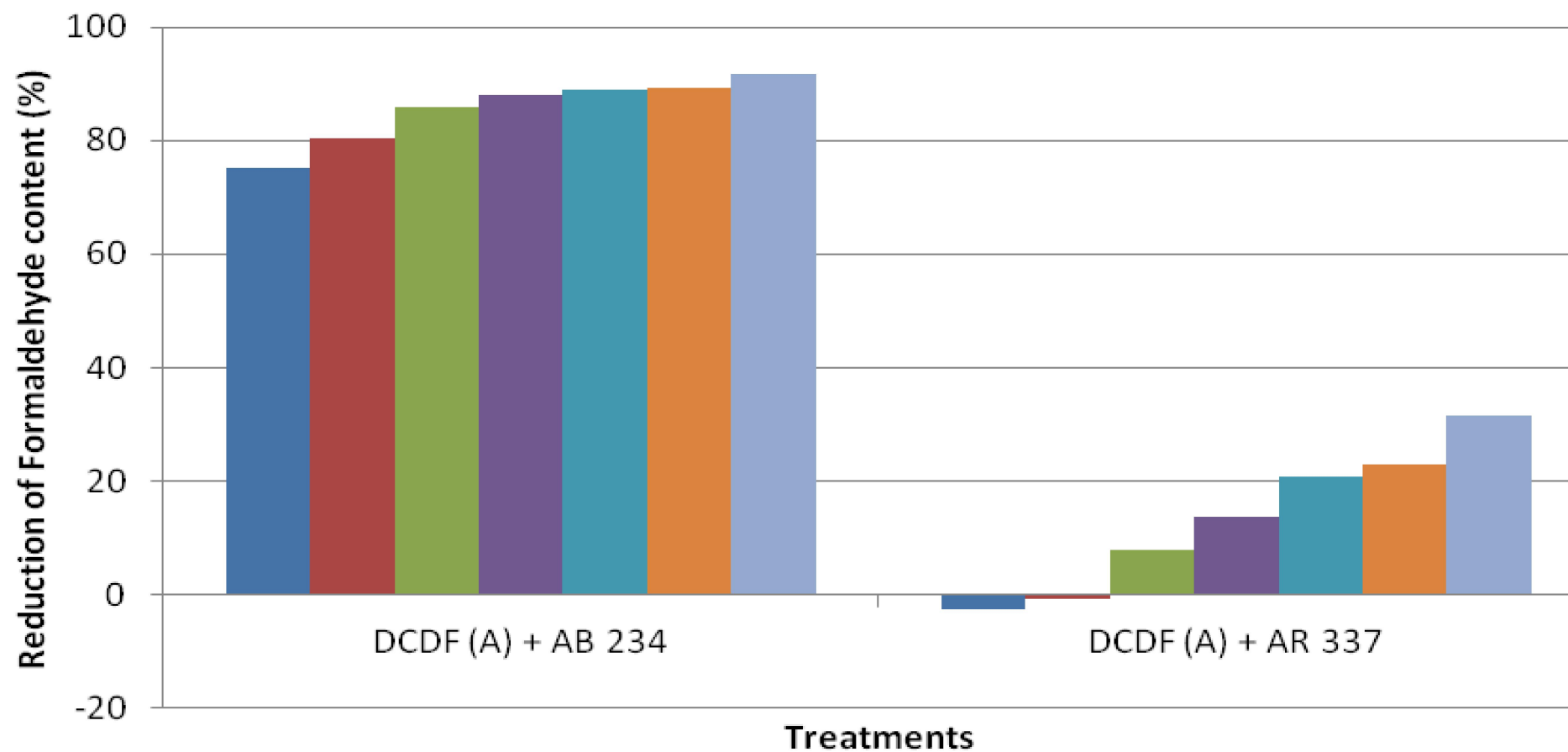




- 7.5 days after treatments    ■ 14 days after treatments    ■ 30 days after treatments
- 61.5 days after treatments    ■ 89.5 days after treatments    ■ 140 days after treatments
- 203.5 days after treatments

