Influence of Emulsifiable Concentrate Formulation on the Physical Properties of the Fluid, Spray Characteristics, and Insecticide Deposits on Stored Grains

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In stored grains, smaller depositions and great variations with regard to theoretical insecticide doses are frequently found. The objective of this work was to evaluate the influence of the emulsifiable concentrate formulation on the physical properties of the liquid, volumetric distribution, droplet spectrum, and insecticide deposits on stored grains. To determine its physical properties, the applied mix was prepared at a concentration of 0.4% of commercial product. Volumetric distribution was used as an evaluation parameter in a model TJ-60 8002EVS hydraulic nozzle study, and clean water and insecticidal mix were used as test fluids. After the effective swath width (esw) had been determined for both fluids, an application system was built to apply theoretical concentrations of 10 and 0.5 mg kg^{-1} of fenitrothion and esfenvalerate, respectively. Mix viscosity was 82% higher than water viscosity; conversely, surface tension in the mix corresponded to 49% of the water surface tension value. For water and mix, esw values were 0.425 and 0.60 m, respectively. Deposits of both insecticides at the 0.60 m esw were significantly higher ($P < 0.05$) than deposits at the 0.425 m esw. The results obtained demonstrate the great influence of emulsifiable concentrate formulation on the physical properties of the fluid, spray characteristics, and insecticide deposits on stored grains.

KEYWORDS: Viscosity; surface tension; application technology; spray nozzle; effective swath width; gas chromatography

INTRODUCTION

Chemical control is an important component in stored-grain integrated pest management programs. For this reason, seeking the best insecticide application method is perhaps more important than biological efficacy studies, because the latter is but one of the factors of interest in stored grain protection. An unsuitable application method will result in great variation of insecticide deposition on the mass of grains and may encourage the occurrence of residue levels above the maximum limit allowed by law and the progression of insect resistance to insecticides, posing a health hazard to the consumer and putting the producer's income in jeopardy. In a spraying system, the nozzle is the most important component, because it is responsible for the flow, generation, and distribution of droplets that will carry the insecticide to the target to be controlled. Knowing the nozzle's transversal volumetric distribution is highly im-

portant in a nozzle's performance analysis and has been the object of study of several researchers (*1−3*). In this respect, the International Organization for Standardization has established that clean water should be used as test fluid (*4*). On the other hand, the fluid's physical properties might affect spray characteristics. Several studies have demonstrated the influence of agricultural adjuvants on the physical properties of the fluid, its volumetric distribution pattern, and droplet spectrum (*5, 6*); however, little information is available about the effect of the insecticide formulation on the above-mentioned parameters (*7−9*). The liquid insecticides used in the treatment of stored grains are formulated mainly as emulsifiable concentrates (EC). Therefore, the objective of this work was to evaluate the influence of emulsifiable concentrate formulation on the fluid's physical properties, volumetric distribution, droplet spectrum, and insecticide depositions on stored corn and wheat grains.

MATERIALS AND METHODS

Application Technology. *Parameters Used in Laboratory Assays.* To determine the fluid's physical properties (surface tension and viscosity), the mix was prepared at a concentration of 0.4% v/v of the commercial product Sumigranplus [500 g of the active ingredient (ai)

