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Permeability of Different Wax Coatings and Their Effect on Citrus Fruit Quality

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Gas and water vapor permeability (WVTR) of seven coatings, used commercially for citrus, was determined by coating these on highly permeable films. Oranges and mandarins were coated with the same seven coatings, and weight loss, appearance, internal gas composition, presence of ethanol and acetaldehyde, and flavor of these fruits were determined. There was a relationship between low concentrations of oxygen, which lead to off-flavors, and the presence of ethanol and acetaldehyde in the fruit. There was also a relationship between WVTR and weight loss of the fruit with most coatings, but no correlation between CO_2 and O_2 permeability of the coatings and concentration of these gases in the fruit. The above findings were validated in a semi-industrial trial.

Keywords: *Wax coatings; permeability; citrus fruits*

INTRODUCTION

Citrus fruit, like all other fruit, are subject to transpiration (loss of water) as well as to respiration after harvest, and, as a result, they are exposed to physical and microbial deteriorations which may result in considerable economic losses. The predominant system used commercially to reduce undesirable changes and extend shelf life involves washing the fruit, disinfecting it, and applying a protective coating into which sometimes a chemical preservative is incorporated. Coating fresh citrus fruit with waxes, to retard weight loss and shriveling, was practiced in China in the 12th century (Hardenburg, 1967). Although many types of fruit coatings have been developed over the years, only recently Hagenmaier and Shaw (1992) and Hagenmaier and Baker (1983) presented data concerning the permeability of a variety of commercial coatings to oxygen, carbon dioxide, and water vapor. Most of these coatings provide an attractive gloss, reduce weight loss, prevent shriveling, and reduce incidence of microbial spoilage. However, in some coated fruit, considerable amounts of ethanol and acetaladehyde were found, which caused undesirable flavor changes (Ben-Yehoshua, 1969). Ahmed and Khan (1987) found significant amounts of ethanol in waxed mandarins accompanied by a change in flavor. These researchers attributed the off-flavor to insufficient supply of oxygen through the wax coating, which caused partial anaerobic respiration. Similar results were reported by Nisperos-Carreido et al. (1990) for wax-coated pineapple oranges.

Thus, while the potential negative effects of citrus coatings on flavor of the edible parts of the fruit are known, their causes have not been investigated so far. Furthermore, little attention has been paid to the effect of coatings on the respiration of the fruit. A good coating should give the fruit a shiny, attractive appearance and reduce weight loss, but at the same time it should affect as little as possible the normal respiration of the fruit and should not cause partial anaerobic conditions.

The objectives of this work were to evaluate the permeability of several wax coatings to oxygen, carbon dioxide, and water vapor, as well as to study their effect on flavor, weight loss, and appearance.

MATERIALS AND METHODS

Fruits. Fresh unwashed and uncoated mandarins of the Sazuma and Michal varieties and unwashed and uncoated Shamuti and Valencia oranges were obtained directly from a packing house.

Coatings. The coatings used in this work were as follows: Britex 505 (Brogde Co., Pomona, CA); PacRite-StorRite 101, which contained polyethylene and shellac, and PacRite-SunShine, which contained shellac (American Machinery Corp., Orlando, FL); Primafresh 30, which contained carnauba wax and shellac (Johnson Wax Co., Racine, Canada); Decco Lustr 202, which contained natural and synthetic waxes and fatty acids (ELF Atochem North America Inc., Munrovia, CA); and Natural Zivdar, which contained a carnauba wax emulsion, and Industrial Zivdar, which contained a polyethylene emulsion (Saif-Pac Ltd., Kfar-Saba, Israel).

Fruit Coating and Storage. The uncoated fruits were washed, dried, and dipped into the respective emulsion which was spread by hand and air-dried at 40 °C, prior to storage at 15 °C. Seven different coatings were used.

Weight Loss. Lots, of at least 15 of the same fruits, stored at 15 °C and 60% relative humidity (RH), were weighed periodically.

Analyses of Ethanol and Acetaldehyde. The internal gas composition of the fruits was evaluated by withdrawing a 2 mL gas sample from the core of the fruit. The sample was analyzed, simultaneously, for ethanol and acetaldehyde in a gas chromatograph (Varian, Model 3700) equipped with a flame ionization detector and a $^1/_4$ in. stainless steel column packed with 10% 20M Carbowax on 60/80 mesh Chromosorb P. Detector temperature was 180 °C, column temperature was 130 °C, and injector temperature was 150 °C. Helium at 50 mL/min was the carrier gas. For each analysis of at least three different fruit were taken.

