

sampled on July 16 and September 16. In a second experiment spray applications were continued bimonthly until August 16, samples being taken on July 16 and September 16. Table II shows the residues of mercury found in replicate samples following analysis.

Some varieties in Table II were not available for the September sampling.

The weight of dried apple burned was about 2 grams, which represented about 10 grams of fresh apple tissue. If a larger weight of tissue was used, combustion was incomplete. Expansion of gases

into the balloon allowed the combustions to be carried on safely. The size of the sample and the rapid rate of burning of cellophane necessitated the use of a balloon, which was replaced after about five combustions. Nearly 200 combustions have been conducted in the flask. About 12 samples can be burned and analyzed in a day.

Acknowledgment

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FUNGICIDE RESIDUES

Effects of Treatment Conditions on *o*-Phenylphenol Residues in Oranges

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Sodium *o*-phenylphenate is effective as a postharvest fungicide in controlling decay of citrus fruits, but it sometimes causes peel injury. A study was made of the effects of treatment conditions on residues of *o*-phenylphenol in oranges. Residues increased with concentration, temperature, and length of treatment, but decreased as pH was raised. By control of treatment conditions residues can be maintained at any desired level. Peel injury was not a problem when residues were below the legal tolerance of 10 p.p.m.

ORTHO-PHENYLPHENOL and its sodium salt are effective as postharvest fungicides for citrus fruits when applied from aqueous solutions (8). A major problem has been injury to the peel by these materials (7). Efforts to prevent this injury have been directed toward adjustment of formulation (9) and use of additives such as hexamethylenetetramine (5). Recently it has been found (6) that both peel injury and fungicidal effectiveness are related to the pH of sodium *o*-phenylphenate solutions used for treatment of oranges.

The authors found (4) that addition of sodium *o*-phenylphenate to the water used for hydrocooling oranges was effective in reducing subsequent decay. The search for optimum conditions has been extended to study the effects of concentration, temperature, pH, and length of treatment on residues of *o*-phenylphenol and extent of peel injury of oranges.

Fruit Handling

Oranges used in these experiments came from groves of the Citrus Experiment Station. The entire series of experiments was run using Pineapple oranges, a midseason variety, and repeated with Valencias, which mature

much later. Fruit was washed, dried, graded, and automatically packed in 4/5-bushel fiberboard cartons using small, commercial-type machinery in

the experimental packinghouse. Storage before and after fungicidal treatments was at 70° F.

Low temperature treatments were

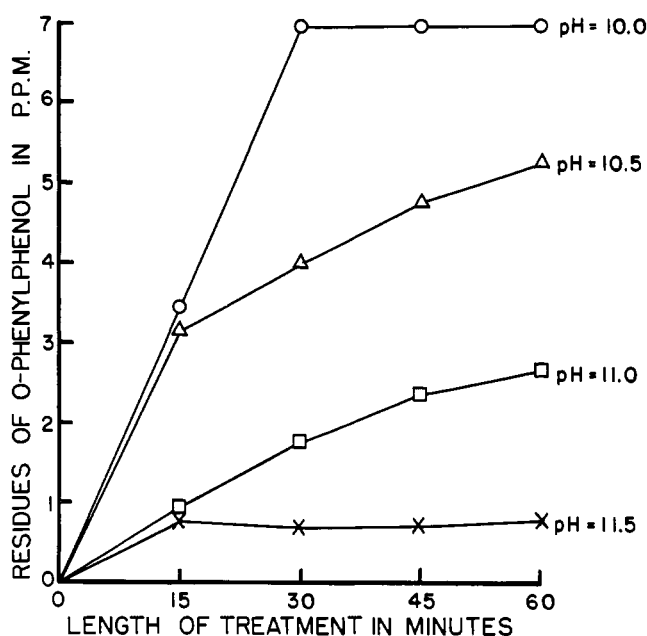


Figure 1. Effect of length of treatment on *o*-phenylphenol residues in oranges treated with 0.1% Dowicide A at 40° F. at various pH levels

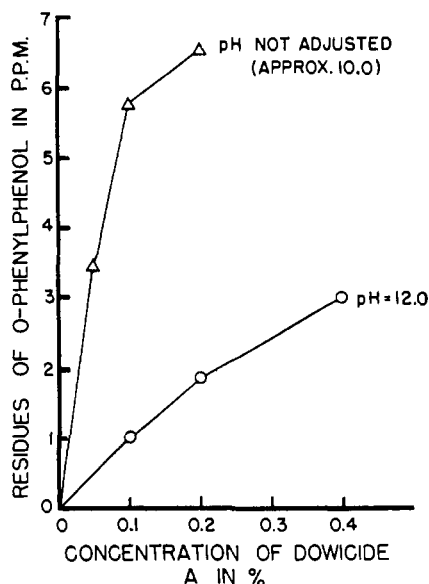


Figure 2. Effect of concentration of Dowicide A on *o*-phenylphenol residues in oranges treated for 30 minutes at 40° F. at two pH levels

carried out in a bin-type hydrocooler (3) having cloth baffles for the fruit and a pump for flooding with fungicidal solutions maintained at 40° F. by mechanical refrigeration. Oranges were coated with a commercial, solvent-type wax and run directly into the hydrocooler for treatment. Samples were removed at scheduled times, packed wet into cartons, and stored at 70° F. for analysis and examination.

