Sodium Lignin Sulfonate and Sodium Orthophenylphenate Interaction on Browning of Pear Fruits

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Summary. Immersion of Anjou pears (*Pyrus communis* L. cv. Beurre d'Anjou) in sodium lignin sulfonate (SLS), a flotation agent used in hydraulic handling of pears, did not cause injury leading to skin browning. Immersion of cut pear slices in SLS discolored pear fruit flesh, but the discoloration derived from SLS pigments does not intensify with time. When the fungicide sodium orthophenylphenate (SOPP) was combined with SLS, necrotic skin mottling occurred with increased immersion times and temperatures. A white precipitate in the SLS SOPP solution accompanied phytotoxicity of pear skin tissue. Acidification of alkaline SOPP solutions (pH 11.3) with 0.01 N HCl down to pH 10 produced mild skin necrosis. Both acid (0.01 N HCl) and alkaline (0.01 N KOH) solutions of SOPP and SLS SOPP combinations caused browning of pear flesh.

The purpose of this investigation was to determine conditions causing injury to pear fruit tissue during hydraulic movement in the grading and packing operation, and to quantify the effects of SLS (sodium lignin sulfonate: Orzan SL-50, ITT Rayonnier, Stamford, Conn.; or Lignosite 458, Georga-Pa-

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cific, Bellingham Wash.) and SOPP (sodium orthophenylphenate: Steri-seal D, Steri-Seal of Washington Inc., Wenatchee, Wash.) at varying concentrations, temperatures, and pH values on pear skin and flesh. Flotation agents are added to the flume water used to convey and reduce injury to pear fruits in packinghouses. The desired specific gravity for pear flotation is between 1.03 and 1.06 (Sugar and Spotts, 1989). Soda ash, sodium sulfate, and sodium silicate have been used as flotation agents. SLS was introduced recently into the industry as a flotation agent and fungicide (Sugar and Spotts, 1986).

SOPP and various chlorine formulations are used in dump tank water as fruit disinfectants (Baker and Heald, 1932; Wellman, 1939), and SOPP has been combined recently with SLS. This combination occasionally has caused a hypersensitive reaction characterized by skin browning and mottling (Apel, 1989; Sugar and Spotts, 1986).

Pear disk treatments. Anjou pears at various stages of maturation and ripeness (Hanson and Mellenthin, 1979) and from different sources were used in 1988 and 1989. Four 27-mm-diameter disks, 12 to 18 mm thick, were removed from a uniform area on an individual pear. Eight to 10 pears were selected at random for the various temperature and pH studies. Injury (tissue darkening) was measured with a reflectance meter (Photovolt Corporation, New York) equipped with tri-green filter (absorbance= 416 nm). Reflectance of both the skin and flesh were assayed on eight to 10 disks per treatment. Initial measurements were taken within 5 min of removal from the pear. Reflectance were measured immediately after treatment and after 20- to 30-min intervals for up to 3 h after removal from the test solutions.

Immediately after the initial reflectance was measured, individual pear disks were placed in 22.3-ml vials containing 10 ml of water, 11% SLS, 2200 mg liter⁻¹ SOPP, or combinations of SLS and SOPP. Solution temperatures were maintained using cold storage rooms (10C) or a Magni Whirl (Blue M Electric Co., Blue Island, Ill.) water bath (25 C, 35 C). After immersion, the disks were strained from the solution with cheesecloth, washed in tap water for 2 to 4 sec, and placed on dry paper towels for subsequent mea-

surements. Reflectance were measured again at intervals of 20 to 30 min for up to 3 h after removal from the test solutions.

Concentration, temperature, and pH treatments with SLS and SOPP on pear skins and disks. The SLS concentrations were diluted with water from the 100% commercial product to 33% and 11%. Pear disks were immersed in the SLS solutions for 90 min at 25C.

Pear disks were immersed in solutions of 11% SLS and 2200 mg liter⁻¹ SOPP, alone and in combination, and in a water control for 10, 20, 30, 90, and 130 min at 10C, 25C, and 35C.

pH effects. Pear disks were immersed in 11% SLS (pH 4.6) and 2200 µg ml⁻¹ SOPP (pH 11.3) and in combination (pH 7.0) with unbuffered 0.01 N HCl and 0.01 N KOH for 30 min in a 25C water bath. Acidic and basic solutions without SLS or SOPP were used as control treatments. The change in pH with addition of SLS and SOPP to the HCl and KOH solutions were measured using a Beckman 071 pH meter (Beckman Instruments, Irvine, Calif.) with a combination electrode.

Concentrations of SLS and pear injury. Ninety-minute immersions in 11%, 33%, and 100% SLS solutions at 25C did not cause skin damage or browning (Fig. 1A). The pear flesh (Fig. 1B) stained during the initial immersion when compared to the water

Fig. 1. Immersion in 0%, 11%, 33%, and 100% sodium lignin sulfonate (SLS) at 25C for 90 min on pear skin (A) and flesh (B) browning (reflectance). Bar = 1 SD.

Fig. 2. Immersion in water, 11% SLS, 2200 mg liter⁻¹ SOPP, and 11% SLS-2200 mg liter⁻¹ SOPP combinations at 25C for 20 min on pear skin (A) and flesh (B) browning (reflectance). Bar = 1 SD.

control. After removal from SLS, the pear flesh did not continue to darken with time.