Analyses of Oxygen and Carbon Dioxide. Samples of 0.5 mL were taken from the core of the fruits (at least three fruit for each determination) and analyzed using a gas chromatograph (Becker Packard, Delft, Holland, Model 406) equipped with a thermal conductivity detector. The carrier gas was helium at 50 mL/min. The column for carbon dioxide, oxygen, and nitrogen identification was a CTR I (Alltech Associates Inc., Deerfield, IL, catalog no. 8700) stainless steel column constructed of an outer column (6 ft × $^1/_4$ in.) packed with activated molecular sieve and an inner column (6 ft × $^1/_8$ in.) packed with a porous polymer mixture. This column

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enables simultaneous analysis of several gases, including oxygen, carbon dioxide, and nitrogen. Column temperature was 40 °C, injector temperature was 50 °C, and detector was at 150 mA.

Sensory Evaluations. The appearance of the fruits was evaluated by means of a sensory hedonic test (Larmond, 1977). Mean hedonic appearance scores, on a scale from 5 (very good) to 1 (very bad) were obtained using at least 10 trained assessors. Analysis of variance and *t*-test were used to analyze the data. The triangular test was used to determine taste differences among samples of juice made from the fruit. Results of the triangle test were analyzed according to the method of Larmond (1977).

Permeability Measurements. Permeability was measured according to the method described by Hagenmaier and Shaw (1991). The liquid wax coating was applied, by means of a film applicator rod (no. 0032), onto a plastic film of known permeability. A poly(vinyl chloride) film, type VF (15 μm thickness) (Borden Chemical Division), North Andover, MA) was used for O_2 and CO_2 permeability determinations, and cellophane (40 μm) for water vapor transfer rate (WVTR) evaluations. The coating thickness needed to calculate the permeability (eq 1) was measured with a micrometer, in at least six locations. The average thickness varied for the different coatings from 25 to 55 μm on the VF films for O_2 and CO_2 permeability measurements and from 4 to 12 μm for WVTR determinations. WVTR of coated and uncoated samples was measured by using the gravimetric dish method according to ASTM (1984). Films were mounted on the dish with the uncoated cellophane on the side with 0% RH and the wax coating on the side with 90% RH.

Permeabilities of films to both O_2 and CO_2 were measured on identical samples, by the concentration method, using a test cell described by Gilbert and Pegas (1969). The test film separated two sections of the cell, one of which was flushed with the test gas and the other with an inert gas. The concentration change of the test gas permeating through the films was monitored by gas chromatography. Permeability was calculated according to Fick's law (Nobel, 1983), which states that flux of gas or water vapor through a barrier varies with permeance (P) and pressure gradient. Permeability is defined as

$$\text{permeability} = P \times \text{thickness} \tag{1}$$

For barriers in series, such as in a laminated film, the permeance through the series (P_s) is related to the permeance of film one (P_1) and film two (P_2) as follows (Crank, 1956):

$$1/P_s = 1/P_1 + 1/P_2 \tag{2}$$

The units for oxygen and carbon dioxide permeance were are mL·mil/(m^2·day·atm) and for water vapor are g·mil/(m^2·day·90% RH).

Permeability of wax coating was calculated from the permeability of coated and uncoated films using eqs 1 and 2.

The water vapor transfer rates (MVTB) were measured at 38 °C and 90% RH and are average values from at least six replicates. The values for O_2 and CO_2 were measured at 25 °C and 60% RH and are averages of at least six samples.

A semi-industrial trial was performed in a pilot packing house of the Volcani Research Cener. The operations in the pilot plant included washing, drying, disinfecting, drying, wax coating, and drying. For this experiment Mandarins of the Nova variety were coated with Zivdar polyethylene, which is the coating presently used by the industry, and PrimaFresh 30.

