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Experiments concerning metal depletion in must and wine by Divergan HM^{TM}

Giorgio Nicolini, Roberto Larcher and Fulvio Mattivi

Istituto Agrario di San Michele all'Adige, Dip. Laboratorio Analisi e Ricerche
I-38010 S. Michele all'Adige (TN), v. Mach 1
E-mail: Giorgio.Nicolini@mail.ismaa.it

Divergan HM^{TM}, a vinylimidazole/vinylpyrrolidone co-polymer produced by BASF, was used in white juice and wine with several doses and different contact times. Metal depletion was more effective when Divergan HM^{TM} was applied in juice than in wine. Depletion was rapid and improved significantly by a perfect mixing of the polymer into the liquid matrix. The highest depletion was for copper, and significant reductions were observed also for iron, zinc and aluminium, mainly when the polymer was added during fermentation. Reduced concentrations of chromium and boron due to the treatments were observed. Divergan HM^{TM} is an effective alternative to blue-fining, particularly in case of technologically high levels of copper and in juices. Divergan HM^{TM} treatment caused a rapid and significant decrease of cinnamate derivatives, mainly trans-caftaric acid, and improved white wine colour stability.
Key words: Grape must, wine, metal depletion, heavy metals, fining, Divergan HM^{TM}, browning.

Versuche zur Reduktion des Metallgehalts in Mosten und Weinen mittels Divergan HM^{TM}. *Divergan HM^{TM}, ein Vinylimidazol/Vinylpyrrolidon Co-Polymer, das von der Firma BASF hergestellt wird, wurde mit unterschiedlichen Dosierungen und Kontaktzeiten bei weißen Mosten und Weinen angewandt. Die Metallreduktion war bei der Zugabe von DiverganHM^{TM} zu den Mosten effektiver als bei der Zugabe zum Wein. Der Abbau erfolgte rasch und wurde durch gründliches Einmischen des Polymers in die flüssige Matrix noch verbessert. Der höchste Abbau erfolgte bei Kupfer, signifikante Reduzierungen wurden auch bei Eisen, Zink und Aluminium beobachtet, hauptsächlich dann, wenn das Polymer während der Gärung zugegeben wurde. Weiters wurden reduzierte Gehalte an Chrom und Bor beobachtet. Divergan HM^{TM} ist eine effiziente Alternative zur Blauschönung, besonders bei hohen Kupfergehalten und in Mosten. Es verursachte auch eine signifikante Minderung der Zimtsäurederivate, hauptsächlich der trans-Kaftarsäure, und verbesserte die Farbstabilität.*
Schlagwörter: Traubenmost, Wein, Schwermetalle, Metallreduktion, Schönung, Divergan HM^{TM}, Bräunung

Essais en vue de réduire la teneur en métal des moûts et vins au moyen de Divergan HM^{TM}. *Divergan HM^{TM}, un copolymère vinylimidazole/vinylpyrrolidone produit par la société BASF, a été ajouté aux moûts blancs et aux vins avec des dosages et des temps de contact différents. Après l'ajout de Divergan HM^{TM}, la teneur en métal des moûts a été réduite de manière plus efficace que celle des vins. La démétallisation s'est effectuée rapidement ; elle a encore été amélioré par un mélange minutieux du polymère avec la matrice liquide. La réduction du cuivre a été la plus prononcée ; une réduction importante a également été observée pour le fer, le zinc et l'aluminium, particulièrement dans le cas où le polymère a été ajouté au cours de la fermentation. En outre, des teneurs réduites en chrome et en bore ont été observées. Divergan HM^{TM} est une alternative efficace au collage bleu, notamment lorsque les teneurs en cuivre sont élevées, et pour les moûts. Il a également entraîné une réduction importante des dérivés de l'acide cinnamique, notamment de l'acide trans-caftarique, et la stabilité de la couleur a été améliorée.*
Mots clés: Moût de raisins, vin, métaux lourds, réduction de la teneur en métaux, collage, DiverganHM^{TM}, brunissement