SLS and SOPP temperatures on pears. SLS did not cause significant pear skin browning through the 25C (Figs. 1A and 2A) or at 10 and 35C temperatures. SOPP without SLS produced a mottled, reddish-brown discoloration on pear skins when treated for 130 min at 10C. When 2200 µg ml⁻¹ SOPP and 11% SLS were used in combination, a milky white precipitate was produced in suspension and a reddish-brown, mottled discoloration developed around lenticels when treated for 60 min at 25C (Fig. 2A) and 130 min at 10C. Generally, cool solution temperatures and/or short exposure times to SOPP, such as 10 min at 35C, 30 min at 25C, and 60 min at 5C, did not brown pear skins significantly.

The pear flesh behaved differently from pear skin tissue when exposed to SOPP and SLS. With SLS alone, SLS pigment staining occurred during the immersion phase of treatment (Figs. 1B and 2B), with no additional browning developing during the observation period. SOPP alone at 2200 µg ml⁻¹ produced flesh necrosis in the following solutions: 25C for 60 min (Fig. 2B), 10C for 130 min, and 35C for 10 min. When SLS was combined with SOPP, necrotic browning was reduced, but it was not significantly (Fig. 2B)

different than treatment with SOPP alone.

pH and SOPP-SLS-treated pears. A white precipitate was formed in SOPP solutions acidified with 0.01 N HCl, pH 2.2. SLS amended with 0.01 N HCl had a pH of 4.4, with no precipitate. Very severe, rapid browning occurred in pear skins treated with 2200 $\mu\text{g ml}^{-1}$ SOPP in 0.01 N HCl (Fig. 3A). When the acidity became less, the SOPP toxicity was reduced. Alkaline (0.01 N KOH) solutions (Fig. 4A), at pH 11.4, gave a very mild skin-browning reaction, with negligible necrosis in a 0.01 N KOH solution (Fig. 4A).

Flesh responses to SOPP, SLS, and SOPP SLS combinations were different from skin reactions. The skin was mottled, while the flesh was an even, brown color. Acidification of SOPP and SOPP SLS combinations increased browning (Fig. 3B) when compared to water and SLS alone. In alkaline (0.01 N KOH) regimes, SOPP alone at 2200 $\mu\text{g ml}^{-1}$ produced severe browning (Fig. 3B).

Sodium lignin sulfonate, when used alone, is remarkably nonphytotoxic over a wide range of concentrations, temperatures, and pH regimes. Moreover, SLS has beneficial flotation and disinfectant properties. After initial immersion, which results in some staining, pear flesh tissue maintains its

Fig. 3. Immersion in 0.01 N HCl, 0.01 N HCl + 11% SLS, 0.01 N HCl + 2200 mg liter^{-1} SOPP, and 0.01 N HCl + 11% SLS-2200 mg liter^{-1} SOPP combinations at 25°C for 30 min on pear skin (A) and flesh (B) browning (reflectance). Bar = 1 SD.

Fig. 4. Immersion in 0.01 N KOH, 0.01 N KOH + 11% SLS, 0.01 N KOH + 2200 mg liter^{-1} SOPP, and 0.01 N KOH + 11% SLS-2200 mg liter^{-1} SOPP combinations at 25°C for 30 min on pear skin (A) and flesh (B) browning (reflectance). Bar = 1 SD.

color. The addition of SLS tended to moderate the phytotoxic properties of SOPP.

SOPP is especially toxic to pear flesh; the tissue darkens and becomes soft (personal observation). The observed flesh reactions were an even brown; while skin symptoms were reddish-brown and mottled. When mixing chemicals, in particular SOPP with SLS and SOPP with 0.01 N HCl, a white precipitate was produced in the aqueous solution. This precipitate may be the result of free phenol, which was toxic to fruit (Apel, 1989). Severe skin mottling seems to have been associated with this precipitate.

High temperature and prolonged treatment of pear tissue with combinations of SLS and SOPP tended to accentuate both skin and flesh necrosis. However, the reactions were manifest even in cool (10°C) solutions, when the exposure time was increased. These reactions were probably the result of enzymatic oxidative browning reactions influenced by temperature and chemical concentrations of SLS and SOPP.

The work of Sugar and Spotts (1986) has shown that SLS has fungicidal properties and our work shows that it does not detract from the appearance of the fruit when used alone. Our work elucidates the hazards of SLS and SOPP combinations, in par-

ticular in acid regimens. The eventual withdrawal of SOPP from the market may not be a serious disadvantage to the pear storage industry, if SLS is able to fill the void left by the lack of SOPP disinfectant. More work is required to study the disinfectant properties of SLS at various concentrations.

In conclusion, SLS, without the addition of SOPP, was not toxic to pear skin or flesh under any of the conditions imposed. Lack of toxicity to the fruit skin was not altered by skin colors ranging from green to yellow-green. Toxicity was not induced by immersion in 100% SLS solutions, nor was it produced by acid or alkaline solutions. Neither high nor low temperatures, nor duration of immersion, caused skin toxicity. Although the fruit flesh was stained by SLS pigments, in the absence of SOPP, the exposed flesh remained free of damage due to concentration, pH, temperature, and immersion time.

SOPP could be damaging to both skin and flesh. Increased concentrations, temperatures, acidity, and immersion time augmented damage. When SOPP was combined with SLS, the toxicity was attenuated.

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