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fenitrothion + 25 g of the ai esfenvalerate/L]. Surface tension was determined by using the burette method, according to the NBR 13241 standard for surface tension determination in agrochemicals (*10*). Viscosity was determined with a Brookfield model LVDV-III Ultra viscometer at 26 °C. A twin-jet model TJ-60 8002EVS hydraulic nozzle (Spraying Systems Co.) was used. A channeled table (patternator) was used to carry out the spray nozzle transversal volumetric distribution analysis experiments, standardized according to the ISO 5682-1:1996 (E) standard. The testing table (3.5 m long, 3.0 m wide) has channels spaced at 0.025 m, positioned at a 5% slope. On the front part of the table, a set of graduated cylinders (250 mL) collects the fluid from each channel. Clean water and an insecticidal mix were used as test fluids. The following parameters were evaluated: actual flow and transversal volumetric distribution, at a pressure of 200 kPa and a nozzle height of 0.5 m. The weighing method was used to obtain actual flow, and the volume collected during 1 min in a plastic container was weighed in a precision balance. To determine transversal volumetric distribution and effective swath width for both test fluids, the nozzle was mounted on the boom and positioned in a perpendicular direction in relation to the assay table. Collection time was set until one of the graduated cylinders reached a volume of 230 mL. This collection time was used for the three replicates. Droplet spectrum studies were conducted after effective swath widths were determined. To that effect, a mobile application system was built containing the nozzle, a manometer, a CO_2 tank, and a tank for the fluid to be applied (water or mix). Three water-sensitive papers (0.076 m long, 0.026 m wide) were distributed on the extreme and central portions of the previously defined effective swath widths. The same height and working pressure adopted for the assay table were used, at a moving speed of 5 km h^{-1}. After spraying, the water-sensitive papers were collected and analyzed using a computerized image analysis system, Gotas, version 1.0 (Embrapa Meio Ambiente, São Paulo, Brazil).

Grain Treatment. Corn and wheat cultivars Sol-da-Manhã and BRS 208 were used, respectively, both developed by Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA-Brazilian Company for Livestock and Farming Research). To determine the mass of grains per unit area, the corn and wheat were spread as a fine layer onto a plastic tarp, covering a 1 m^2 area, and were then weighed. Values of 5.0 and 4.0 kg m^{-2} were thus obtained for corn and wheat, respectively. A plastic tarp was placed between the rails, and the grains were uniformly spread on the tarp. The swath widths where the grains were spread were established on the basis of the nozzle's transversal volumetric distribution study performed previously. To check on the intended application rate, three glass slides (0.1 m length, 0.05 m width) were placed on the grains for subsequent quantification of deposition using gas chromatography. Insecticide losses were evaluated by collecting and analyzing seven plastic tarp samples (0.1 m length, 0.1 m width). Fenitrothion and esfenvalerate were applied to produce theoretical concentrations of 10 and 0.5 mg kg^{-1}, respectively. During application, the mobile system was moved along the material to be treated (**Figure 1**); the nozzle's operational specifications were the same as in the laboratory tests. The system's moving speed was calculated for an application volume equivalent to 5 L t^{-1}; under these conditions, the insecticidal emulsion contained 0.4% of the commercial product. Three replicates were made, generating 6 experimental plots, and two insecticides were analyzed, totaling 24 subplots. The same procedure was adopted for the control treatment, but in this case the spray consisted of water only. The temperature and relative humidity during spray were 26.2 °C and 76%, respectively.

Deposition Analysis. Half an hour after the spray, the grains were collected and processed together with dry ice. To achieve this, a model TRF70 forage chopper was used. The dry ice was mixed with the grain at a 1:1 ratio prior to grinding, to maintain a temperature value that would minimize insecticide degradation during the operation.

