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Treatment of White Wine of Browning Color Material with Nylon 66

by

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White table wines frequently develop too much brown color during aging, it is thus desirable to find an agent removing excess color in such a manner altering neither flavor nor bouquet. Using carbon, casein and polyvinyl pyrolidone (P. V. P.) to remove color from browning white wines has been throughly reviewed by Ibarra and Cruess (7), O'Neal *et al.* (8) and Cruess (3). Casein as color removal agent was preferred to carbon since casein seemed to have less effect on wine quality. Using P. V. P. as removal agent in preference to casein and large molecular browning material showed to have less effect on wine quality (A. Caputi *et al.*, 2).

De Villiers (4) demonstrated an improve in color and flavor when treating a young white wine with 1% nylon combined with an increased resistance to oxidative browning. Cantarelli (1) showed that nylon not only removes browning precursors but also reduced the total content of anthocyans and tannins of white wines. He also found that carbon or proteins such as casein, gelatin and albumin had a similar effect on wine, but at a reduced rate in terms of weight per unit volume. Three of four materials — protein, carbons, P. V. P. and nylon — reduced the optical density of wine.

Materials and methods

Wines fermented in the experimental cellars at Tokachi-Ikeda Experiment Station of the Viticulture and Enology and commercial samples were used for these tests. The wines were clarified with 1 kg of celite per 1 hl and the latter with 0.5 kg. All wines were filtered through a leaf filter. Lee-fermented wine was in contact with crushed berries upto 24 hrs.

Two types of nylon powders were used. One of them, Type 66, manufactured by the Toyo Rayon Co. Ltd., was used as received from the manufacturers and the other type, a polyamide, manufactured by Openhymer Co., was prepared from a sample of Nylon 66. As the nylon could not be ground to a fine enough powder the paste was prepared by dissolving the nylon in formic acid and precipitating it by gradual addition of water. The resulting paste was collected on a filter, boiled with water, diluted with sodium hydroxide, and then repeatedly with distillated water until the filtrate was free of soluble matter and tasteless. The nylon paste was sucked as dry as possible on a filter to about one part of nylon to four parts of water. Any attempt to receive it still more dry resulted in a hard product that had lost its ability to suspend in water and to adsorb polyphenols.

One hundred ml of wine were treated through each of the 0.5 g nylon pastes. Nylon pastes were regenerated with 10 ml of methanol containing 4 drops of HCl per 100 ml and the other 10 ml of 5% solution of NaOH. All nylon pastes were rinsed free of the regenerating solution with distilled water. Alkali washing solution was adjusted to pH 3.5 with 10% HCl, and again rinsed with distilled water.

Table 1

Analysis of Wines

Variety of Wine	Alcohol %	Extract %	Total acid (tartaric) %	Volatil acid %	Sample number
Kôshû*)	13.2	2.1	0.856	0.098	1.
Kôshû**)	12.3	3.9	0.768	0.136	2.
Seibel 9110	11.4	2.0	1.218	0.102	3.
Seibel 10076	11.2	1.8	1,3275	0.096	4.
Johannesburg, Riesling	12.0	3.8	0.611	0.244	5.
Semillon	12.5	3.6	0.570	0.108	6.
Kôshû × Afus-Ali**)	15.5	1.7	0.630	0.129	7.
Kôshû × Afus-Ali*)	14.7	2.3	0.795	0.135	8.
Delaware**)	13.9	2.7	0.8325	0.165	9.
Delaware*)	13.0	2.6	0.7725	0.090	10.

*) Lee-fermented, **) Free-run-fermented

All optical densities were measured at wave lengths of 320—600 mμ and 440 mμ with Bausch and Lomb Spectronic 20 using 12 mm diameter colorimeter tubes.

For accelerated browning rates all wines were stored in closed glass triangle flasks of 200 ml volume at a temperature of 45 ± 2° C. All flasks were filled with 120 ml of wine, leaving a half volume headspace. Optical density was measured before and after heating. A control sample was stored in an ice box at a temperature of 10° C. The heating period lasted 10 days at 45° C after the first measurement of browning.