According to ESCHNAUER and NEEB (1988) for the elemental composition of juice and wine a "primary content" - due to the natural transfer "soil-root-grape-wine" - and a "secondary content" - due to geogenous (natural) and anthropogenic (artificial) contamination - can be defined. Frequently, the natural amounts of metals are affected and overlapped by artificial contaminations (SEPPI and SPERANDIO, 1978; MEDINA and SUDRAUD, 1980; MCKINNON et al.,1992; OUGH, 1993; ESCHNAUER and SCOLLARY, 1995; PINAMONTI et al.,1999). Although checking the amount of several elements in grape juices and wines can have other reasons, i.e. origin authentication (SCARPONI et al.,1982; ETIEVANT et al.,1988; HERRERO-LATORRE and MEDINA, 1990; DAY et al.,1994; LATORRE et al., 1994; GREENOUGH et al.,1997; BAXTER et al.,1997), the main reasons lie in the medical field, i.e. the potential toxicity or role in the human diet of some of them (e.g. Pb, Cd, Al) (ELINDER et al.,1988; TEISSÈDRE et al.,1996; CERUTTI, 1999; TERRÉS et al., 2001), and in the technological field, i.e. the effects of potassium, calcium, iron, copper, zinc, and aluminium on wine stability (GAROGLIO, 1981; RIBÉREAU-GAYON et al.,1980; RANKINE, 1983; BOULTON et al.,1995).
The removal of surplus metal cations, especially iron and copper, with methods alternative to the traditional precipitation with potassium ferrocyanide is of particular interest because of the potential toxicity of ferrocyanide, the use of which is strictly regulated. Further concerns about the security of a massive distribution and storage of potassium ferrocyanide were raised, when in February 2002 the product traditionally employed for the blue-fining was discovered among the materials prepared for a terrorist attack on the US embassy in Rome. For the removal of iron and copper, FUSSNEGGER et al. have proposed since 1992 a 9:1 co-polymer between 1-vinyl-imidazole and 1-vinyl-pyrrolidone (PVI). In the USA, since July 2001, the Food and Drug Administration included PVI in the list of food contact substances (FDA, 2001) under the name of polyvinylimidazol (CAS Reg. No. 87865-40-5). It was authorized "as a component of matrix filter sheets, for removal of metals and sulfides in alcoholic beverages using repeat-usage filtering equipment". At present, the polymer is not allowed in the European Community.
Some technological peculiarities of the polymer were investigated previously (MATTIVI et al.,1994; MATTIVI et al., 2000; EDER et al., 2001). This paper reports the effects on mineral elements, cinnamate derivatives content and wine colour stability of the optimized PVI, marketed under the name of Divergan HM^{TM} (BASF, Ludwigshafen, Germany), applied in white grape juice and wine with several doses and for different contact times.

Materials and Methods

Laboratory scale trials

All trials were carried out both in white juice and wine, adding Divergan HM^{TM} into bottles.
The effects of increasing doses (10-20-30-50-100 g/hl) of the polymer were investigated compared to an untreated control (experiment "dose"). After the addition of Divergan HM^{TM}, bottles were gently overturned (15 rotations for 1 minute) and samples were taken after natural settling one day later.
The effects of the contact time were studied by submitting bottles of juice and wine, to which Divergan HM^{TM} had been added (25 g/hl), to continuous gentle overturning for a variable duration (experiment "stirring time"). At defined intervals (10-20-30-60-120-240 min), one bottle was taken, immediately centrifuged and the clear sample was stored until analysis.

Semi-industrial scale trials

Seven white wines were produced from a juice clarified to brightness in order to test the effectiveness of the treatment with Divergan HM^{TM} in three different steps of the winemaking: on juice, during fermentation and on wine. The flowchart of the trial is reported in Figure 1.