Grain. The analytical method was adapted from Ohlin (*11*). Ten grams of homogenized sample was placed in a 100 mL Schott bottle for residue extraction. Fifty milliliters of ethyl acetate and 10 g of sodium sulfate were added and later homogenized in a stirring table for 1 h at 360 cycles min^{-1}. After this operation, the extracts were centrifuged for 5 min at 2600 rpm for better separation of the liquid phase from suspension materials. Ten-milliliter aliquots of the super-
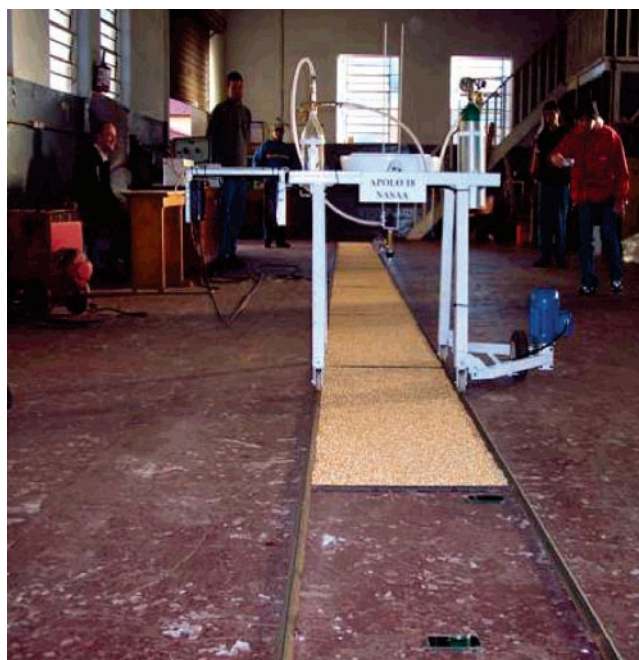

Figure 1. Grain treatment.

natant were transferred to 12-mL test tubes, corresponding to 2 g of the original sample, and then 50 μL of dodecane was added. The extracts were evaporated in a Turbo-Vap evaporator, in a water bath at 30 °C aided by moving air previously dried through a blue silica gel desiccant filter. Later, the insecticide residues were resuspended in 5 mL of a cyclohexane/ethyl acetate mixture (1:1, v/v), homogenized in a vortex mixer/ultrasound, and filtered through a Millipore, FG, 0.2 μm pore membrane filter mounted on a plastic hypodermic syringe (5 mL). The extracts were cleaned by gel permeation chromatography (GPC) and eluted with a cyclohexane/ethyl acetate mixture (1:1, v/v). After this operation, the extracts were evaporated in a Turbo-Vap evaporator to which 50 μL of dodecane had previously been added and were later resuspended in 20.0 and 1.95 mL of the cyclohexane/ ethyl acetate mixture (1:1, v/v) for the fenitrothion and esfenvalerate residues, respectively. The samples were analyzed by gas-phase chromatography, with a Thermo Electron Corp. model Finnigan Trace Ultra gas chromatograph, equipped with an electron capture detector (ECD, Ni^{63}) and a Restek Corp. RTX-5MS chromatography capillary column (30 m long, 0.25-mm diameter, and 0.25-μm film thickness), with injections made in the splitless mode. The chromatograph was operated under the following conditions: column temperature = 100 °C (start), then raised to 280 °C at 25 °C min^{-1}, remaining at this temperature for a period of 10 min; injector temperature = 230 °C; detector temperature = 320 °C; purge time = 1 min; gas flow (mL min^{-1}), H$_2$ (carrier) = 1.2; N$_2$ (make up) = 45; and purge flow = 65. Under these conditions, retention time was 6 min and 20 s for fenitrothion and 10 min and 25 s for esfenvalerate, approximately. Residue amounts were calculated using the ChromQuest version 4.0 software, by comparing the chromatographic peak heights for the samples against the chromatographic peak heights for the corresponding analytical standards.

Glass Slide. Three glass slides were placed into 600-mL flasks. Five hundred milliliters of ethyl acetate was added, and the insecticides were later extracted by ultrasound for 15 min. After this operation, 2-mL aliquots were transferred to 12-mL test tubes, and then 50 μL of dodecane was added. The extracts were evaporated in a Turbo-Vap evaporator, in a water bath at 30 °C aided by moving air previously dried through a blue silica gel desiccant filter. Later, the insecticide residues were resuspended with 2 mL of the cyclohexane/ethyl acetate mixture (1:1, v/v) (1:1 mL), homogenized in a vortex mixer/ultrasound, and then diluted at a rate of 1 mL of extract + 9 mL of the cyclohexane/ ethyl acetate mixture (1:1, v/v), followed by injection in the chromato-graph system.