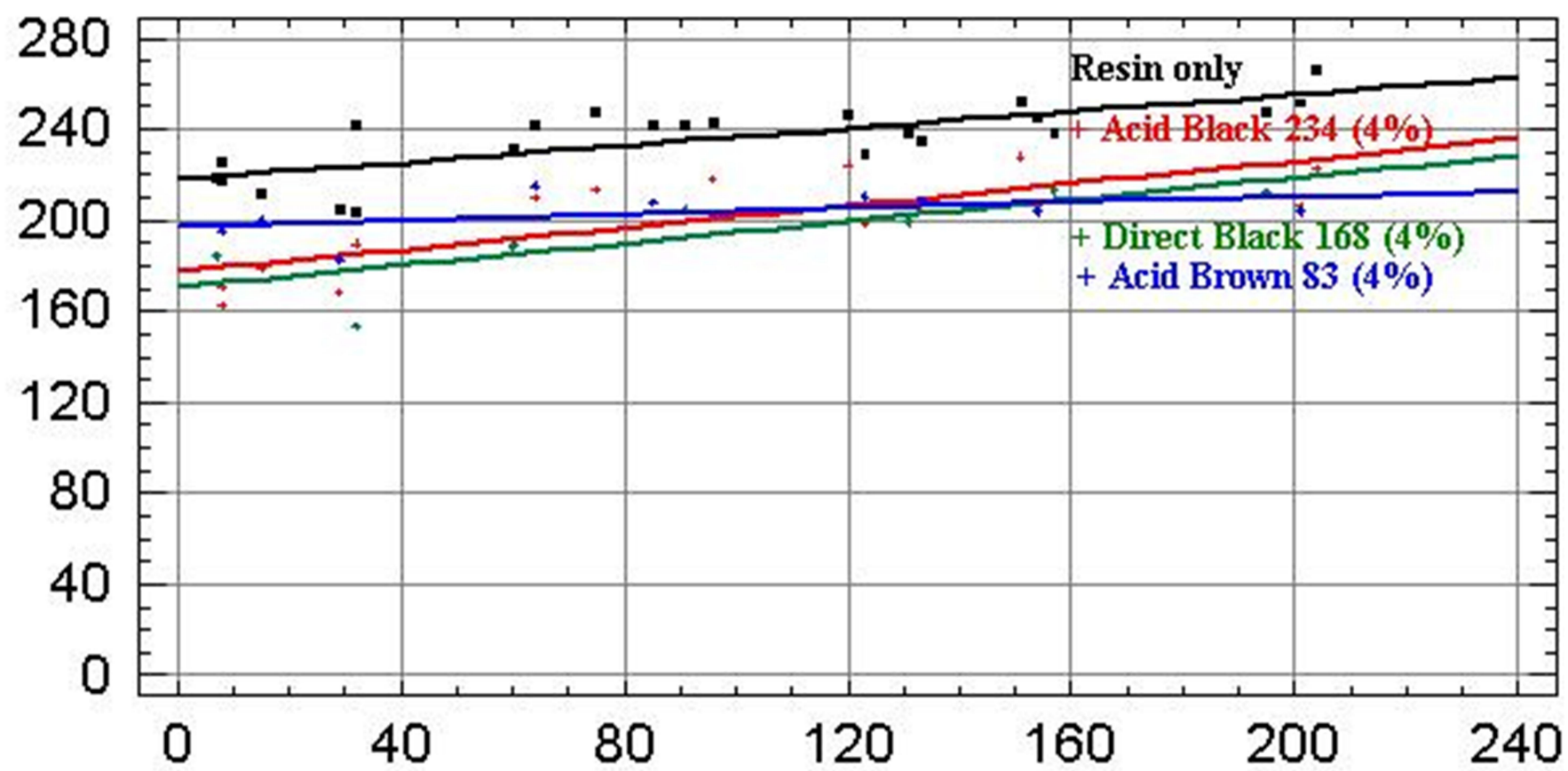
Formaldehyde content (mg/kg)



