# ZINC OXIDE AND LIQUID ZINC CHELATE SPRAYS AND LEAF DIPS FOR CORRECTION OF ZINC DEFICIENCY IN CITRUS

C. D. LEONARD

*IFAS Agricultural Research and Education Center*
Lake Alfred
and

FRANK H. MYER

*Griffin Fertilizer Company*
Frostproof

*Abstract.* **A field experiment comparing low-volume foliar sprays of Zn oxide at 6.9 lb. Zn, a liquid Zn chelate (THIS containing 7% Zn) at 0.70 lb Zn, and a second liquid Zn chelate (THIS Citrus Mix containing 1.75% Zn) at 0.26 lb. Zn per acre for correction of Zn-deficiency was conducted in a 'Pineapple' orange grove near Frostproof, Florida.**

**All the Zn-chlorotic leaves were completely greened on 97, 40 and 70% of marked twigs by the ZnO, THIS Citrus Mix, and THIS sprays respectively. Leaves on the marked twigs in the check plots remained chlorotic.**

**In another experiment in the same grove, Zn-chlorotic leaves were dipped into various Zn mixtures. Some of the chelate treatments using low concentrations of Zn were as effective as much higher concentrations of Zn in the ZnO treatments. The addition of the wetting agent Vatsol OT and/or urea enhanced Zn uptake from the chelates but not from the ZnO mixtures.**

## Introduction and Literature Review

Periodic application of a zinc (Zn) foliage spray is the most economical and most widely used method of supplying nutritional Zn and controlling Zn deficiency or frenching in Florida citrus groves. Zinc sprays are reasonably effective in controlling Zn deficiency in most groves, even though this metal does not translocate from the sprayed leaves to new leaves that develop later (6). Broadcast applications of zinc sulfate, zinc chelates or other sources of Zn to acid, sandy soils in central Florida have not been effective in correcting Zn deficiency in bearing citrus trees. However, a mixture of 5 lb. zinc sulfate and 5 lb. calcium chloride per tree applied in high concentration on small areas of soil beneath trees of bearing size will readily correct Zn deficiency (4, 5). This method costs more in both materials and labor than Zn spray applications. It may, however, have limited use in unsprayed groves on a biological pest control program if Zn deficiency occurs.

Four inorganic Zn sources, including zinc sulfate with hydrated lime, zinc oxide, zinc oxysulfate and basic zinc carbonate at either 5 or 10 lb. Zn and zineb, an organic fungicide (zinc ethylenebis-dithiocarbamate) at either 0.77 or 1.54 lb. Zn per 500 gal. gave good correction of severe Zn deficiency when applied postbloom as dilute sprays. There was no evidence of leaf or fruit burn from any of the Zn sprays (2).

Liquid Zn chelates, derived from by-products of wood processing, have been available to Florida growers for 2 or 3 years. These liquid chelates are much more expensive per pound of Zn than the inorganic Zn sources commonly used for nutritional sprays. Hence the chelates must be sprayed at much lower rates of Zn per acre than the inorganic Zn sources if the costs of the 2 types of spray materials are to be comparable. The use of liquid Zn chelates in nutritional sprays applied with low-volume spray equipment appeals to many growers because the chelates virtually eliminate the danger of clogging the sprayer. Some growers have had trouble with clogging such sprayers due to settling out of high concentrations of insoluble inorganic Zn sources such as Zn0 and Zn oxysulfate. Zinc sulfate, which is water soluble, will burn the leaves if sprayed without adding hydrated lime or soda ash. Growers using low-volume sprayers may prefer to use a non-toxic soluble Zn source such as the liquid Zn chelates at low Zn levels even though insoluble inorganic Zn sources applied at higher Zn levels might give better control of Zn deficiency. The work reported here was carried out to compare the effectiveness of zinc oxide sprays and leaf dips with that of 2 liquid Zn chelates applied at much lower rates of Zn per acre.

