Color and Texture of Acidified Ripe Olives in Pouches

P. García, M. Brenes, C. Romero, and A. Garrido

ABSTRACT
The effects of pouch material (aluminum, plastic), packing pH (3.8, 4.3), acidifying compound (lactic, gluconic), and storage temperature were tested on polyphenol content and color of holding brines, surface color, and firmness of ripe olives. Using pouches of plastic films, pH 4.3–4.0 holding solution, and lactic or gluconic acid products with color and texture similar to traditional canned ripe olives were produced. They could be properly stored at room temperature (25°C). As storage temperature rose, color improved but texture was seriously degraded at 50°C.

Key Words: olives, color, brines, acidity, plastic pouches

INTRODUCTION
OlivEs May Be ProCessed to Produce three main table products known as Spanish-type green olives, naturally black olives, and ripe (dark) olives. The industrial procedure for production of ripe olives consists of successive treatments of fruit with dilute NaOH. During intervals between NaOH treatments, fruits are suspended in water through which air is bubbled (García et al., 1991). Throughout this operation, olives darken progressively due to oxidation of orthodiphenols, hydroxytyrosol (3,4-dihydroxyphenyl ethanol) and caffeic acid (Brenes et al., 1992). To prevent deterioration of color during storage, various compounds such as ferrous gluconate (National Canners Association, 1965; García et al., 1991) and ferrous lactate (García et al., 1988) were used in the darkening step. The product is canned and sterilized, as appropriate for a low-acid food (pH equilibrium 6.0–7.0) (Anonymous, 1995).

Packing such olives at pH <4.6 may qualify the product as acidified food (Anonymous, 1995), which would require only pasteurization. This change could be advantageous since it would save energy, provide the possibility of new packing materials (such as pouches), and reduce investment in retorts. However, pH<6.5 could affect color, producing discoloration and brown tines in the oxidized fruit (Garrido and Sánchez, 1982; Brenes et al., 1995), which may negatively affect consumer acceptance.

The aim of this work was to study the feasibility of packing ripe olives in acidic conditions and to investigate changes in surface color of the fruits, color and polyphenol content of the brines, and texture when the product is packed as acidified food in pouches.

MATERIALS & METHODS
Olives and darkening treatments
Experiments were carried out on fruits of Hojiblanca cultivar (Olea europaea L.) previously preserved in aerobic conditions (Brenes et al., 1986) for a period of 8 mo. Olives (14 kg) were treated on two consecutive days with 20L NaOH solutions (lyes) of 1.5 and 1.0% (w/v) which were permitted to penetrate either 1 mm into the flesh or to the pit, respectively. After each lye treatment, tap water (20L) was added and air was bubbled every day to complete a 24h cycle (lye treatment plus washing). On the third day, the pH of the washing liquid was maintained at 7.5 by an automatic controller (Crismon, pH/mV controller, Spain). CO2 being added to neutralize excess NaOH. On the fourth day, olives were immersed in 0.08% (w/v) ferrous gluconate solution (Fluka, Switzerland) for another 24h. Details of the darkening process were as described by Fernández et al. (1985).

Packing of olives
Pitted fruits (75g) were packed in plastic or complex aluminum pouches (layers of plastic and aluminum foil) and covered with 105 mL of solution containing 4% (w/v) NaCl, 0.03% (w/v) ferrous gluconate, and either lactic (Paneac, Spain), or gluconic acid (Sigma, USA) to adjust the equilibrium pH. The equilibrium pH’s studied were 7.0, 4.3, 4.0, and 3.8. Unless explicitly stated in other treatments, pH was corrected with lactic acid. Pouches prepared to reach pH 7 at equilibrium were sterilized at 121°C for 15 min (lethality value F0 = 15) in a computer-controlled Sterilflow retort (Madinox, Barcelona, Spain). When the pH at equilibrium was 4.3 or 3.8, pouches were pasteurized in the same apparatus at 80°C for 5 min or at 90°C for 4 min (in one treatment). In both cases, pouches reached the same lethality value, UP2,4 = 25. Pouches with pH 4.0 at equilibrium were sterilized or pasteurized, with the same conditions. Plastic pouches (comprising layers of polyester, saran and polyethylene) and complex aluminum (central layer) based films were provided by Soplaril Hispania (Barcelona, Spain).