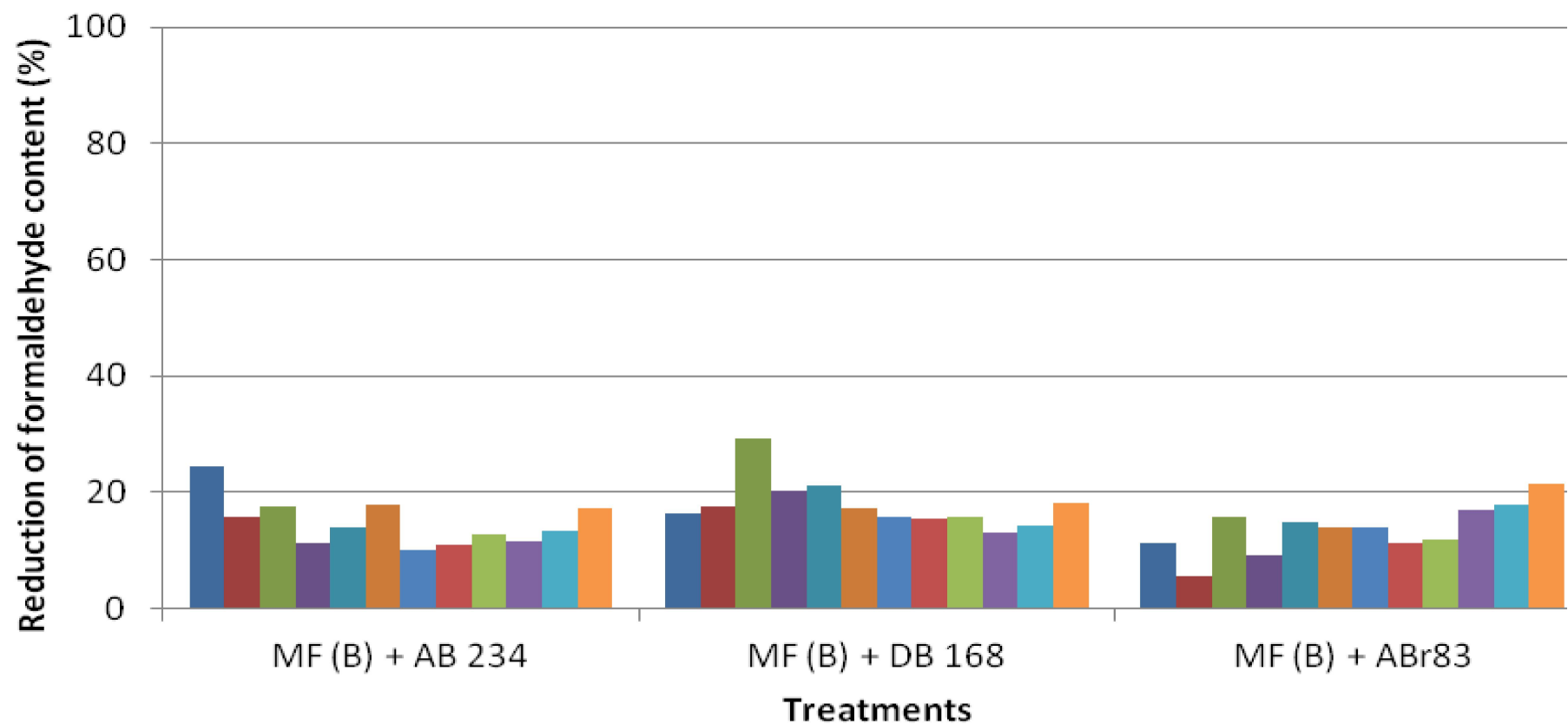


- 7 days after treatments
- 13 days after treatments
- 31 days after treatments
- 60.5 days after treatments
- 90 days after treatments
- 110 days after treatments
- 204.5 days after treatments

Formaldehyde content (mg/kg)



