The Effects of Particle Size and Distribution on Performance of the Fungicide Chlorothalonil

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ABSTRACT

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Flowable preparations of chlorothalonil (tetrachloroisophthalonitrile) prepared by wet milling had reduced particle sizes and better fungicidal performance than standard air-milled preparations. Fungicidal efficacy in the field was affected more by distribution profile of particles than by absolute numbers of particles, or total surface area per gram. Field applications of 30-50% lower dosages of wet-milled formulations of chlorothalonil provided control equivalent with full dosages of the commercial air-milled formulation. Wet-milling and particle-size distribution studies provide a key to increasing performance of chlorothalonil, and possibly to many other fungicides of low water solubility.

Additional key words: pesticide persistance, disease control, *Cercospora, Cercosporidium*, peanuts, fungicide formulation.

Particle size of fungicides, particularly of elemental sulfur, has long been known to affect fungicidal performance; formulations with similar-sized particles produced by a Raymond roller mill or an air-milling process did not differ in innate toxicity (5). Feichtmeir (2) speculated, however, that although small particles were more fungicidal in the laboratory, under field conditions small particles would not withstand weathering as well, possibly allowing the somewhat larger grinds to be the best performers. Thus, Feichtmeir postulated the existence of a U-shaped relation of particle size to field performance. This theory assumes that fungicidal activity increases as particle size is decreased, but the activity decreases as particles are reduced still further. This hypothesis was later supported by research with the fungicide dichlone (2, 3-dichloro-1, 4-napthoquinone) (1); results indicated that the major factor in inactivation for this fungicide was ultraviolet radiation, and though finely ground preparations were very fungitoxic, they were more sensitive to photodecomposition.

Horsfall (3) proposed the existence of toxicant gradients between fungicide particles and spores on the leaf surface. Further, he speculated that the frequency of the particles dictated the potency of the surrounding toxicant. Inherent in this supposition is that small particles with greater surface area per gram would dissolve or errode more quickly and thus disappear sooner.

This study was undertaken to answer three questions relating to the performance of the fungicide chlorothalonil (tetrachloroisophthalonitrile): (i) is wet milling superior to air milling for achieving a smaller particle size, (ii) are wet-milled preparations superior in control of peanut leafspot, and (iii) what physical parameters other than particle size affect disease control?

MATERIALS AND METHODS

Flowable formulations of chlorothalonil were prepared by wet-mill grinding of the technical product in the flowable matrix. Grinding was achieved by the shearing action of metal balls rotating under pressure in a steel chamber. Particle size is inversely related to time of grinding in the chamber. Samples were removed after 3, 9, and 13 hours, adjusted to 54% active ingredient (w/w), and particle size and distribution determined with a Coulter Model TA-2 counter equipped with a 30-μm orifice. Median particle size, total surface area per gram, and numbers of particles per gram of active ingredient were estimated assuming a spherical particle shape (Fig. 1, 2).

For tests conducted in 1974, wet-milled formulations were compared to the commercial air-milled formulation for physical properties and for field performance. In the 1975 test the same procedure was used, but a wet-milled sample was selected that had physical parameters similar to that of the standard air-milled product; a second wet-milled sample that had a mean particle size approaching that found to be most effective in 1974 also was tested in 1975.

Field tests.—Fungicidal performance was evaluated in 1974 and 1975 on field plots of peanuts (*Arachis hypogaea* L. 'Florunner') for control of *Cercospora arachidicola* Hori and *Cercosporidium personatum* (Berk. & Curt.) Deight. Experiments were conducted using rates of 0, 0.42, 0.84, and 1.26 kg/ha of active ingredient for each formulation, delivered in a spray volume of 21 liter/ha at a pressure of 4.2 kg/cm². In addition, a rate of 0.56 kg/ha of each formulation was tested during the 1975 season. Each plot consisted of four 15.2-m rows spaced 0.9 m apart. The spray program commenced approximately 45 days after planting and were applied at 14-day intervals for a total of seven applications. Yields of peanuts were determined by harvesting the two center rows of each plot 145 days after planting. Disease was evaluated 1 week before harvest on 10 vertical stems (runners) removed at random from the center two rows of each plot. The runners were evaluated