Shelf life and color of packed olives
Pouches were stored at 25 or 50°C in two thermostatic chambers (Selecta, Barcelona, Spain); periodically (two replicates) the physical-chemical characteristics were analyzed. Colorimetric measurements on the olives were performed using a BYK-Gardner Model 9000 Color-view spectrophotometer (Silver Spring, MD). Interference by stray light was minimized by covering samples with a box having a matt black interior. Color was expressed as reflectance at 700 nm (Fernández and Garrido, 1971). Lower reflectance values indicated darker colors.

Texture of olives
Firmness was measured using a Kramer shear compression cell coupled to an Instron Universal Testing Machine (Canton, MA). The cross head speed was 200 mm/min. The firmness of the olives was expressed as the mean of 8 measurements, each of which was performed on 4 pitted olives. Shear compression force was expressed as N/100g pitted olives.

Color of liquids and physico-chemical analysis
Color was determined as the difference of absorbances at 440 and 700 nm (Montaño et al., 1988). Previoulsy, liquids were centrifuged at 12000×g for 10 min. Sodium chloride, pH, free acidity, and total polyphenols in liquids (determined by the Folin-Ciocalteau reaction method and expressed as ppm of caffeic acid) were analyzed as described by Fernández et al. (1985).

Permeability of pouches
Measurements were made with a Micro-Oximax O2/CO2 respirometer (Columbus Instruments, Columbus, OH). Two sealed pouches containing olives and liquid were placed inside 2L jars and incubated in a thermostatic chamber (Selecta, Barcelona). Experiments were run in triplicate and O2 was
monitored every 6h. After each measurement, the air in the jars was replaced with fresh dry air. Thus, the permeability of the containers was tested in an "open" system.

**Statistical analysis**

Statistical analysis of results was performed using the Statistica package software (StatSoft, 1996). Comparisons between treatments were made by the multiple Duncan’s range test. Significance of differences was defined at $p \leq 0.05$.

**RESULTS & DISCUSSION**

**SURFACE COLOR OF Ripe Olives**

packed in sterilized or pasteurized complex aluminum (Al) and plastic (P) pouches, at pH 7.0 and 4.0, showed important changes (Fig. 1). In Al pouches, the fruits packed at pH 7.0 and sterilized (pH7;ST;Al), which can be considered the normal industrial product (control), practically maintained color throughout storage, as has been reported in canned ripe olives (García et al., 1986). The color values (% reflectance) were always $<10$, which can be rated as 2 (good color) in the ripe olive scale established by Fernández and Garrido (1971). They defined very good color (1) as values $<6.5$. In the same containers, there was discoloration when the pH at equilibrium was 4.0. The discoloration was more evident for sterilized fruits (pH4;ST;Al), in which the effect was produced mainly during heat treatment. Reflectance (%) values were just below 16, which was considered a poor color (4) according to the same scale. In pasteurized fruits, there was an initial color recovery and then a progressive discoloration, although color was always darker than in sterilized fruits. A similar effect of pH on surface color had been reported by Brenes et al. (1995).

In contrast, in P pouches, the surface color of olives packed at pH 7.0 and sterilized improved throughout storage and led to the darkest final color. When the pH at equilibrium was 4.0, sterilized olives (pH4;ST;P) showed a considerable color improvement throughout most of the storage, especially up to day 90. After that there was a slight discoloration, although the final color was similar to that of the control (pH 7; ST;Al). At pH 4.0, the surface color of pasteurized olives (pH4;PS;P) was only slightly less intense than that in the normal product (pH7;ST;AL). This indicated the potential for packing acidified ripe olives in pouches while maintaining the normal color of the product.