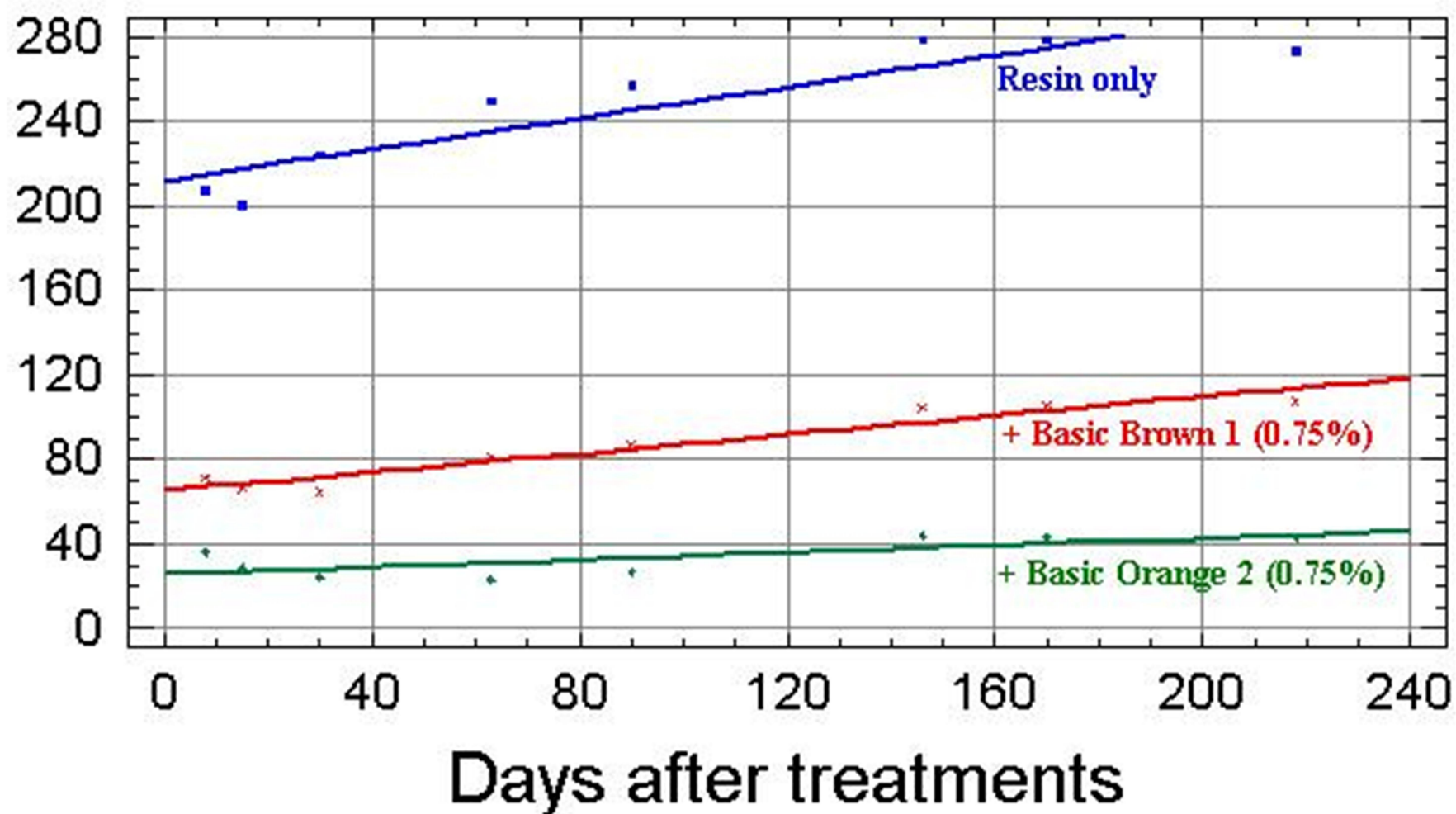
Days after treatments

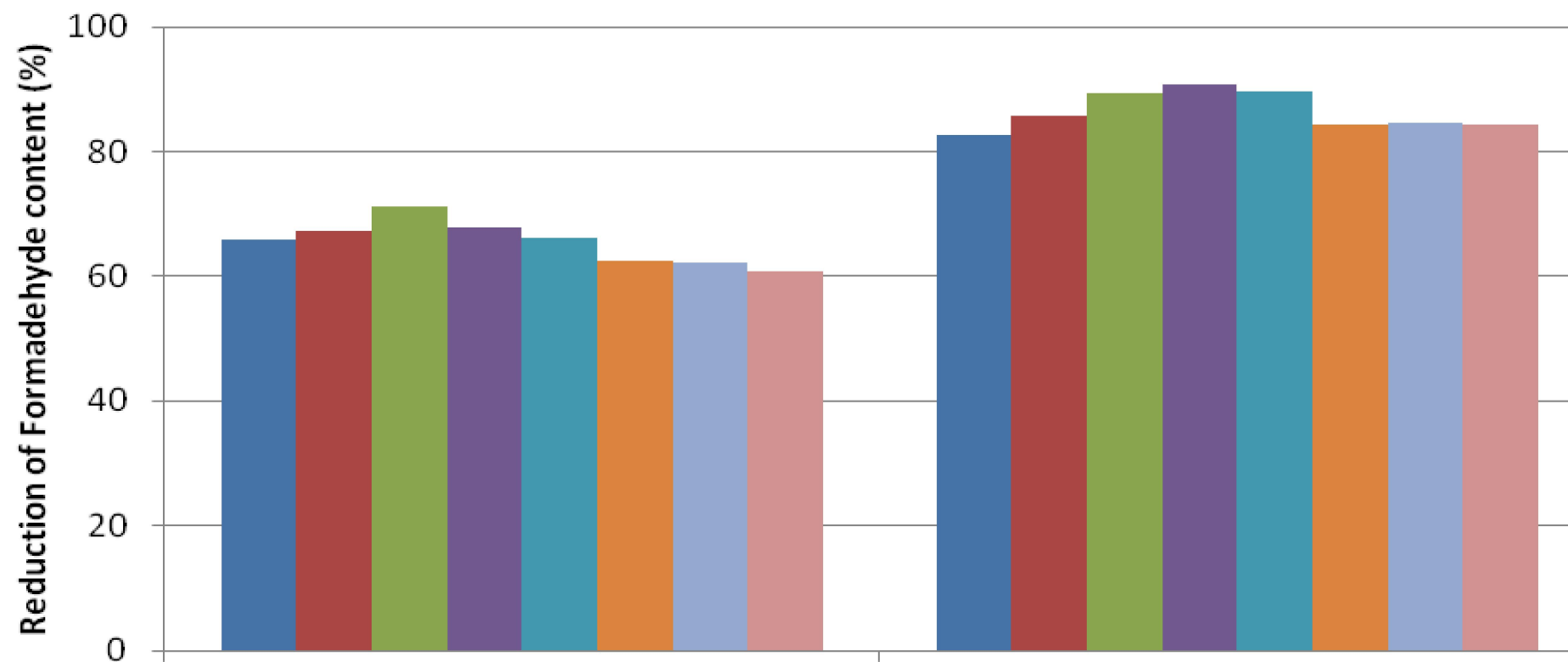


- 7.5 days after treatments
- 15 days after treatments
- 31 days after treatments
- 62 days after treatments
- 75 days after treatments
- 85 days after treatments
- 93.5 days after treatments
- 121.5 days after treatments
- 132 days after treatments
- 154 days after treatments
- 195 days after treatments
- 202.5 days after treatments



Formaldehyde content (mg/kg)





MF (B) + Basic Brown 1

MF (B) + Basic Orange2

Treatments

- 8 days after treatments    ■ 15 days after treatments    ■ 30 days after treatments
- 63 days after treatments    ■ 90 days after treatments    ■ 146 days after treatments
- 170 days after treatments    ■ 218 days after treatments



**1**



**2**



**3**

**Table 1**

Processing of leathers. Formulation applied.

Starting material: Butts of 1.5 mm wet-blue splits

All of the offers refer to the shaved wet-blue weight

Process	%	Chemical	°C	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'	
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

\* 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)

**Table 2**

Percentage of inorganic matter  $\pm$  95% confidence intervals in the studied dyes and amount of amino residues for 100 g of dyed leather.

Dye	Offer (%)	Inorganic matter (%)	Total amino residues/ 100g leather (g)	Amino residues with reduced reactivity/ 100 g leather (g)	“Free” amino residues/ 100 g leather (g)