## Materials and Methods

*Spray experiment.* A field spray experiment

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was established in 1973 in a grove of Zn-deficient 8-year-old 'Pineapple' orange trees growing on acid sandy soil near Frostproof, Florida. There were 5 Zn spray treatments and one check spray treatment that received no Zn (Table 1). All sprays, including the check, contained chlorobenzilate for mite control and Plyac as a wetter-sticker. The 2 Zn chelates used were THIS containing 7% Zn and THIS Citrus Mix (THIS-CM) containing 1.75% Zn. The check treatment, THIS, THIS-CM and zinc oxide (ZnO) were applied at rates of 0, 0.70, 0.26 and 6.92 lb. Zn per acre respectively in 50 gal of spray with a low-volume Kinkelder sprayer. Two dilute Zn spray treatments with ZnO and THIS were applied at 10.4 and 0.70 lb. Zn per acre respectively in about 500 gal of spray. Rates of Zn used were higher than that usually applied in groves because many branches on the experimental trees showed severe Zn deficiency (footnote z, Table 1). The experimental design was one of randomized blocks with 4 replications. The plots consisted of 8 trees in each of 5 adjacent rows, or 40 trees per plot.

Four trees showing extensive Zn deficiency in the interior rows of each plot were selected for sample trees, to avoid possible effects of spray drift from plot to plot. Most of the 1973 spring flush twigs showing Zn deficiency on each of the sample trees were marked shortly after application of the treatments for later use in *checking* the effectiveness of the treatments.

Current spring flush leaf samples were taken from marked twigs on the sample trees of each plot. Chlorophyll was extracted with 80% acetone from the fresh leaves and the optical density was measured at 652$\mu$ (1). Significance of the mean differences in percent of chlorotic twigs greened and percent chlorophyll in leaves was determined by analysis of variance and the Duncan multiple range test.

*Leaf dipping experiments.* (a) *First experiment.* Mixtures for leaf dipping were prepared in 1 gal amounts for each of the following Zn sources: THIS-CM, THIS, ZnO (65% Zn) and KE-NU (6.5% Zn). KE-NU is another of the liquid Zn chelates. Several concentrations of Zn were used for each Zn source. Other variations included the use of chlorobenzilate miticide (which contains a wetting agent), Plyac as a wetter-sticker, Vatsol OT (Na dioctylsulfosuccinate) as a wetting agent, and urea as a penetrating agent (Table 2). On July 24, 1973, 4 twigs with Zn-deficient spring flush leaves on trees other than the designated sample trees in the check plots were tagged, numbered and dipped into the appropriate mixture in a 3-gal bucket. Other twigs with Zn-deficient 1973 summer flush leaves were dipped on August 17.

(b) *Second experiment.* An additional series

Table 1. Effect of foliar sprays of zinc oxide and liquid zinc chelates on correction of zinc deficiency and on chlorophyll content of 'Pineapple' orange leaves.

| Trt. No. | Zinc source: Name | Zn, % | lb./A | Zn lb./A | Spray: Concn[z] | Spray: Gal/A | Greened leaves,%[y] | Chlorophyll in leaves,%[y] |
|---|---|---|---|---|---|---|---|---|
| 1 | None | -- | -- | -- | -- | 50 | 0 d | .0937 c |
| 2 | THIS | 7 | 10 | .70 | 20x | 50 | 71 b | .1283 b |
| 3 | THIS-CM | 1.75 | 15 | .26 | 20x | 50 | 40 c | .1256 b |
| 4 | ZnO | 52 | 13 | 6.92 | 13x | 50 | 97 a | .1834 a |
| 5 | ZnO | 52 | 20 | 10.4 | 2x | 500 | 98 a | .1782 a |
| 6 | THIS | 7 | 10 | .70 | 2x | 500 | 65 b | .1431 b |

[z]Manufacturer's recommended rate to control moderate zinc deficiency is considered the "x" rate for THIS and THIS citrus mix. The Florida Citrus Spray and Dust Schedule's recommendation of 5 lb. Zn per 500 gal of dilute spray is considered the "x" rate for inorganic zinc sources.

[y]In the same column, mean values not followed by the same letter differ significantly at P = 0.05.

of dip mixtures with THIS-CM, THIS, and ZnO, was prepared with variations in Zn concentration and in wetting agents but without urea. Eight twigs with Zn-deficient leaves were dipped with each mixture on August 22, 1973.

## Results and Discussion

*Spray experiment.* Early in September, 1973, the percentage of marked twigs on which all the leaves had greened up was determined for each plot. Averages for each treatment are shown in Table 1, column 8. Both the concentrate and dilute ZnO sprays (Treatments 4 and 5) produced significantly more greening of Zn-deficient leaves than the sprays with THIS or THIS-CM (Treatments 2, 3 and 6). Sample leaves from the ZnO-sprayed trees also contained significantly more chlorophyll than leaves from the trees sprayed with THIS or THIS-CM (Table 1, column 9).