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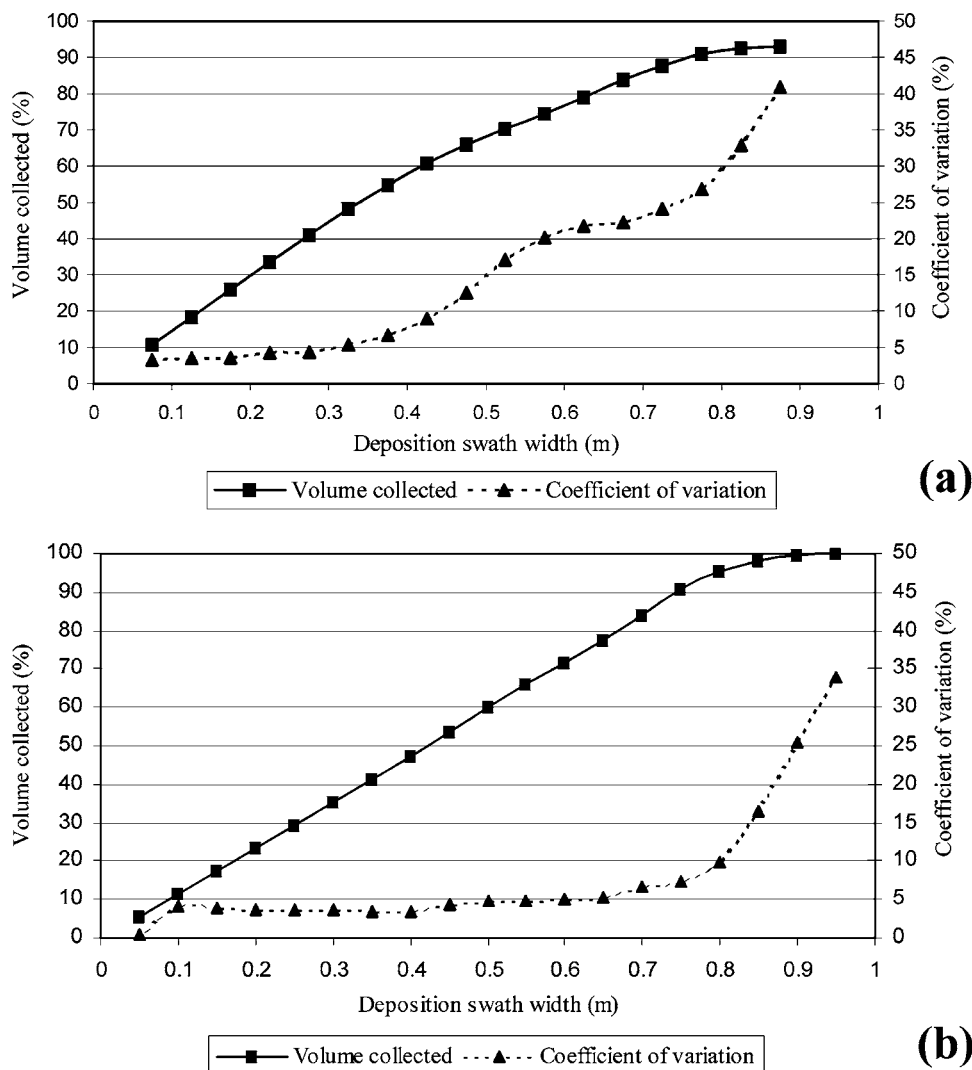
Figure 2. Transversal volumetric distribution of a TJ-60 8002EVS nozzle using clean water (**a**) and insecticidal mix (**b**).