Mineral element analysis

Thirty ml of sample and 2 ml of 65 % nitric acid (superpure for trace analyses) in polypropylene vial were heated on a boiling bath to remove ethanol and minimize matrix interferences. The residue was made up to its original volume with deionized water (Milli-Q water) and analysed by Inductively Coupled Plasma - Optical Emission Spectrometry (Perkin Elmer Optima 3300 Dual View) according to the method detailed in LARCHER and NICOLINI (2001). Flow conditions for gases were: (a) plasma 15 l/min; (b) auxiliary 0.5 l/min; (c) nebulizer 0.55 l/min. Power was at 1400 Watt.

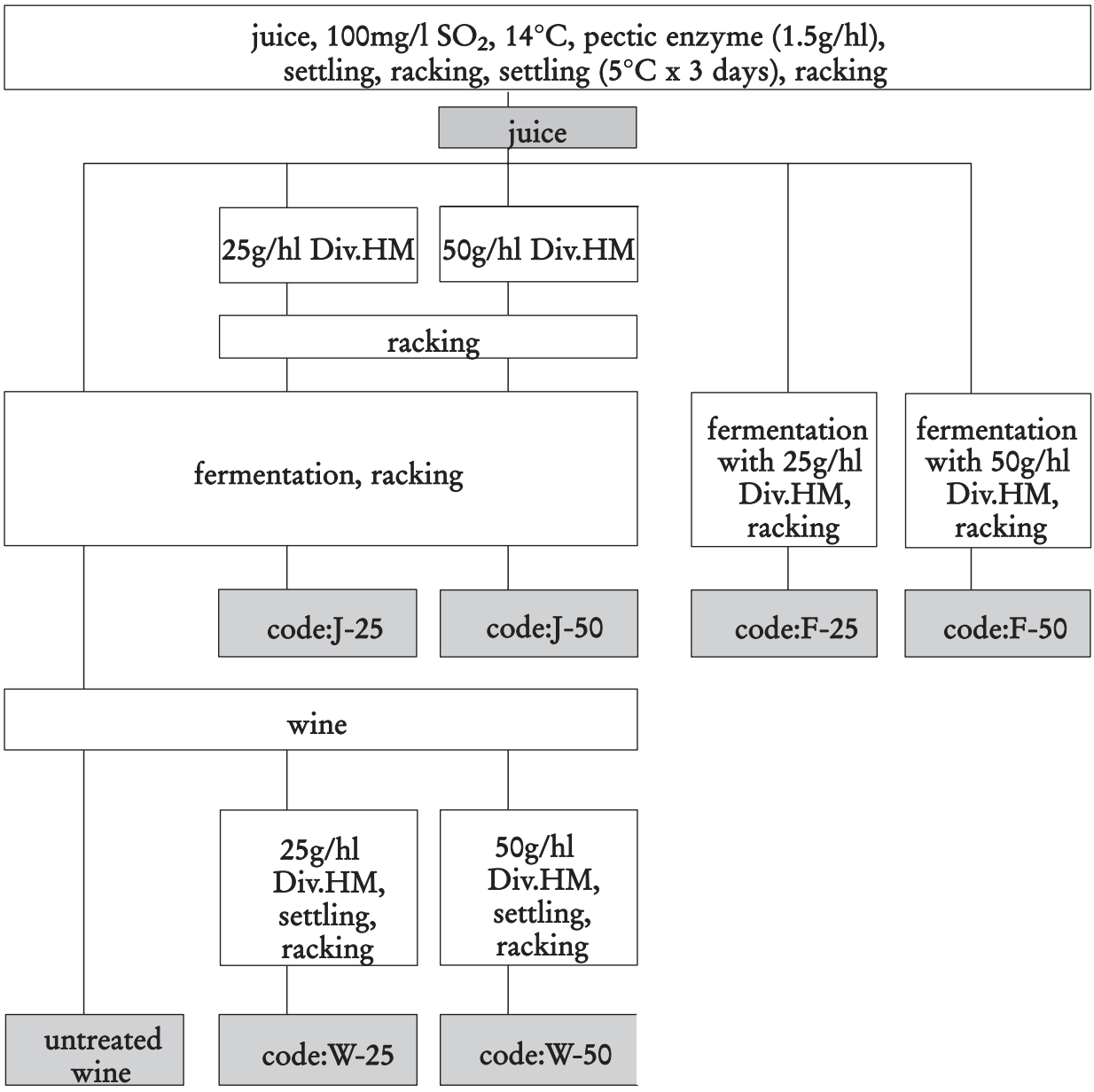

Figure 1: Flowchart of the fining treatments applied in the trials on semi-industrial scale

Other analyses

Cinnamate derivatives were analysed by direct injection into the HPLC, under the conditions described by NICOLINI et al. (1991). The free hydroxycinnamic acids were quantified at 320 nm by a calibration curve obtained with pure standards, while their tartaric acid esters were quantified as caffeic acid equivalents, mg/l.

The colour parameters of the white wines were measured with Chroma Meter CT 310 (Minolta, Osaka, Japan) on 20 mm optical path length cell, with light source "Standard C" (MATTIVI et al., 2002). The measured absolute data were reported using the colour system L*C*h, and the overall colour difference between samples was expressed as $\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ (MINOLTA, 1994; CAGNASSO, 1997).

Table 1:
Mineral element composition of the untreated samples

Element (mg/l)	Experiment "dose"		Experiment "stirring time"	
	Juice	Wine	Juice	Wine
Al	0.83	0.60	0.72	0.67
B	7.24	5.82	5.66	6.11
Ba	0.16	0.11	0.13	0,1
Ca	89	79	89	79