Table 2. Effect of dipping Zn-deficient 'Pineapple' orange leaves into different Zn spray mixtures on greening of the leaves.

| | | Per 500 gal | | | | Percent greened[y] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Summer flush | | Spring flush | |
| Trt. No. | Zinc source[z] | Zn lb. | Urea lb. | Vatsol pints | Plyac pints | 42 days | 59 days | 66 days | 83 days |
| 1 | THIS-CM | .13 | -- | -- | 5 | 54 | 70 | 74 | 80 |
| 2 | THIS-CM | .13 | 15 | 3 | -- | 100 | 100 | 88 | 85 |
| 3 | THIS-CM | .26 | -- | 3 | -- | 83 | 88 | 60 | 71 |
| 4 | THIS-CM | .26 | 15 | 3 | -- | 94 | 96 | 70 | 86 |
| 5 | THIS-CM | 1.04 | -- | -- | 5 | 56 | 73 | 86 | 86 |
| 6 | THIS-CM | 2.08 | -- | -- | 5 | 70 | 86 | 89 | 93 |
| 7 | THIS | .35 | -- | -- | 5 | 75 | 95 | 74 | 79 |
| 8 | THIS | .35 | 15 | 3 | -- | 94 | 96 | 79 | 81 |
| 9 | THIS | .70 | -- | -- | 5 | 45 | 69 | 84 | 88 |
| 10 | THIS | .70 | 15 | 3 | -- | 65 | 83 | 65 | 73 |
| 11 | THIS | 1.40 | -- | -- | 5 | 68 | 80 | 83 | 84 |
| 12 | THIS | 2.80 | -- | -- | 5 | 84 | 89 | 65 | 88 |
| 13 | KE-NU | .65 | -- | -- | 5 | 70 | 84 | 56 | 66 |
| 14 | KE-NU | .65 | 15 | 3 | -- | 91 | 96 | 92 | 90 |
| 15 | KE-NU | 1.30 | -- | -- | 5 | 67 | 78 | 80 | 80 |
| 16 | KE-NU | 2.60 | -- | -- | 5 | 80 | 91 | -- | -- |
| 17 | ZnO | 5.2 | -- | -- | 5 | 88 | 96 | 57 | 73 |
| 18 | ZnO | 5.2 | -- | 3 | -- | 74 | 84 | 81 | 84 |
| 19 | ZnO | 5.2 | 15 | 3 | 5 | 93 | 96 | -- | -- |
| 20 | ZnO | 10.4 | -- | 3 | -- | 93 | 95 | 62 | 78 |
| 21 | ZnO | 2.6 | -- | -- | 5 | 91 | 93 | 63 | 76 |
| 22 | ZnO | 1.3 | -- | 3 | 5 | 71 | 88 | 97 | 100 |

[z]THIS-CM = THIS, citrus mix; it contains 1.75% Zn and some manganese (Mn), iron (Fe), and magnesium (Mg). THIS contains 7.0% Zn. KE-NU contains 6.5% Zn. The ZnO used contains 65% Zn.

[y]Column heading "days" indicates number of days after dipping.

*Leaf dipping experiments.* (a) *First experiment.* The dipped leaves were examined on September 28 and on October 15 for the percentage of the chlorotic leaf area that was greened. The averages of the 4 dipped twigs for each treatment are shown in Table 2. The amount of greening of Zn-deficient summer flush leaves dipped in mixtures without urea did not increase with increased Zn concentration except for the 2 lowest Zn levels in THIS-CM (Treatments 1 and 2) and the highest Zn level in KE-NU (Treatment 16). Spring flush leaves greened more slowly than

Table 3. Effect of wetting agent in mixtures applied as foliar dips on greening of Zn-deficient summer flush orange leaves.