RESULTS

Five different coatings were evaluated with regard to weight loss, appearance, and internal oxygen concentration in Sazuma mandarins and Shamuti oranges. The five coatings were Natural Zivdar, Primafresh, Decco, Britex, and Pacrite-StorRite 101. On the basis of these results, only two coatings (Natural Zivdar and Primafresh) and a new coating, PacRite-Sunshine, were used in further studies. In the final, semi-industrial trial, only Primafresh was compared with the Industrial Zivdar (Zivdar polyethylene), which is the coating used by the industry in Israel).

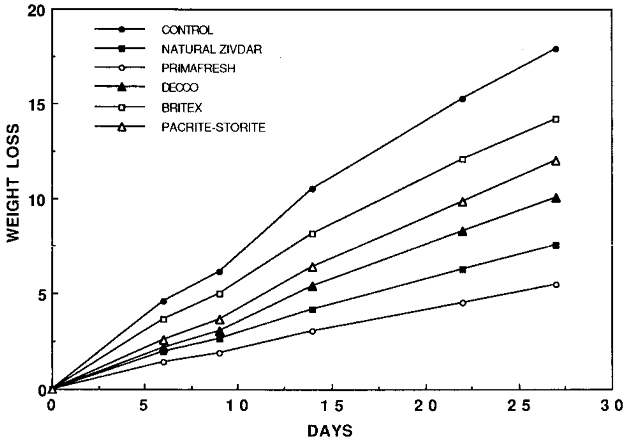

Figure 1. Weight loss of Sazuma mandarins with five different coatings at 15 °C.

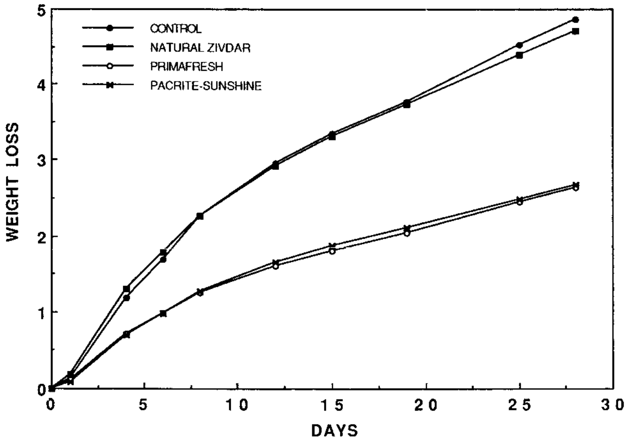

Figure 2. Weight loss of Valencia oranges with three different coatings at 15 °C.

Weight Loss. Results presented in Figure 1, for Sazuma mandarins, show that the lowest weight loss was manifested in Primafresh-coated fruit, while the highest loss was recorded for the uncoated (control) fruit followed by fruit coated with Britex, PacRite-StorRite, Decco, and Natural Zivdar coatings. Similar results (data not shown) were obtained with Shamuti oranges. Data for Valencia oranges show that the weight loss for fruit coated with Primafresh and PacRite-Sunshine coating was lower than that for Natural Zivdar-coated fruit (Figure 2). The above results indicate that the Primafresh coating was the best with regard to weight loss.

Internal Oxygen Concentration. Figure 3 illustrates internal oxygen concentrations in Sazuma mandarins, with five coatings during storage at 15 °C. The lowest internal oxygen concentrations were found in fruits coated with Natural Zivdar, while the highest concentrations were in control fruits, followed by fruits coated with PacRice-StorRite and Decco. Primafresh- and Britex-coated fruits had a slightly lower oxygen concentartion than control fruits. Similar results were obtained with Shamuti oranges and Michal mandarins (results not shown).

Valencia oranges coated with PacRite-Sunshine also had low internal oxygen concentrations similar to those

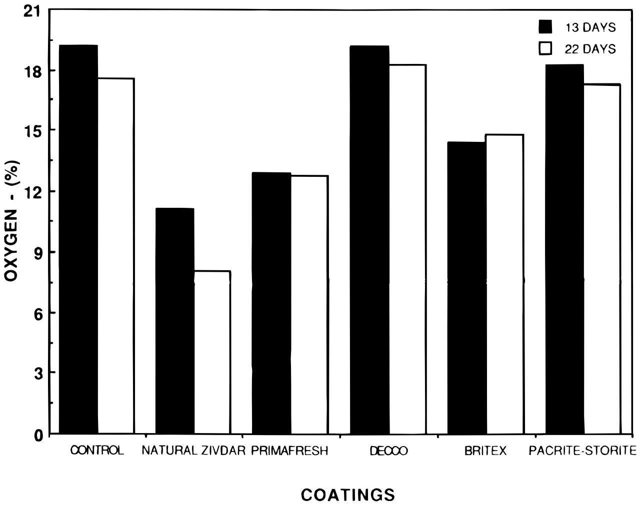

Figure 3. Internal oxygen concentration in Sazuma mandarins with five different coatings.