At higher temperatures, a flood-type, color-add tank with a thermostatically controlled steam coil for heating the solution was used. Fruit was placed on a roller conveyor running at a speed adjusted to give an exposure time of 3 minutes under the flooding solution, rinsed in a water spray, dried, waxed, packed in cartons, and stored at 70° F.

Fungicidal Solutions

A calculated amount of Dowicide A, a technical grade (97%) of the tetrahydrate of sodium *o*-phenylphenate, was added to a known volume of water in the tank to give a solution of the lowest concentration required for a given series of treatments. More Dowicide A was added when higher concentrations were desired in the same series.

The pH was adjusted by slowly adding a 25% solution of sodium hydroxide using the color change of pHydrion test papers as a measure of pH. Samples at the lowest pH were run first and the level was increased as necessary by addition of more alkali.

Residue Analysis

Two oranges were taken at random from each treatment sample, cut into

pieces, and ground in a Waring Blender. A 20-gram portion was transferred, using 90 ml. of water, to a 250-ml. flask containing 2 grams of citric acid and a drop of Dow Corning Antifoam B. The flask was placed on an electric heater and connected by a distilling head to a vertical condenser dipping into 25 ml. of 0.025% sodium carbonate solution in a 150-ml. beaker. Boiling was continued until 50 ml. had distilled, making a total volume in the beaker of 75 ml. This solution containing the fungicide was filtered, to remove peel oil, into a 100-ml. volumetric flask, 15 to 20 ml. of sodium carbonate solution being used for washing. This simplified steam distillation method gave an 85 to 90% recovery of *o*-phenylphenol from ground oranges at levels up to 8 p.p.m.

Color was developed by the method of Gottlieb and Marsh (2) using 4-aminoantipyrine and potassium ferricyanide. Absorption of standard and unknown solutions was measured at 500 m μ with a Bausch & Lomb Spectronic 20. A standard sample containing 160 γ of *o*-phenylphenol had an absorbance of 0.128 when read in a half-inch square cell. Results were calculated as parts per million of *o*-phenylphenol and corrected for the apparent 1.2 p.p.m. shown consistently by untreated oranges. Averages of the residues found in the two orange varieties were used for plotting graphs showing results of experiments. No varietal differences were observed.

Experimental and Results

Experiments were run in the hydrocooler at 40° F. using a Dowicide A

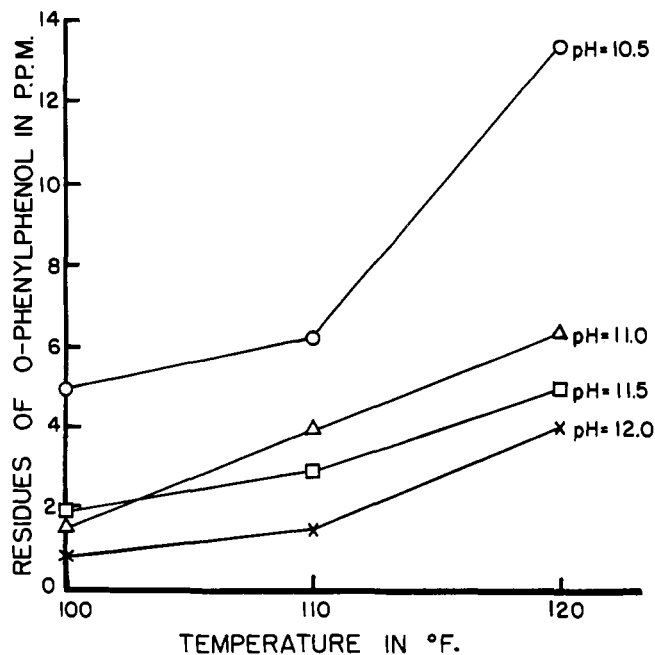


Figure 3. Effect of temperature on *o*-phenylphenol residues in oranges treated for 3 minutes with 0.1% Dowicide A at various pH levels

concentration of 0.1% with samples of oranges removed at 15-minute intervals over a period of 1 hour. This series was repeated at four pH levels varying by increments of 0.5 pH unit from 10.0 to 11.5. Results in Figure 1 show that *o*-phenylphenol residues increase with length of treatment but approach or achieve a limit inversely related to the pH of the solution.

In a second low temperature series the concentration of Dowicide A was varied from 0.05 to 0.4% for a 30-minute treatment at 40° F. This series was run once without pH adjustment (approximately 10.0) and again at pH 12.0. Figure 2 shows that *o*-phenylphenol residues increase with concentration of Dowicide A, but are much lower at the higher pH level.