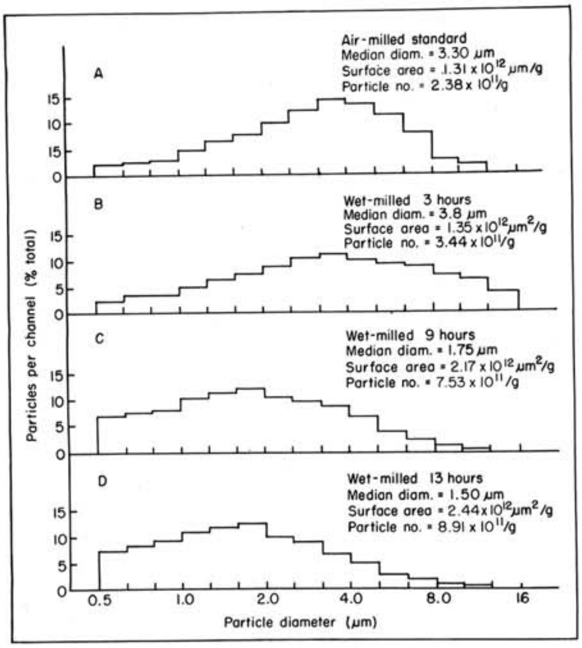

Fig. 1. Effects of air milling (commercial formulation) or wet milling of technical chlorothalonil on particle-size distribution (1974 samples).

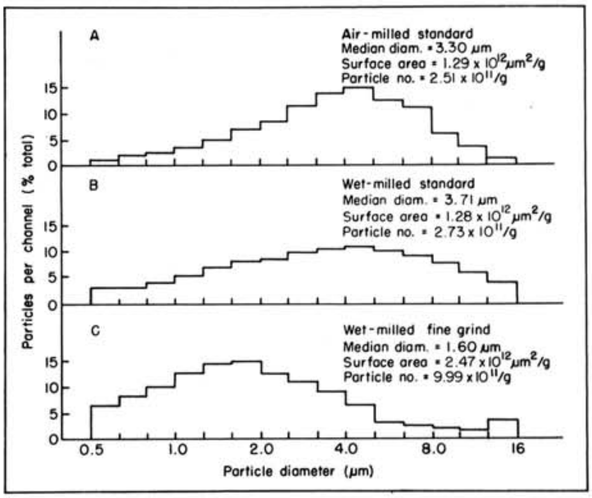

Fig. 2. Effects of air milling (commercial formulation) or wet milling of technical chlorothalonil on particle-size distribution (1975 samples).

TABLE 1. Cercospora leafspot infection (A) and defoliation (B) of Florunner peanuts treated with various rates and formulations of 54% flowable chlorothalonil—1974

A.	Infection[x,y] (%)			
Formulation/rate[z]	0.42 kg/ha	0.84 kg/ha	1.26 kg/ha	Formulation means
Air-milled	59.0 b	42.3 cde	32.2 ghi	44.5 A
Wet-milled				
3 hours	56.0 bc	41.4 def	25.1 hij	40.8 AB
9 hours	50.1 bcd	32.6 gh	21.0 j	34.6 B
13 hours	48.6 cde	34.2 fgh	27.8 ij	35.2 B
Rate means	53.4 X	37.6 Y	25.3 Z	

B.	Defoliation[x,y] (%)			
Formulation/rate[z]	0.42 kg/ha	0.84 kg/ha	1.26 kg/ha	Formulation means
Air-milled	39.2 b	24.5 def	19.0 fgh	27.6 A
Wet-milled				
3 hours	32.9 bc	23.9 ef	15.5 gh	24.1 A
9 hours	31.5 cd	17.2 fgh	14.1 h	20.9 B
13 hours	27.2 cde	22.9 egh	15.4 gh	21.8 B
Rate means	32.7 X	22.1 Y	16.0 Z	

[x]Control value = 73.8% infection and 50.4% defoliation.
[y]Values followed by different letters (lower case) are significantly different ($P \leqslant 0.05$) using Duncan's multiple range test; mean values followed by different upper case letters are significantly different ($P \leqslant 0.05$).
[z]Active ingredient rate per hectare.

by the following criteria: (i) total leaflets = number of leaf nodes × 4; (ii) percent defoliation = number of leaflets lost ÷ total leaflets × 100; (iii) total leaflets infected = number of leaflets lost + number of leaflets infected; and (iv) percent infection = leaflets infected ÷ total leaflets × 100. This method assumes that defoliation occurred because of leafspot infection.

Field plots were in a randomized complete block design. The inherent factorial arrangement permitted development of Duncan's multiple range comparisons (4) of formulation means, rate means, and treatment means.