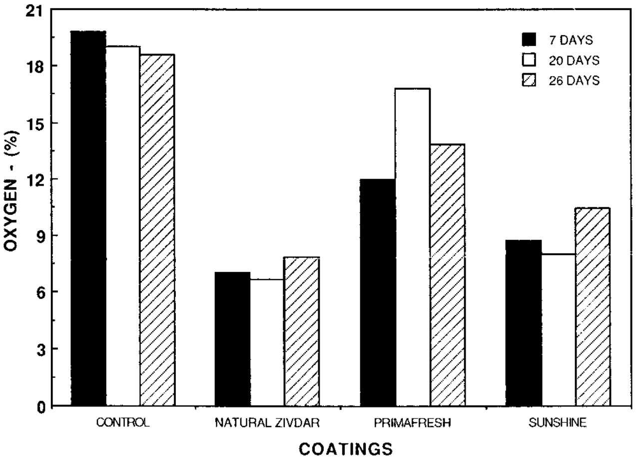

Figure 4. Internal oxygen concentration in Valencia oranges with three different coatings.

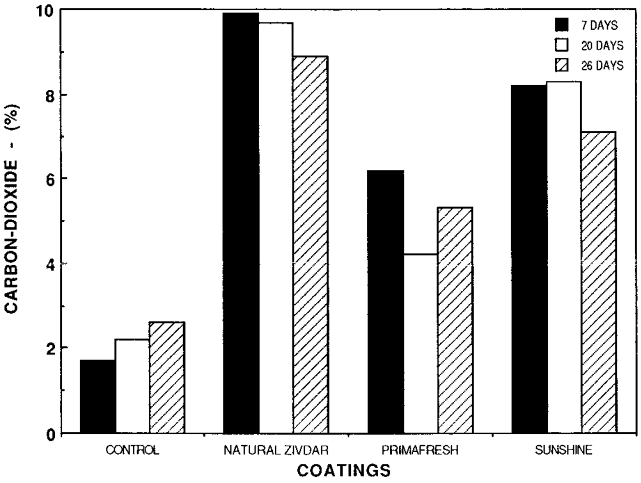

Figure 5. Internal carbon dioxide concentration in Valencia oranges with three different coatings.

of oranges with Natural Zivdar (Figure 4), while Primafresh-coated oranges had a significantly higher (better) O_2 concentration.

Internal carbon dioxide concentration was highest in oranges coated with Natural Zivdar followed by PacRite-Sunshine coatings and was lowest in oranges coated with PrimaFresh (Figure 5). There was a correlation between low concentrations of oxygen (Figure 4) and high carbon dioxide concentrations (Figure 5). The explanation for these observations is that the coatings serve as barrier for gases so that the amount of oxygen which can pass into the oranges is reduced and the CO_2, which is a product of respiration, accumulates inside the fruit (Ben-Yehoshua, 1969).

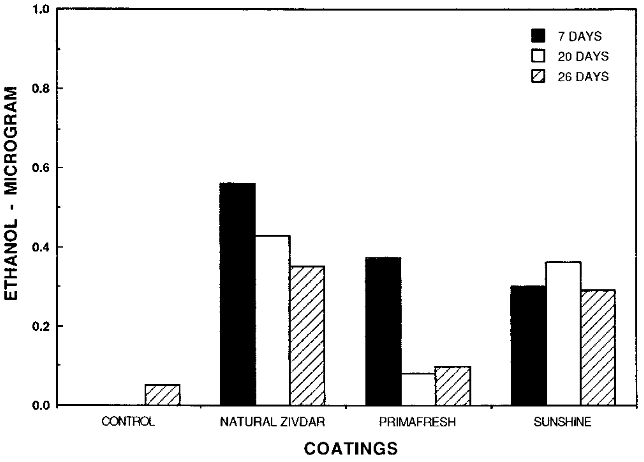

Figure 6. Ethanol accumulation in Valencia oranges with three different coatings.