Basic Brown 1	0.75	38.09 $\pm$ 0.10	0.072	0.036	0.036
Basic Orange 2	0.75	0.57 $\pm$ 0.02	0.096	0.048	0.048
Acid Black 234	4.0	38.23 $\pm$ 0.08	0.138	0.092	0.046
Direct Black 168	4.0	30.31 $\pm$ 0,08	0.099	0.099	---
Acid Red 337	4.0	17.89 $\pm$ 0,01	0.121	0.121	---
Acid Brown 83	4.0	37.07 $\pm$ 0.06	0.081	0.081	---

**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/Dyeing Treatments	$[FC]_0$ (mg/kg)	$[FC]_{rate}$ (mg/kg)	r
Figure 3	MF (A)	51.51±4.86	+0.20±0.04	+0.95
	MF (A) + Acid Black 234 (4%)	17.77±4.20	-0.04±0.06	-0.81
	MF (A) + Acid Red 337 (4%)	58.15±7.53	+0.10±0.06	+0.90
Figure 5	DCDF (A)	34.49±2.51	+0.07±0.02	+0.91
	DCDF (A) + Acid Black 234 (4%)	6.67±1.53	-0.02±0.03	-0.81
	DCDF (A) + Acid Red 337 (4%)	34.66±3.12	-0.01±0.03	-0.42

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/Dyeing Treatments	$[FC]_0$ (mg/kg)	$[FC]_{rate}$ (mg/kg)	r
Figure 7	MF (B)	218.04±8.61	+0.19±0.08	+0.76
	MF (B) + Acid Black 234 (4%)	177.23±13.38	+0.24±0.12	+0.76
	MF (B) + Direct Black 168 (4%)	170.55±24.60	+0.24±0.21	+0.79
	MF (B) + Acid Brown 83 (4%)	197.28±12.39	+0.07±0.11	+0.46
Figure 9	MF (B)	211.86±20.16	+0.37±0.17	+0.91
	MF (B) + Basic Brown 1 (0.75%)	65.09±7.58	+0.22±0.06	+0.96
	MF (B) + Basic Orange 2 (0.75%)	25.51±9.35	+0.09±0.08	+0.73

MF: Melamine-Formaldehyde;

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

r: linear correlation coefficient