Cr (µg/l)	13	8	16	14
Cu	3.78	0.24	3.19	0.23
Fe	1.14	0.78	0.87	0.79
K	1592	968	1541	924
Mg	96	84	85	83
Mn	1.6	0.9	0.7	1.2
Na	15.3	14.0	13.9	15.0
Ni (µg/l)	30	10	20	12
Pb (µg/l)	63	7	41	11
Sr	0.10	0.07	0.06	0.10
Zn	0.67	0.45	0.44	0.52
Rb	4.8	3.2	5.4	3.0

Accelerated browning tests were performed according to the procedures proposed by SIMPSON (1982), which correlate with the natural browning of wine observed in long-storage tests (VRHOVSEK and WENDELIN, 1998).

Results

The elemental composition of the untreated control samples is shown in Table 1. Among the 16 elements measured, only those modified by the fining treatments will be discussed. In the figures, the results are expressed as percentage of each element remaining after treatment, compared to the original amount (100 %) in the untreated control.

Laboratory scale trials

Experiment "dose"

The results of the experiment "dose", where the polymer was put in contact with juice and wine for a very short time, are shown in Figure 2. The effect of depletion in juice is clear even with the lowest amount of the fining agent, and increases with the dose. In particular, the metal depletion is remarkable for copper and iron. The highest dose of polymer reduced aluminiun and zinc up to 60 and 70 % of their original content, respectively, while the removal of chromium was less effective. Applied in wine, the treatment was less effective than in juice. In fact, only iron and copper could be reduced significantly, but using the highest doses of Divergan HM™. The polymer did not remove any significant amount of calcium, potassium, magnesium, manganese, sodium and lead, either in juice or in wine, and fixed maximum 19 % of boron when used at 100 g/hl.