Ethanol Accumulation. Low concentrations of oxygen lead to partial anaerobiosis and thus to ethanol and acetaldehyde production. Figure 6 illustrates the amount of ethanol (micrograms/2 mL) found in the core of Valencia oranges as a function of the various coatings. Ethanol, in various amounts, accumulated in all coated fruits; however, in control fruits it accumulated only after long storage periods. Fruits coated with Primafresh contained the lowest quantity of ethanol (except after 7 days), while in PacRite-Sunshine- and Natural Zivdar-coated fruits higher amounts of ethanol were found.

Traces of acetaldehyde (data not shown) were found in most coated fruits. There was a relationship between amounts of ethanol and existence of traces of acetaldehyde and low concentrations of oxygen. Accumulation of ethanol and acetaldehyde in the fruit can be attributed to creation of partial anaerobic conditions and the barrier properties of the coatings to these compounds.

Sensory Evaluation. Freshly squeezed juices were presented to the trained taste panel within 1 h from juice extraction. There was a statistically significant difference in triangle taste evaluations (13 correct answers from 18) between juices made from fruit coated with PacRite-Sunshine and Natural Zivdar in comparison to juices from uncoated fruits. However, there was no significant difference in the taste of juices made from Primafresh-coated oranges and juices made from uncoated oranges. The difference in the former juices was apparently due to a slight off-taste in these fruits, which was absent in the Primafresh and control fruits.

Permeability of the coatings to O_2, CO_2, and water vapor and their standard deviations are presented in Table 1. Since the standard deviations were rather high, the evaluations were carried out at least six times on different samples. However, the same samples were used for gas as well as WVTR analyses. The results in Table 1 are averages of at least six determinations. The differences in gas permeabilities of the various coatings were relatively small and cannot explain variations in the gas concentrations inside the fruits. Furthermore, the permeability of the coatings to carbon dioxide was

Table 1. Permeability of Seven Wax Coatings to O_2 and CO_2 at 25 °C and WVTR at 38 °C

	permeability					
	O_2 (60% RH)		CO_2 (60% RH)		WVTR (90% RH)	
coating	mL·mil/ m^2·day· atm	SD[a]	mL·mil/ m^2·day· atm	SD	g·mil/ m^2·day	SD
Britex	2030	570	3980	550	3.83	0.5
Decco	3000	10	2450	40	0.95	0.1
PacRite-Sunshine	1650	59	1850	83	1.26	0.5
Natural Zivdar	1750	229	400	140	3.02	0.7
Zivdar PE	2270	460	2460	430	1.61	0.3
PacRite-StorRite	2040	560	1380	520	0.67	0.03
Primafresh	3400	109	2660	110	0.45	0.04

[a] SD, standard deviation.

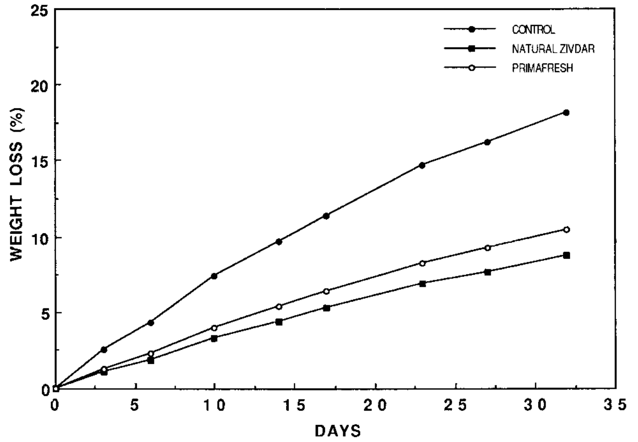

Figure 7. Weight loss of Nova mandarins with two coatings at 15 °C.

Table 2. Hedonic Appearance Scores of Coated Fruits

coating	score	coating	score
Natural Zivdar	5.0	Britex	3.4
Primafresh	4.5	Decco	2.3
PacRite-Sunshine	4.5	control	2.5

not always higher than that of oxygen, as normally seen in polymeric films. The Primafresh coating had the lowest WVTR and gave the best results with regard to weight loss and at the same time also had a good appearance (score 4.5, Table 2).