Leuco-anthocyanins were determined by photometric determination of the color intensity produced by acid hydrolysis. 5 ml of the solution, suitable diluted, were added to 2 ml of 6N HCl in a test-tube with ground glass reflux tube and maintained in boiling water in the dark for 40 minutes. After cooling the cyanin produced was extracted three times with 2 ml of iso-amyl alcohol. The amylic extracts were collected in a 25 ml calibrated glass tube and diluted up to the given volume with ethanol. Absorbance was determined at 650 mμ to avoid interference with chlorophyll, as leuco-anthocyanins have an absorbance at 550 mμ. Pure cyanidin chloride was used as a standard. A linear relationship was found for concentrations up to 5 mg per 25 ml.

Results and Discussion

Sample of white wines are given in Table 1.

Reduction of color: Table 2 gives the absorption at 420 mμ of the 8 samples before and after treatment with nylon paste. Nylon treatment at the tested level

Table 2

Reduction of color by treatment with Nylon paste

(optical density value at the 420 m μ)

Sample number	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Before treatment	0.537	+	0.155	0.087	1.250	1.850	0.207	0.097	0.162	0.187
After treatment	0.244	—	0.097	0.046	0.980	0.150	0.092	0.041	0.061	0.051

Table 3

Treated Nylon 66 of Wine and pH change

Sample Number	Tannin content (mg/l) Non-treated	After treatment	pH value Non-treated	After treatment
1.	0.447	0.252	3.3	3.8
2.	0.281	0.186	3.6	3.8
3.	0.109	0.092	3.0	3.8
4.	0.022	0.017	3.0	3.8
5.	0.182	0.097	3.5	3.8
6.	0.305	0.206	3.6	3.8
7.	0.361	0.029	3.6	3.8
8.	0.487	0.034	3.4	3.8
9.	0.148	0.032	3.4	3.8
10.	0.196	0.051	3.4	3.8

tended to reduce optical density to one-third of its original value. It is thus possible to improve the color of a browned wine by removing essentially the undesired brown pigments formed by oxidation only.

Accelerated storage tests: Figure 1 shows the optical densities at 420 mμ of the treated wines and controls at 20 days intervals during accelerated storage at 50^{0} C $\pm$ 2^{0} C in the presence of an excess of oxygen. The treated wines take considerably longer to reach the optical density limit, even under the forcing conditions of accelerated storage, which show conclusively that treatment of a white table wine with nylon paste increases its resistance to browning during storage (Figure 1).

Figures 2 and 3 show the ultraviolet absorption of the four representative wines before and after treatment with nylon. The optical density is reduced to 220 mμ and 360 mμ in each treated wine, but the shape of the curve was not altered significantly. As the reduction in absorption is virtually constant at any wave length, it is supposed that a constant proportion of the chromophoric material has been removed. Thus,

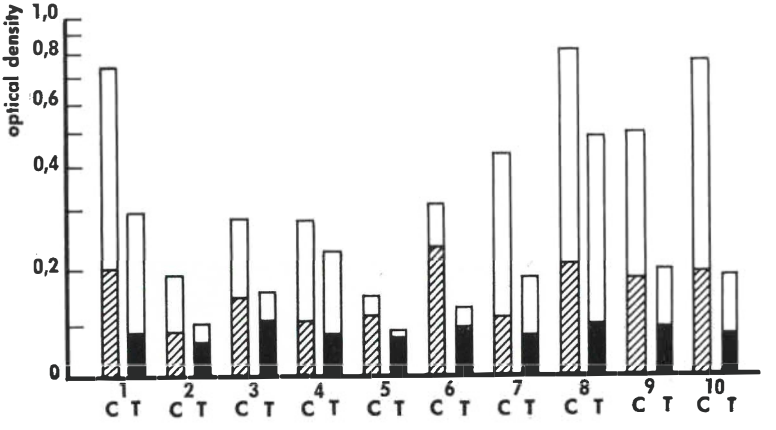

Fig. 1: Absorption of wine at 420 mμ at 30 days intervals during accelerated storage test before and after treatment with nylon. C: untreated, hatched column; T: treated, black column; open colum: change of density.