Variability in the color and firmness of fruits as well as in the polyphenol content and color of holding brines may be expected using acidic conditions. This was studied by comparing probable extreme values of pH (4.3 and 3.8) and storage temperature (room or 25°C, and 50°C). The effect of the type of pouch on polyphenol content in the brine was negligible (Fig. 2), with similar effects in plastic and aluminum. There was a rapid increase of polyphenols in the brines of olives packed in either P or Al during the first 10 days. Then, a clear effect of storage temperature was observed throughout the rest of the period, with the polyphenol content higher in pouches maintained at 50°C. Differences due to pH were less. At the end of storage, olives kept at pH 3.8 always showed lower polyphenol content.

Brine color rapidly increased (darkening) during the first 10 days (Fig. 3), corresponding to the initial polyphenol content increase (Fig. 2). Then, there was a discoloration in all

---

**Fig. 1—Effect of pouch material (aluminum, Al; plastic, P), packing pH (4.0, 7.0), and heat treatment (pasteurization, PS; sterilization, ST) on the changes in surface color of ripe olives during storage at 25°C. Where standard deviations are not visible, they were within the range of the symbols on the graph.**

**Fig. 2—Effect of pouch material (aluminum, plastic), packing pH (4.3, 3.8), and storage temperature (25°C and 50°C) on the total polyphenol concentration (expressed as ppm of caffeic acid) in the holding solutions of ripe olives during storage. Where standard deviations are not visible, they were within the range of the symbols on the graph.**

**Fig. 3—Effect of pouch material (aluminum, plastic), packing pH (4.3, 3.8), and storage temperature (25°C, 50°C) on the color of the holding solutions of packed ripe olives. Where standard deviations are not visible, they were within the range of the symbols on the graph.**
Color and Texture of Acidified Ripe Olives . . .

treatments, the effects of pH and temperature being considerably higher in P than in Al pouches. Throughout storage, darker colors were observed in olive brines packed at pH 4.3 than in those at pH 3.8, with the same levels of the other components. This may be due to the pH effect on color of the polyphenol solutions (Brenes et al., 1995), although a greater oxidation might also have occurred at higher pH. Note that colors of brines stored at 25°C were similar in both types of pouches and at both pH’s of packing. In contrast, a storage temperature of 50°C gave rise to differences between color of brines packed in P or those in Al pouches. The color in P pouches at pH 4.3 was considerably darker. This darkening may be due to a higher polyphenol oxidation, provoked by the high oxygen permeability of the plastic at that temperature.

Surface color of ripe olives packed in P pouches was considerably affected by pH and storage temperature (Fig. 4). A first effect of pH was observed during heat treatment (pasteurization). Olives packed at pH 4.3 were darker (lower reflectance) than those at pH 3.8. There was a rapid darkening in all treatments during the first days after packing, corresponding to initial brine darkening (Fig. 3). This darkening (Fig. 4) was more intense in olives kept at 50°C. Color changes throughout the rest of storage were evident but slower, showing different patterns due to temperature and pH. Storage at 50°C led to progressive darkening, which was more intense in fruits packed at pH 3.8. The color of those kept at pH 4.3 was always darker, although differences were not appreciable after 150 days. Storage at 25°C did not appreciably alter the color of fruits when the pH of the holding brine was 3.8. In contrast, when the equilibrium pH was 4.3, an initial improvement was observed up to day 60; then, there was a slight discoloration followed by stabilization. In any case, note that olives stored at 25°C and packed at pH 4.3 always had considerably darker (about 1.5% reflectance values) color than those packed at pH 3.8. Color of fruits stored at 25°C and packed in Al did not change during storage when the pH was 4.3 (reflectance values were 8 to 9) and had a slight discoloration at pH 3.8 (reflectance rose from 9 to 13). When stored at 50°C, there was a progressive discoloration and fruits passed from 9 reflectance value to 17 and 20 for pH 4.3 and 3.8 respectively. These colors at end of the storage (150 days) would not be acceptable for ripe olives (Fernández and Garri-do, 1971).

The darkening of ripe olives in plastic films must have been due to oxidation of polyphenols by oxygen diffused through the plastic film (Exama, 1993; Leiris, 1996). Oxygen diffusion was ten times higher in plastic films stored at 50°C than in samples maintained at 25°C (Table 1). (p<0.001). Diffusion through the P film was independent of storage time (p>0.01), and was the same (p>0.05) for pouches pasteurized at 80 and 90°C (Table 1) when the storage temperature was 50°C. Diffusion through Al complex film was negligible in all treatments.