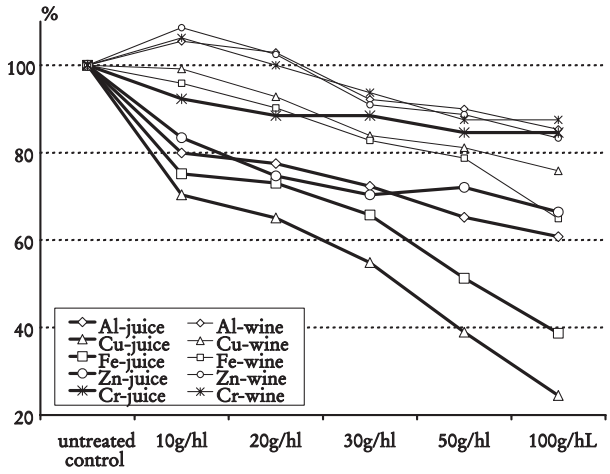

Figure 2: Percentage of the original content of mineral elements remaining in juice and wine after the fining treatment with increasing doses of Divergan HM (experiment "dose")

Experiment "stirring time"

More prolonged stirring times of the liquid with a low dose (25 g/hl) of polymer significantly enhanced depletion (Figure 3). At 20 min, the content of aluminium and chromium measured in juice and wine was roughly 65 to 75 % of the original concentration. This reduction was more effective than that obtained by settling in the experiment "dose" using 100 g/hl of fining agent. The same behaviour was observed for zinc in wine, while a clear decreasing trend could not be observed for this element in juice (data not reported). With juice, the polymer fixed roughly 90 % of copper and iron, being slightly more effective than in wine, where it fixed 35 to 40 % of copper and 75 % of iron. After 20 min,

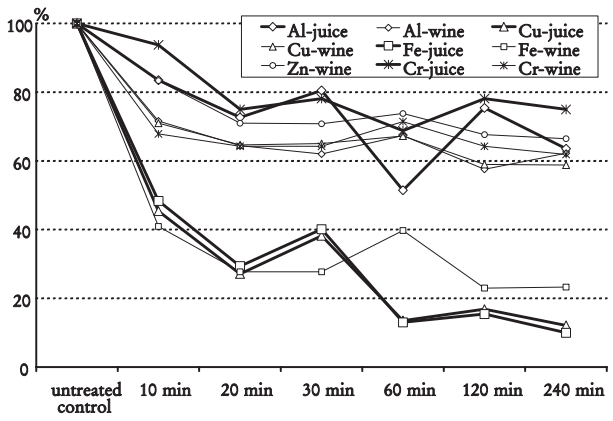

Figure 3: Percentage of the original content of mineral elements remaining in juice and wine after the fining treatment with 25 g/hl Divergan HM applied for increasing contact times (experiment "stirring time").

roughly 30 % of chromium were removed in juice and in wine.

Semi-industrial scale trials

The comparison of the concentrations measured in juice and wine (Table 2) shows that the simple fermentation phase caused significant decreases of all the elements reported, particularly copper (- 92 %) and aluminium (- 50 %).
Mainly, Divergan HM^{TM} had a remarkable capability of reducing copper, aluminium, iron and zinc, in particular when used for further clarification and stabilisation of the juice or, particularly for aluminium and zinc, during fermentation. The polymer confirmed to be less effective against copper if used in wine instead of juice, while the ability to reduce the iron content seems to be less matrix dependent. The ability to reduce the amount of chromium and boron was higher when Divergan HM^{TM} remained in the wine during fermentation.

Effects on cinnamate derivatives

The PVI polymer confirmed its effectiveness in reducing the content of cinnamate derivatives, as proved in previous research (Mattivi et al., 1994 and 2000; Eder et al., 2003). Depletion due to Divergan HM^{TM} treatment was higher in wine than in juice, and higher on the *trans*-caftaric acid content than on the sum of other cinnamates (Figure 4). Besides, depletion was rapid, with 50 to 70 % of the total removal achieved in the first ten minutes (Figure 5).