Preparations of air-milled and wet-milled chlorothalonil used in 1975 were suspended in water and filtered onto Millipore filter membranes (0.22-μm pore size), dried at 40 C for 10 hours, shadowed with gold, and viewed and photographed on an AMR Model 1000 scanning electron microscope to determine particle surface configuration and size.

TABLE 2. Cercospora leafspot infection (A) and defoliation (B) of Florunner peanuts treated with various rates and formulations of 54% flowable chlorothalonil—1975

A.	Infection[y] (%)					
Formulation/rate[z]	0 kg/ha	0.42 kg/ha	0.63 kg/ha	0.84 kg/ha	1.26 kg/ha	Formulation means
Air-milled	61.2 ab	56.5 abc	54.6 bc	50.4 cd	41.6 efg	52.9 A
Wet-milled	62.8 ab	56.2 abc	44.2 def	43.7 def	35.3 gh	48.4 B
Wet-milled (fine)	64.6 a	49.0 cde	45.8 def	37.4 fgh	31.4 h	45.6 B
Rate means	62.9 W	53.9 X	48.2 Y	43.8 Y	36.1 Z	

B.	Defoliation[y] (%)					
Formulation/rate[z]	0 kg/ha	0.42 kg/ha	0.63 kg/ha	0.84 kg/ha	1.26 kg/ha	Formulation means
Air-milled	38.7 a	35.1 abcd	33.4 abcd	33.5 abcd	26.9 d	33.5 X
Wet-milled	39.0 a	35.1 abc	29.7 cd	27.7 d	27.7 d	31.8 X
Wet-milled (fine)	37.0 ab	31.5 bcd	30.6 bcd	29.4 cd	26.6 d	31.0 X
Rate means	38.2 A	33.9 B	31.3 B	30.2 BC	27.1 C	

[y]Values followed by different letters (lower case) are significantly different ($P \leq 0.05$) using Duncan's multiple range test; mean values followed by different upper case letters are significantly different ($P \leq 0.05$).
[z]Active ingredient rate per hectare.

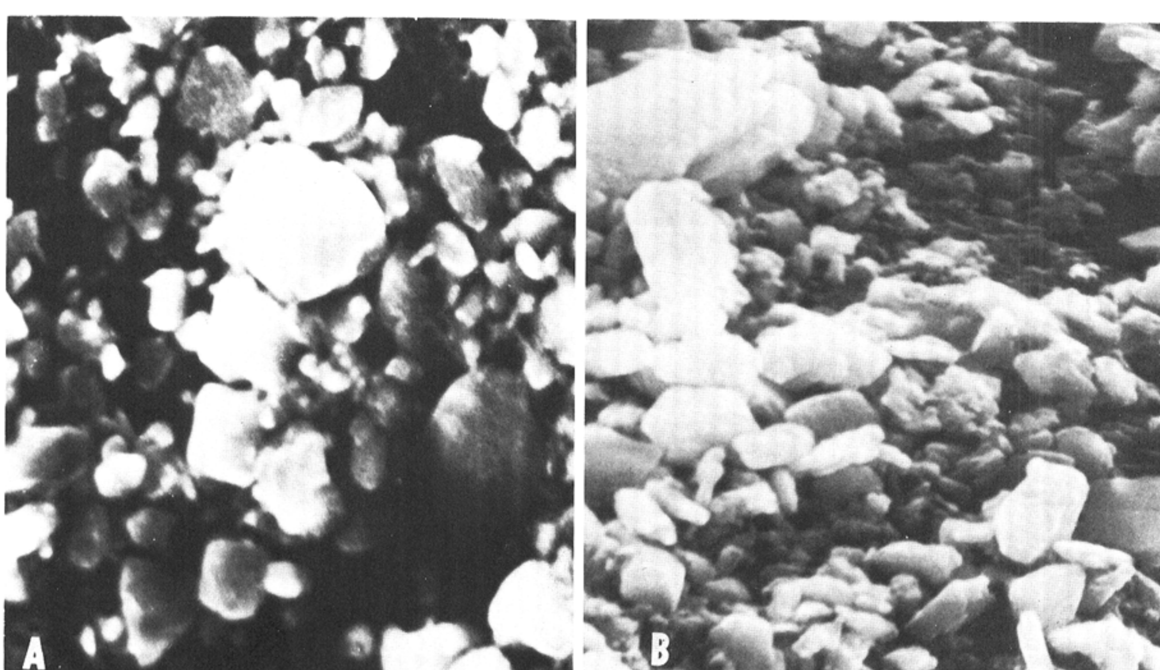

Fig. 3-(A, B). Scanning electron micrographs of **A)** air-milled and **B)** wet-milled chlorothalonil preparations (× 5,200).