Three series of experiments were run at higher temperatures in the color-add applicator, with treatment time fixed at 3 minutes by the conveyor speed.

Oranges were treated with 0.1% Dowicide A solution at 100°, 110°, and 120° F. for pH levels of 10.5, 11.0, 11.5, and 12.0. The increase in residues of *o*-phenylphenol with temperature is shown in Figure 3, and the inverse relationship of residues to pH is again evident.

In a second series fruit was treated with 2.0% Dowicide A solution for 3 minutes at 90° F. at various pH levels between 11.0 and 11.8. The results shown in Figure 4 indicate the importance of pH control in determining the level of residues in oranges.

The final series was run at 110° F. with a pH of 11.5 for concentrations of Dowicide A ranging from 0.1 to 1.0%.

The straight-line curve which resulted shows that under the conditions of the experiment the *o*-phenylphenol residues vary directly with concentration of the treatment solution.

All samples were examined for chemical peel injury after storage for 1 week at 70° F. Only the few samples having residues of *o*-phenylphenol greater than 15 p.p.m. had appreciable peel injury.

Discussion

Residues of *o*-phenylphenol in oranges increase with concentration, temperature, and length of treatment but decrease as the pH of the Dowicide A solution is raised. By proper control of treatment conditions almost any desired level of residues can be maintained. The time-tested Dowicide A-hexamine method (5) gives good control of decay at residue levels of about 2 p.p.m. and the legal tolerance for *o*-phenylphenol in citrus fruits (7) is 10 p.p.m. As no peel injury was found at levels below the legal limit, residues in this range should give good decay control without injury. For hydrocooling of oranges, a 30-minute treatment at 40° F. with 0.1% Dowicide A at pH 10.5, resulting in a residue level of about 4 p.p.m., has been found satisfactory.

These experiments have shown the importance of pH control in the use of Dowicide A as a fungicide for oranges. This factor is especially critical, as the pH of the solution tends to decrease because of absorption of carbon dioxide from the air and reaction with citric acid from damaged fruit. Unless checked, this could lead to residues in excess of the legal tolerance, serious peel injury, and ultimate precipitation of the fungicide.

The pronounced effect of pH on residues is probably due to absorption by the fruit of fungicide in the form of

free *o*-phenylphenol which is formed by hydrolysis of the sodium *o*-phenylphenate in solution. Lower pH would tend to favor this hydrolysis and higher pH to suppress it. The absorption of fungicide by waxed fruit in the hydrocooling experiment supports this view.

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FERTILIZER TECHNOLOGY

High-Analysis Superphosphate by the Reaction of Phosphate Rock with Superphosphoric Acid

A NEW SUPERPHOSPHATE that contains about 54% available P_2O_5 has been introduced to the fertilizer industry by TVA. Because of its higher grade, this material is referred to as "high-analysis superphosphate." It is produced by acidulating phosphate rock with superphosphoric acid. Superphosphoric acid, also a TVA development, is

an electric furnace acid that contains about 76% P_2O_5 , which is equivalent to about 105% orthophosphoric acid (H_3PO_4). This compares with 54 to 56% P_2O_5 for the usual furnace and wet-process phosphoric acids used in the fertilizer industry. Chemically, the superphosphoric acid contains about 49% of its phosphate as orthophosphate,

42% as pyrophosphate, and the remainder as higher polyphosphates. TVA has done considerable work in studying the production, properties, and use of superphosphoric acid (3, 5, 6); first application was in liquid fertilizer processes.

In considering the use of superphosphoric acid in the production of super-

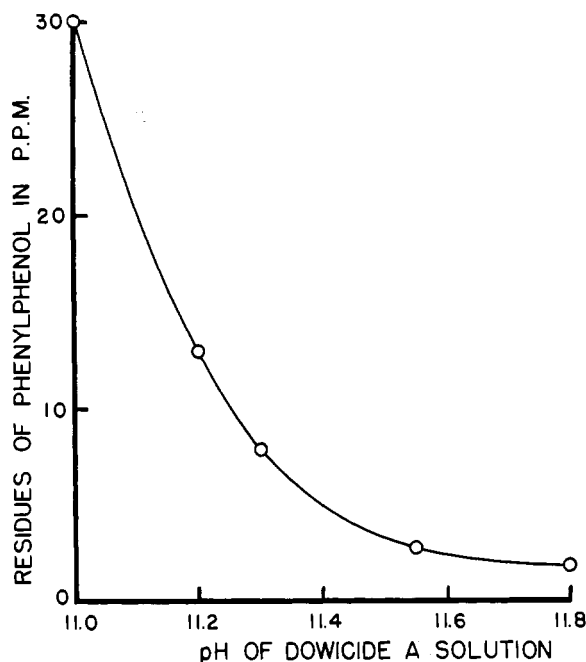


Figure 4. Effect of pH on *o*-phenylphenol residues in oranges treated for 3 minutes with 2.0% Dowicide A at 90° F.