The effect of pH on ripe olive color was considerable, as has been reported by Garri-do and Sánchez (1982). In our studies, fruits packed at pH 4.3 and stored at 25°C gave darker surface color, possibly due to faster polyphenol oxidation (García et al., 1992) and a darker color of the Fe-phenol complex (Brenes et al., 1995) as pH increased. In fruits packed at pH 3.8 and stored at 50°C, there was progressive darkening. Differences due to pH must have been due to oxidation of polyphenols by oxygen diffused through the plastic film (Exama, 1993; Leiris, 1996). Oxygen diffusion rates were separately compared (Table 3). At 50°C storage, fruits in Al pouches at pH 7...
(sterilized) and pH 4.3 had similar texture (p<0.01) while those packed at pH 3.8 were softer (p<0.05). At 25°C, fruits in Al pouches at pH 7 (sterilized) were the softest. Differences between pasteurized Al pouches at pH 4.3 and 3.8 were significant (p<0.05) and had acceptable texture.

Ripe olives in pasteurized P pouches produced the softest fruits at 50°C. However, when stored at 25°C they maintained higher texture than the sterilized product (pH7). This may be of interest for preparing ripe olives from cultivars with low consistency. At 25°C, texture differences occurred between fruits packed at 4.3 and 3.8 (p<0.05).

The effect of pH was expected, and confirmed results of Brenes et al. (1994), who showed that the softening rate of acidified olives increased as pH decreased and temperature rises. However, differences in firmness due to material of pouches were clear. Texture degradation might have been enhanced by the presence of oxygen, which diffused through the P film and was negligible in Al packages. Texture losses in ripe olives may be related to pectic substance losses (Chung et al., 1974, Jiménez et al., 1993). They could be influenced by degradation of other polymers in the olive cell wall (García et al., 1994). Oxygen diffusion through the plastic film might have increased such an effect.

For acidification, gluconic and lactic acids were tested but industrial experts advised against the use of vinegar (acetic acid) because of negative sensory considerations. The effects of acids on the olive surface color were apparent (Fig. 5). There was an initial effect during pasteurization, lactic producing darker olives than gluconic. Afterwards, surface color was maintained at 25°C, and was darker (lower reflectance) for olives packed with lactic than for those with gluconic. In both cases, there was a slight tendency for color to improve at the end of storage. Throughout storage at 50°C, the effect of the two acids were parallel, with both darkening marked for about 30 days. Then, the darkening rate decreased considerably, but olives packed with lactic always remained darker. Thus, irrespective of changes during storage, initial differences due to type of acid continued.

The effect of using lactic or gluconic, at the same pH, on firmness at 25°C and 50°C was negligible (Fig. 6). However, at 50°C there was rapid texture degradation during the first 10 days, after which softening slowed. The risk of deterioration of acidified ripe olives packed in P pouches increased when stored at high temperatures. In contrast, at 25°C texture losses with time were only moderate, and comparable to those reported for green olives (Sánchez et al., 1997).

Titratable acidity reached equilibrium concentrations of 2.0 to 2.2 g L⁻¹. Sodium chloride should thus be 20–25 g L⁻¹, as usual in normally canned ripe olives. Higher or lower values of salt may lead to unbalanced concentrations similar to those reported in green olives (Fernández et al., 1985). The presence of lactic acid usually introduces a sour taste different from that of traditional ripe olives.

CONCLUSIONS

RIPE OLIVES COULD BE PACKED AS ACIDIFIED FOODS (pH<4.6) IN PLASTIC POUCHES, APPLYING PASTEURIZATION for preservation. In that case, pH should be kept slightly below 4.3 where color and texture were well preserved throughout storage at room temperature (25°C). Lactic and gluconic showed parallel effects with respect to texture, although lactic led to more acceptable surface color although it produced a slightly lower pH.

REFERENCES


Volume 64, No. 2, 1999 — JOURNAL OF FOOD SCIENCE 251