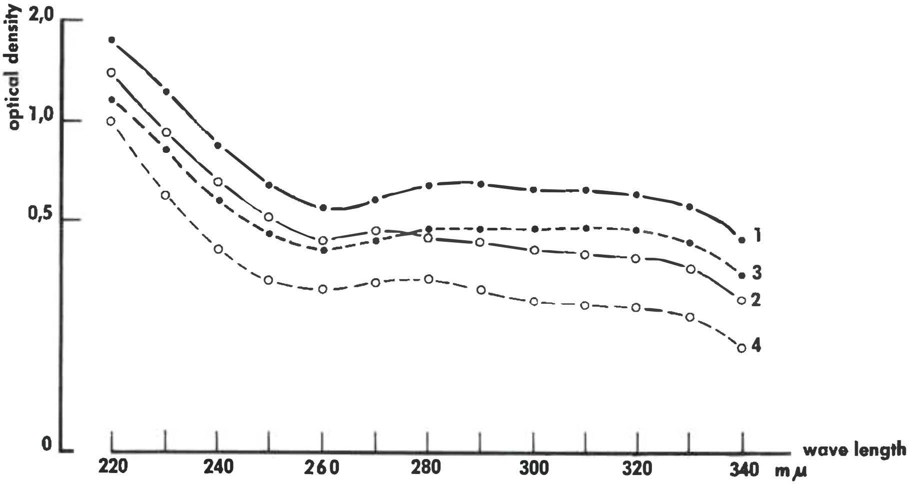

Fig. 2: Absorption spectra of wines number one and two before (1, 2) and after (3, 4) treatment with nylon. Kôshû wine, lee-fermented (1, 3); free-run-fermented (2, 4).

the leuco-anthocyanins being precursors of cyanidine were quantitatively removed from the wine by nylon. This specific removal of cyanidine precursors corresponds to experimental results of Harris and Ricketts (6) who found only cyanidine and delphinidine precursors from beer but no other leuco-anthocyanins.

Nylon is a specific absorber of polyphenols and their oxidation products and, besides improving the color of a browned wine, it improves its flavor by removing the flat unpalatable oxidized taste.

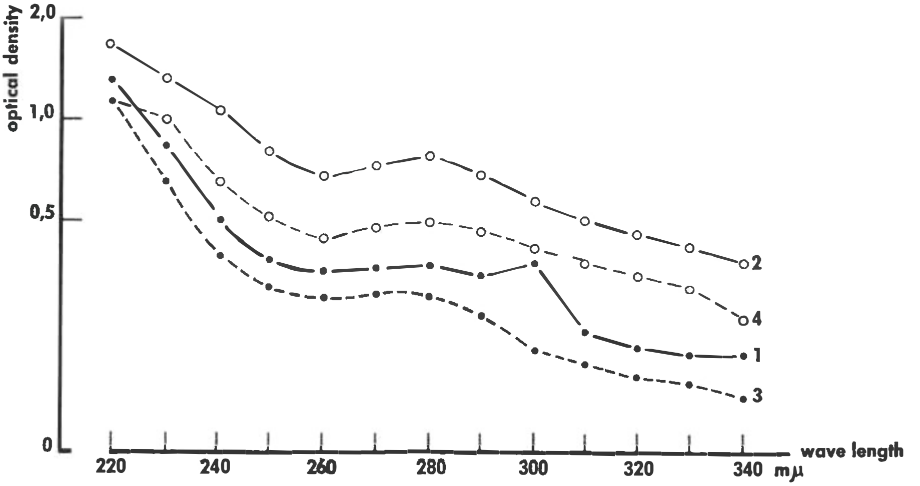

Fig. 3: Absorption spectra of wines number five and six before (1, 2) and after (3, 4) treatment with nylon. Johannesburg Riesling (1, 3); Semillon (2, 4).

Summary

It has been found that a partial removal of polyphenols from a white table wine by treatment with nylon paste reduces color and considerably increases its resistance to browning during storage.

This confirms that the browning of white wines is due to oxidation of polyphenolic material and not to melanoidin formation by sugar and amino acid interation, the common cause of browning in the food industries.

Brownish pink color of the skin of Kôshû and Delaware grape berries proved that these species contained too much polyphenol substances; consequently wines of these two grapes get browning more quickly. Treatment of the wine with nylon paste is simple to carry out and, since nylon is chemically inert, it neither dissolves in wine nor reacts with it. Nylon removes a part of the phenolic material by adsorption. Nylon paste can easily be regenerated by treating with alkali and washing with water. All experiments were made with young and aged wines, but the process could probably be applied with advantage at an earlier stage of vinification. Nylon treatment is complementary to the usual process of wine making and does not supercide sulfiting or fining. It was introduced in the process of wine making because it is very economical and useful to the preservation of materials.

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