Plastic Tarp. Seven 100 cm^2 samples were cut into small pieces and placed in 100-mL Schott bottles. Fifty milliliters of ethyl acetate was added, and the insecticides were later extracted by ultrasound for 15 min. Upon completion, 5-mL aliquots of the solution were filtered through a Millipore, FG, 0.2-μm pore membrane filter mounted on a plastic hypodermic syringe (5 mL) and then diluted at proportions of 0.1 mL of the extract $+$ 19.9 mL of ethyl acetate for fenitrothion analysis and 0.1 mL of the extract $+$ 0.9 mL of ethyl acetate for esfenvalerate, followed by chromatographic analysis.

Validation of the Analytical Method. The analytical method used for corn and wheat grains was validated by means of matrix fortification at the levels of 0.05, 0.5, and 10.0 mg kg^{-1} for fenitrothion and 0.05, 0.1, and 1.0 mg kg^{-1} for esfenvalerate, with three replicates for each level (nine fortified samples for each matrix). Recoveries between 70 and 120% were considered to be acceptable.

Statistical Analysis. The data were submitted to analysis of variance, using a mathematical model for a completely randomized design in a split-plot arrangement, and the *F* test was used to evaluate the significance of factors (grain species, effective swath width, insecticide, and interactions) in the model of Pimentel-Gomes (*12*).

RESULTS

Application Technology. Surface tension and viscosity in the insecticidal mix reached values of 35.47 mN m^{-1} and 1.82 mPa s, respectively. The mix surface tension value corresponded to 49% of the water surface tension value (71.97 mN m^{-1}). Conversely, mix viscosity was 82% higher than water

viscosity (1.0 mPa s). The nozzle's actual flow was 0.660 and 0.672 L min^{-1} for water and the mix, respectively; in both cases, the variation between actual and nominal flow (0.650 L min^{-1}) was within the acceptable limit, as according to the WHO (*13*), the acceptable flow variation limit of a spraying nozzle is ±4% in relation to the nominal flow indicated by the manufacturer. At the experiment's working conditions, the total deposition swaths for water and the mix were 0.88 and 0.95 m, with coefficients of variation (CV) of 40.9 and 34%, respectively (**Figure 2**). From **Figure 3**, it can be seen that the nozzle's volumetric distribution pattern using clean water as test fluid was asymmetric, with an oval aspect and higher volume concentration in the central region. For the insecticidal mix, the volumetric distribution pattern was symmetric, with a trapezoidal aspect and more uniform distribution of the fluid across the deposition swath. However, in both cases, the CV for total swath width was higher than the 7% limit established by the prEN 12761-2 international standard (*14*). To obtain an insecticidal mix distribution as uniform as possible, and considering that in Brazil a CV of up to 10% is acceptable, we determined effective swath width and CV values of 0.425 m and 8.9% for water and 0.6 m and 5.1% for the mix, respectively. The effective swath width and CV values for the mix were 0.8 m and 9.9%, respectively, but the spraying system had a swath width application capacity of up to 0.6 m;

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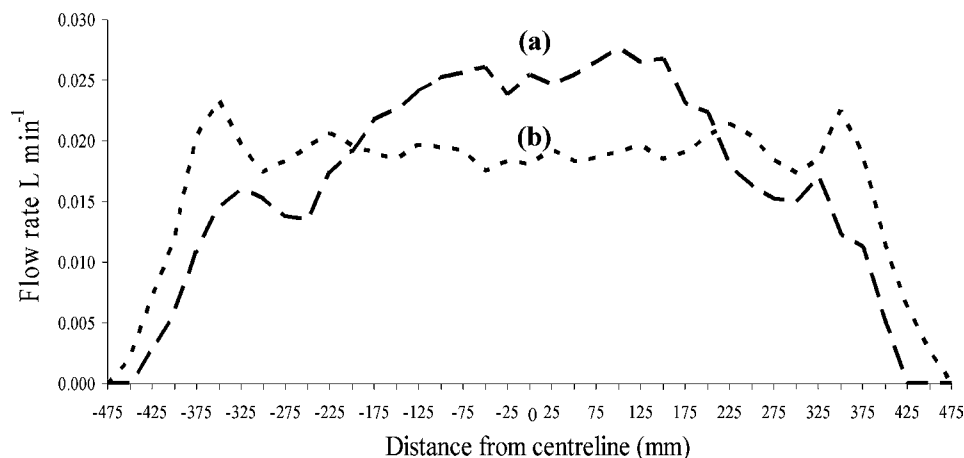
Figure 3. Transversal volumetric distribution pattern of a TJ-60 8002EVS nozzle using clean water (**a**) and insecticidal mix (**b**).