Effects on colour stability

In the wines analysed before accelerated aging (Table 3), Divergan HM^{TM} caused, in particular, slightly higher lightness (L*) and lower colour saturation (chroma, C*). The overall colour difference (ΔE*) due to the fining treatment was limited, and increased with the dose of the polymer or the duration of the treatment. The colour differences were ascribed to a diminution of the colour saturation and increase of the lightness.
Compared to the data measured before aging, accelerated aging caused, as expected, remarkable decreases in lightness and increases in chroma and hue (h), but ΔE* decreased in the treated wines compared to the controls. About 50 % of the colour difference ΔE* was

Table 2:
Changes in the elemental composition of wine due to the fining treatments applied according to the flowchart presented in Figure 1.

Element (mg/l)	Juice	Untreated wine	J-25	J-50	F-25	F-50	W-25	W-50
Al	0.68	0.35	0.27	0.20	0.09	0.03	0.25	0.18
B	6.38	5.41	5.10	4.87	4.89	4.24	4.90	4.42
Cr (µg/l)	9.7	7.4	6.8	6.3	5.4	4.6	6.4	6.1
Cu	3.72	0.29	0.10	0.09	0.09	0.07	0.23	0.21
Fe	0.99	0.71	0.52	0.37	0.53	0.45	0.51	0.35
Zn	0.56	0.44	0.45	0.42	0.26	0.20	0.39	0.41

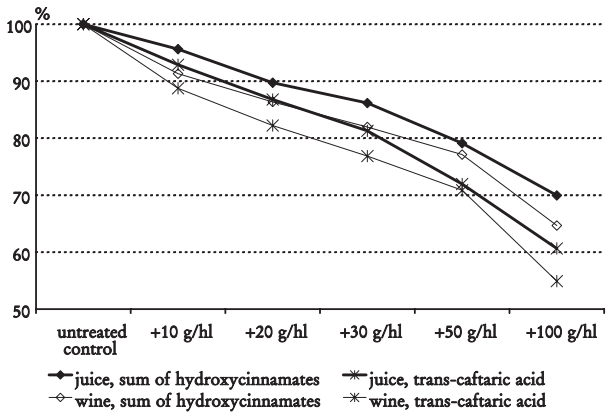

Figure 4: Percentage of the original content of hydroxycinnamates remaining in juice and wine after the fining treatment with increasing doses of Divergan HM (experiment "dose") (Sum of hydroxycinnamates = *trans* caftaric acid + *cis* coutaric acid + "GRP" + *trans* coutaric acid + fertaric acid + *trans* caffeic acid + *trans p*-coumaric acid + *trans* ferulic acid.)

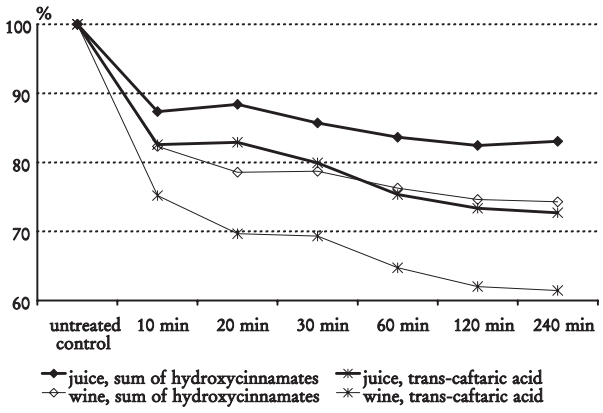

Figure 5: Percentage of the original content of hydroxycinnamates remaining in juice and wine after the fining treatment with 25 g/hl Divergan HM applied for increasing contact times (experiment "stirring time"). (Sum of hydroxycinnamates = see Figure 4)

due to a lower initial colour of the wine, while the remaining 50 % of reduction of the colour difference can be explained by a reduced browning. This improvement of the colour stability of white wines can be attributed to the concomitant depletion of metals, cinnamates and, although here not measured but already observed (MATTIVI et al., 2000), low-molecular weight flavanols reactive to vanillin, all involved in chemical or enzymic reactions of oxidative browning.