RESULTS

Coulter counter analyses of wet-milled chlorothalonil preparations and the standard air-milled product indicated that wet milling (WM) produced a more finely divided product than did air milling (Fig. 1, 2). Near minimal particle size and maximal surface area were achieved after 9 hours of wet milling.

Results from tests conducted to determine optimal rate for effective control of Cercospora and Cercosporidium leafspot in peanuts revealed that the 9-WM and 13-WM preparations generally were significantly ($P \leqslant 0.05$) more effective than the air-milled standard in reducing infection and defoliation (Table 1). Further, results indicated that rates of 0.84 kg/ha of 9-WM were as effective as 1.26 kg of the air-milled standard. The 3-WM, with a larger median particle size, less total surface area, and fewer particles per gram, consistently controlled disease better than the air-milled formulation.

Evaluation of 1975 disease control data confirmed results obtained in 1974 (Table 2). Again, disease control from the finely ground wet-milled preparation applied at rates between 0.63 and 0.84 kg/ha was equivalent to the air-milled standard applied at a rate of 1.26 kg/ha. The wet-milled standard, with particle size, and surface area very similar to that found for the air-milled, was significantly more effective than the air-milled product in controlling disease. Peanut yields indicated significant differences ($P \leqslant 0.05$) (data not presented) and were inversely related to disease incidence in both 1974 and 1975.

Scanning electron micrographs of air-milled and wet-milled chlorothalonil preparations revealed that the wet-milled sample contained somewhat more fractured, angular, and greater numbers of smaller-sized particles than did the air-milled sample (Fig. 3). In addition, major differences in size distribution were apparent.

DISCUSSION

Wet-milled chlorothalonil consistently had many more particles < 1 μm in size, even after only short periods (3 hours) of grinding. An unexpected result was that chlorothalonil formulations ground for shorter times in the wet-mill (3-WM and wet-milled standard) consistently decreased disease more than air-milled formulations with similar physical parameters. These results indicate that particle size distribution affects fungicidal efficacy more than the average particle size, surface area, or particle numbers. Wet-milled formulations had more small particles, but also usually had more particles in the largest category compared to the air-milled formulation. The resultant "lower profile" (no defined peak) of particle size distribution in the preparations offers a possible explanation for the unexpectedly good performance of the 3-WM and the wet-milled standard formulations. The role in disease control of any extra surface area contributed by particle surface characteristics observed under electron microscopy has not been determined. Surface areas as calculated here were based on the assumption that particles were smooth-surfaced spheres; any contribution of surface irregularities was ignored by the Coulter counter. Assuming that smaller particles weather faster, the standard air-milled formulation would quickly be comprised mostly of larger particles. However, if the size distribution in the formulation has a flat profile without a well-defined peak, intermediate-sized particles continuously will be eroded to smaller particles, thus maintaining a pool of small particles. This relates to the studies of Feichtmeir (2) and Burchfield and McNew (1) who theorized a U-shaped response of field effectiveness for sulfur as particle size is reduced. In their conclusions, optimum performance was thought to be found at intermediate particle size, whereas control was less effective with very small and very large particles. Their studies, however, only considered particles of one size separated in a sedimentation column and not a profile of particles as studied here. Burchfield and McNew (1) in studying the fungicide dichlone interpreted their data as indicating the following mechanism: ". . . where the smaller particles serve to establish complete control because of good coverage and greater availability at the sites of incipient infection, . . . the larger particles constitute a reserve supply of toxicant that will operate over a longer period owing to better resistance to erosion and photochemical deterioration." The data presented here support their hypothesis with field data and indicate that they apply to fungicides other than dichlone. Use of the Coulter counter provides and plots data on particle size distribution not available in 1950. The resultant "profiles" developed here demonstrate visually how various particle-size blends may result in improved performance of many water-insoluble fungicides. The resultant decrease in rates required for disease control could significantly reduce the total pesticide load in agricultural areas.

Whether chlorothalonil activity is most affected by the distribution of particle sizes or surface configuration of particles was not determined. Regardless, formulations should have smaller particles with a reserve of larger particles to weather down continually to the more biologically active small particles.

Three physical factors relating the nature of chlorothalonil particles to fungicidal efficacy have been determined in this study: (i) particle size; (ii) the distribution of particle sizes; and (iii) surface configuration of the individual particles. The standard air-milled formulation affects only particle size advantageously, whereas wet milling improves chlorothalonil efficacy through all three components.

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