Table 1. Droplet Analysis for a TJ-60 8002EVS Nozzle

| test fluid | parameter | position of water-sensitive paper on effective swath width | | |
		left	center	right
clean water	volume (L ha^{-1})	153.5 ± 17.9	87.1 ± 13.9	127.8 ± 18.6
	density (n^0 cm^{-2})	125.7 ± 12.5	122.4 ± 5.6	122.9 ± 12.7
	uniformity	1.8 ± 0.2	1.8 ± 0.005	1.8 ± 0.1
	VMD (μm)^a	378.7 ± 14.6	320.4 ± 14.8	362.8 ± 15.5
	NMD (μm)^b	214.1 ± 10.6	178.9 ± 8.5	201.0 ± 3.0
	coating (%)	29.6 ± 2.8	18.9 ± 2.5	25.5 ± 3.3
insecticidal mix	volume (L ha^{-1})	121.8 ± 6.2	130.3 ± 7.7	142.8 ± 15.5
	density (n^0 cm^{-2})	127.8 ± 14.7	125.0 ± 1.1	120.3 ± 10.9
	uniformity	1.8 ± 0.01	1.9 ± 0.1	1.9 ± 0.1
	VMD (μm)	362.4 ± 9.2	370.4 ± 15.5	384.5 ± 32.6
	NMD (μm)	194.0 ± 4.2	196.9 ± 2.4	206.9 ± 8.0
	coating (%)	24.7 ± 1.6	25.7 ± 0.8	27.4 ± 1.7

^{a} Volumetric mean diameter. ^{b} Numeric mean diameter.

consequently, we chose to use the previously mentioned value. Under these conditions, 65.4 and 71.6% of the water and mix volumes sprayed were collected within their corresponding effective swath widths (**Figure 2**). Therefore, the spraying equipment was calibrated to apply a total effective volume of 5 L t^{-1} in each effective swath width. The droplet spectra for water and for the mix using the evaluated nozzle, working at pressure and moving speed values of 200 kPa and 5 km h^{-1}, respectively, are presented in **Table 1**.

Deposition Analysis. The insecticide recovery percentages in the fortified corn and wheat grains were acceptable (70−120%), thus validating the analytical method. Neither of the two insecticides was recovered from the control, indicating that the grains were free from contamination by those compounds. The *F* test detected significant effect ($P < 0.05$) for effective swath width and insecticide, either on grains or on glass slides. Moreover, it had a significant effect ($P < 0.05$) of the grain species and of the interactions of grain species with effective swath width and insecticide on the deposition in the grains. In relation to the deposition in the glass slides, it was influenced significantly by the interaction of insecticide with grain species. **Tables 2−4** show insecticide deposition means and standard errors on grains and glass slides for two-by-two combinations of factors. It can be seen that the 0.6 m effective swath width provided greater depositions of both insecticides, either on grains or on glass slides (**Tables 2** and **4**). Fenitrothion deposition was significantly higher ($P < 0.05$) than that of esfenvalerate, both on grains and on glass slides (**Table 3**). Nevertheless, this difference was not significant ($P > 0.05$) for the 0.425 m effective swath width (**Table 4**). Insecticide

Table 2. Means and Standard Errors of Insecticide Depositions on Grains and Glass Slides for Different Grain Species and Swath Widths^a

| effective swath width | grain species | |
	corn	wheat
	Deposition on Grains (%)	
0.425 m	40.2 ± 1.58 aB	40.1 ± 1.58 aB
0.6 m	52.0 ± 2.82 bA	64.2 ± 2.82 aA
	Deposition on Glass Slides (%)	
0.425 m	59.9 ± 3.09 aB	54.4 ± 3.09 aB
0.6 m	92.4 ± 3.09 aA	101.0 ± 3.09 aA

^{a} Means followed by different lower case letters in the rows are significantly different by the *F* test ($P < 0.05$); means followed by different upper case letters in the columns are significantly different by the *F* test ($P < 0.05$).