Appearance of fruits coated with Natural Zivdar, Primafresh, and PacRite-Sunshine was shiny and very attractive. Table 2 shows hedonic appearance scores of fruits with the various coatings, on a scale from 5 (very good) to 1 (very bad).

Results of the semi-industrial trial are summarized in Figures 7 and 8. Weight losses of Nova mandarins coated with Primafresh and Industrial Zivdar were almost the same and considerably lower than that of uncoated controls (Figure 7). Internal oxygen concentration was highest in control fruits, as expected, and lowest in Industrial Zivdar-coated fruits (Figure 8). Mandarins with Primafresh had an intermediate, satisfactory oxygen concentration (not causing partial anaerobiosis and appearance of off-flavors). There was no significant difference in carbon dioxide concentrations between fruits coated with both coatings (Figure 8). The carbon dioxide concentration in uncoated control fruits was slightly lower than that in coated fruits (3−6%) but was considerably higher than in fruits coated in our laboratory (2−3%, Figure 5). This could be due to the fact that fruit in the plant received considerable mechanical abuse on the semi-industrial line in comparison with smooth handling in the laboratory. Only traces of ethanol and no acetaldehyde were found in these fruits. Appearance of all coated fruit was good, and there was no difference in taste between coated and control fruit.

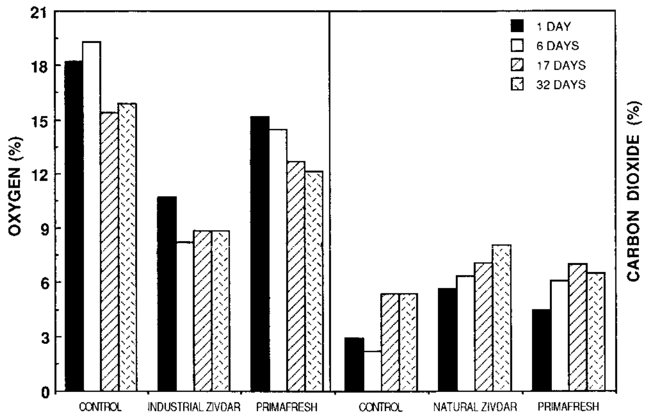

Figure 8. Internal oxygen and carbon dioxide concentrations in Nova mandarins with two coatings.

DISCUSSION

Certain amounts of ethanol and traces of acetaldehyde, which can be a measure for the appearance of undesirable flavors, were found in all coated fruits. There was a relationship between the amounts of these compounds and low oxygen and high carbon dioxide concentrations in these fruits. The fruit coatings apparently reduced passage of oxygen through the peel and thus created partial anaerobic conditions in the fruit, which resulted in the formation of products of anaerobic respiration, e.g., ethanol and acetaldehyde. The coatings also prevented the exit of carbon dioxide, ethanol, and acetaldehyde from the fruit, which led to undesirable flavor changes of the fruit segments or of the juice made from them.

There was no relationship between the gas permeability of the coatings and the concentrations of oxygen and carbon dioxide inside the fruits. This finding indicates that the CO_2 and O_2 gases do not leave the fruit according to their permeability values but that there is apparently another pathway through which the passage of the gases takes place. Hagenmaier and Shaw (1993) claim that there are two pathways for gas exchange: (1) the coating forms an additional barrier on the peel through which the gas must be permeate or (2) the coating plugs openings in the peel. The mechanism that prevails depends on the pathway for gas exchange in the uncoated fruit. Their conclusion was that resistance to gas exchange of coated fruit is strongly influenced by the coating's ability to block pores on the surface of the fruit and the coating thickness is less important. In contrast to gas exchange, the resistance of the peel to water vapor transport is more dependent on the coating thickness than on the type of coating. In our work, the coatings that contained a polyethylene emulsion and carnauba wax had high permeabilities to O_2 and CO_2, but they probably blocked the fruit pores and thus reduced the gas exchange. Other coatings used in our work had the same permeabilities, or even lower, to O_2 and CO_2 but did not block the pores, and thus the gas exchange was not affected significantly.

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