Discussion and conclusion

The composition of wine with respect to mineral elements, which are technologically important, has improved definitely over the last decades (LARCHER and NICOLINI, 2001). Nevertheless, sometimes juices and wines still can have high content of copper, mainly as residues of Bordeaux mixture treatments on grapes and copper sulphate additions in wine to eliminate sulfide related off-flavours. Besides, there is a tendency of the winemakers to avoid blue-fining, both for reasons related to the legal regulation of this practice and to the low effectiveness of the treatment when technologically high levels of copper are combined with low contents of iron. In this context, alternatives to blue-fining (SCHLEMMER, 1986; KERN and WUCHERPFENNIG, 1991 and 1993; GREEN et al., 1995; EDER et al., 2001) are welcome, also in the light of the fact that, at present, blue-fining is not allowed on juice and no other specific treatment for metal depletion is allowed in juice and wine according to the European regulations.

The metal depletion achievable using the new polymer Divergan HM™ proved to be technologically important. Generally, metal depletion caused by Divergan HM™ was more effective when the treatment was applied in juice than in wine. It was rapid and even more efficient when the polymer was mixed perfectly into the liquid matrix. The highest depletion was observed for coppper, and significant reductions were measured also in the content of iron. Zinc and aluminium were also affected significantly by the treatment, being reduced mainly when the polymer was added during fermentation. Reduced concentrations of chromium and boron due to the treatments with Divergan HM™ were observed both in juice and in wine. The polymer proved to be an effective alternative to blue-fining, particularly against high levels of copper and in juices. Treatments with Divergan HM™ improved the colour stability of white wine.

No other technologically significant change ascribable to the treatment with Divergan HM™ could be observed for the content of barium, calcium, potassium, magnesium, manganese, sodium, nickel, lead, strontium

Table 3:
Chromatic characteristics of the wines before and after accelerated ageing. (Legenda (1) = reference for computation of ΔE*)

treatment	before accelerated ageing					after accelerated ageing				
	abs. 420 nm (10 mm)	L*	C*	h	E*	abs. 420 nm (10 mm)	L*	C*	h	E*
experiment "dose"										
Control	0.191	86.06	24.31	55.0	0.0 (1)	0.873	62.46	59.42	73.4	44.0
10 g/hl	0.185	86.49	23.48	55.2	0.9	0.749	66.60	55.90	74.8	39.2
20 g/hl	0.180	86.93	22.97	55.9	1.6	0.754	66.62	55.89	75.0	39.2
30 g/hl	0.175	87.18	22.42	56.0	2.2	0.723	68.03	54.71	75.7	37.7
50 g/hl	0.171	87.35	21.85	56.4	2.8	0.702	68.92	53.99	76.0	36.7
100 g/hl	0.159	88.45	20.29	57.5	4.8	0.644	71.96	51.47	77.8	33.6
experiment "stirring time"										
Control	0.195	85.94	24.63	55.2	0.0 (1)	0.751	66.25	56.04	74.5	39.1
10 min	0.175	87.34	22.54	55.9	2.5	0.681	70.04	53.89	76.5	35.9
20 min	0.174	87.36	22.38	55.9	2.7	0.654	70.94	52.71	76.8	34.6
30 min	0.170	87.58	22.17	55.7	3.0	0.632	71.69	51.75	77.0	33.5
60 min	0.165	87.94	21.63	55.5	3.6	0.614	73.37	51.12	78.1	32.5
120 min	0.159	88.26	21.15	55.4	4.2	0.570	75.47	49.29	79.1	30.4
240 min	0.157	88.46	20.89	55.2	4.5	0.549	76.04	48.03	79.4	29.2

and rubidium. Changes in the amount of silver, previously observed by EDER et al. (2001), could not be observed in these trials because of the very low content of silver (trace level) in the untreated control samples.

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