Table 3. Means and Standard Errors of Insecticide Depositions on Grains and Glass Slides for Different Grain Species and Insecticides^a

| insecticide | grain species | |
	corn	wheat
	Deposition on Grains (%)	
esfenvalerate	42.9 ± 1.96 bB	47.4 ± 1.96 aB
fenitrothion	49.3 ± 1.96 bA	56.9 ± 1.96 aA
	Deposition on Glass Slides (%)	
esfenvalerate	74.1 ± 2.22 aB	74.0 ± 2.22 aB
fenitrothion	78.1 ± 2.22 aA	81.3 ± 2.22 aA

^{a} Means followed by different lower case letters in the rows are significantly different by the *F* test ($P < 0.05$); means followed by different upper case letters in the columns are significantly different by the *F* test ($P < 0.05$).

deposition means were significantly different for grains only. The highest deposition values occurred on wheat grains (**Table 3**), except at the 0.425 m effective swath width, for which corn and wheat were not significantly different ($P > 0.05$) (**Table 2**). Depositions on the pieces of plastic tarp corresponded on average to 8.9 ± 2 and 6.5 ± 0.4% of the theoretical insecticide dose in corn and wheat, respectively.

DISCUSSION

The results demonstrate the great influence of the EC formulation on the fluid's physical properties. On the other hand, the mix behaved characteristically as a Newtonian fluid. At a given temperature, the shear force applied to the mix, by means of either the tank agitators or the pressure received as the fluid passes through the spray tip's orifice, will not change its

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Table 4. Means and Standard Errors of Insecticide Depositions on Grains and Glass Slides for Different Insecticides and Swath Widths[a]

	insecticide	
effective swath width	esfenvalerate	fenitrothion
Deposition on Grains (%)		
0.425 m	38.2 ± 1.58 aB	42.1 ± 1.58 aB
0.6 m	52.2 ± 2.29 bA	64.0 ± 2.29 aA
Deposition on Glass Slides (%)		
0.425 m	54.9 ± 2.22 bB	59.4 ± 2.22 aB
0.6 m	93.2 ± 2.22 bA	100.1 ± 2.22 aA

[a] Means followed by different lower case letters in the rows are significantly different by the *F* test ($P < 0.05$); means followed by different upper case letters in the columns are significantly different by the *F* test ($P < 0.05$).