| Trt. No. | Zinc source | Per 500 gallons: Zn lb. | Per 500 gallons: Wetting agent Name[z] | Per 500 gallons: Wetting agent Pints | Percent greened[y] 37 days | Percent greened[y] 54 days |
|---|---|---|---|---|---|---|
| 1 | THIS-CM | .13 | C | 1 | 53 | 70 |
| 2 | THIS-CM | .13 | C,P | 1,5 | 47 | 68 |
| 3 | THIS-CM | .13 | C,V | 1,3 | 53 | 80 |
| 4 | THIS-CM | .26 | C | 1 | 31 | 61 |
| 5 | THIS-CM | .26 | C,P | 1,5 | 23 | 54 |
| 6 | THIS-CM | .26 | C,V | 1,3 | 59 | 78 |
| 7 | THIS-CM | 2.6 | C | 1 | 32 | 56 |
| 8 | THIS-CM | 2.6 | C,P | 1,5 | 50 | 64 |
| 9 | THIS-CM | 2.6 | C,V | 1,3 | 91 | 98 |
| 10 | THIS | .35 | C | 1 | 69 | 79 |
| 11 | THIS | .35 | C,P | 1,5 | 66 | 81 |
| 12 | THIS | .35 | C,V | 1,3 | 89 | 94 |
| 13 | THIS | .70 | C | 1 | 74 | 84 |
| 14 | THIS | .70 | C,P | 1,5 | 60 | 81 |
| 15 | THIS | .70 | C,V | 1,3 | 90 | 96 |
| 16 | ZnO | 5.2 | C | 1 | 81 | 93 |
| 17 | ZnO | 5.2 | C,P | 1,5 | 81 | 91 |
| 18 | ZnO | 5.2 | C,V | 1,3 | 50 | 78 |
| 19 | ZnO | 10.4 | C | 1 | 57 | 81 |
| 20 | ZnO | 10.4 | C,P | 1,5 | 48 | 74 |
| 21 | ZnO | 10.4 | C,V | 1,3 | 63 | 81 |

[z]C = chlorobenzilate (miticide); P = Plyac wetter-sticker; V = Vatsol-OT.

[y]Each percentage is the average of 8 dipped twigs.

summer flush leaves. In every case with summer flush leaves and in every case except Treatment 10 with spring flush leaves, Zn chelate mixtures that contained urea gave faster and more extensive greening than similar mixtures without urea. However, the ZnO mixture with urea showed little or no increase in greening over similar ZnO mixtures without urea. The average greening of summer flush leaves 42 days after dipping by the 6 treatments containing urea and the 6 similar treatments without urea were 90 and 69% respectively, and after 59 days were 95 and 84% respectively. Comparable averages for spring flush leaves 66 days after dipping for treatments with and without urea were 79 and 70% respectively and 83 days after dipping were 83 and 77% respectively. These data show the value of urea as a penetrating agent to increase the absorption of Zn and to increase the greening of the leaves and is in agreement with previous leaf-dipping work with a liquid chelate of iron (3). Some Zn chelate dips gave results comparable to ZnO dips, despite large differences in Zn concentration.

The results with urea reported here do not necessarily indicate that similar improvement would be obtained by adding urea to concentrate sprays applied with low-volume equipment. The dipping results were obtained by complete wetting of the leaves—a condition that does not result from low-volume application of concentrate sprays. Urea was not used in the Zn spray experiment reported above. It is believed that its possible value as a penetrating agent with low-volume nutritional sprays of Zn chelates should be determined in a field experiment.

The data in Table 2 (summer vs. spring flush) show clearly that young Zn-deficient leaves will absorb foliar-applied Zn much faster, and consequently will green up much faster, than older, hardened leaves. This emphasizes the importance of applying Zn (and other nutritional sprays) during the postbloom period when the heavy new spring flush is still young, as recommended in the Florida Spray and Dust Schedule. There were apparent differences in the ages of some of the summer flush leaves that were dipped, as indicated by variations in the softness of the leaves. Since the younger, softer leaves tended to green up faster than slightly hardened leaves receiving the same dip treatment, such leaf age variation may at least partly explain some of the apparent inconsistencies in the results.

(b) *Second experiment.* The dipped leaves were examined on September 28 and October 15 for the percentage of the chlorotic area that was greened. The averages of the 8 dipped twigs for each treatment are shown in Table 3. In every case except one, the Zn chelate mixture containing Vatsol OT gave more greening of the leaves than similar mixtures without Vatsol OT. The effect of Vatsol OT was greatest at the 20x concentration in Treatment 9. This is the same concentration that was applied with the low-volume Kinkelder sprayer in the spray experiment.

The average figures for greening of the leaves 54 days after dipping by the Zn chelate mixtures with chlorobenzilate alone, combined with Plyac, and combined with Vatsol OT, were 70, 70 and 89% respectively. However, Vatsol OT in combination with the ZnO mixtures failed to increase the uptake of Zn. A similar effect was noted with urea in the first dipping experiment.

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