viscosity. Differences in volumetric distribution pattern of flat-fan nozzles were observed when different types of mixes were used, including water, particularly at low pressure values (*5*). The nozzle model studied is a continuous deposition type and is used only in swath applications. The problem presented above will cause irregular deposition of insecticides, and consequently the grains will receive under- or overdoses depending on their location within the total deposition swath. A number of studies (*15−17*) have demonstrated that great insecticide deposition variation occurs in stored grains. Pesticide sprays are generally classified on the basis of droplet size, with particular reference to VMD or $D_{0.5}$, that is, volumetric mean diameter (*18*). According to the manufacturer's brochure, the TJ-60 8002EVS nozzle yields fine droplets under all recommended work pressures; however, large droplets were obtained in the present study. The droplet size categories used in this experiment were the same as in the international ASAE (X-572) and BCPC standards. The differences in droplet diameter and consequently in droplet size category were possibly caused by the measurement technique used, because the international standards specify a laser system to evaluate the droplet spectrum. In this work, we used water-sensitive paper to obtain droplet marks and to make diameter measurements at a later time using specific software. In the case of water, it can be seen that at the center of the effective swath width droplets were smaller when compared with droplets at the extreme points of the swath. In the droplet formation process, the fluid's hydraulic energy is transformed into droplet kinetic energy (*19*). One explanation for these results is that larger droplets have greater mass and therefore acquire greater kinetic energy. Consequently, large droplets have a greater capacity to overcome air resistance to horizontal movement and may travel longer distances when compared with smaller droplets. In the same way, the volume and coating values at the center of the effective swath were lower than at the ends. This was probably due to the vortex effect generated by the spray system moving at a speed of 5 km h^{-1}; very small droplets would then be dispersed outside the treatment area by air turbulence. For the mix, it can be observed that the droplet spectrum was uniform across the entire effective swath width, in addition to the fact that droplets had greater diameter than water droplets. One explanation for these results is that the physical properties of the mix increased droplet size. Butler Ellis et al. (*6*) demonstrated that emulsions cause a rapid fluid sheet disintegration with the formation of large droplets. The insecticidal mix volumetric distribution was the same both in the laboratory test and in the grain treatment. This would explain the greater deposit of insecticides obtained at the 0.6 m effective swath width. On the other hand, the volumetric distribution of clean water in the laboratory test

suffered alterations during grain treatment, as a function of changes in the fluid's physical properties. Consequently, the extrapolation of volumetric distribution data obtained with water for insecticide application was the main factor responsible for the lower-than-intended deposition values obtained.

In spite of the fact that the physicochemical properties of these insecticides would determine greater esfenvalerate stability, more fenitrothion was recovered. The environmental conditions during spray were adequate for this operation, and processing of the corn and wheat samples included the use of dry ice. Consequently, all steps that preceded the analytical stage prevented losses of both insecticides; therefore, the greater recovery of fenitrothion was due to the higher sensitivity of the chromatograph detector to this molecule. The highest deposition value on wheat was due to its grain morphology; wheat provided a higher specific contact surface area for droplets than corn. On the other hand, the insecticide recovery effectiveness of the analytical method was slightly higher for wheat when compared with corn. Depositions of both insecticides were always higher on the glass slides when compared with depositions on the grains. These results demonstrate that some droplets reached the plastic tarp through the empty spaces between the grains, therefore resulting in depositions lower than those intended. The sum between grain and plastic tarp depositions should have been near the glass slide deposition values, but was considerably lower. One explanation for these results is that the analytical procedure for grains is much more complex than for glass slides, and some degree of insecticide loss occurred in the agronomic matrix. A greater effectiveness of the artificial target in collecting pesticides in agricultural nozzle performance studies is therefore demonstrated.

In a storage facility, grains are usually treated on a conveyor belt, where hydraulic nozzles are mounted for this purpose. Under these conditions, smaller depositions and great variations with regard to theoretical insecticide doses are frequently found. To improve the quality of sprays generated by hydraulic nozzles, a number of methods have been developed under laboratory conditions, but with little success when it comes to solving the above-mentioned problem. In this respect, the International Organization for Standardization (ISO) has established that clean water should be used as test fluid to study performances of hydraulic nozzles, but in this work we demonstrate the great influence of emulsifiable concentrate formulation (the main insecticidal formulation use in stored grain protection) on the fluid's physical properties, volumetric distribution, droplet spectrum, and insecticide deposition on stored grains. Consequently, evaluations of technical characteristics of agricultural nozzles using clean water as test fluid are useful only to compare performances between different tip models. Therefore, the use of insecticidal mix is recommended to evaluate spray characteristics and subsequently calibrate the spray system on the basis of such data. This work contributes to knowledge about the application technology of insecticides in stored grains under laboratory conditions. The practical application of this study will be presented in the next step of the work, in which the application technology will be analyzed in association with conveyor elements responsible for revolving the grain.

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