*PS10-4 – 6182*

# Influence of emulsifiable concentrate formulations on the physical properties of the fluid, spray characteristics, and insecticide deposits on stored grains

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## Abstract

The influence of emulsifiable concentrate formulations on the physical properties of the spraying fluid (viscosity and surface tension), volumetric distribution, droplet spectrum, and insecticide depositions on stored grains was studied. In order to determine its physical properties, the applied mix was prepared at a concentration of 0.4 % of commercial product (Sumigranplus® EC). 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 determining effective swath width (e.s.w.) for both fluids, an application system was built to apply a rate equivalent to 5 L $t^{-1}$ and thus obtain theoretical concentrations of 10 and 0.5 mg $kg^{-1}$ of fenitrothion and esfenvalerate, respectively. For application, the corn and wheat grains were spread out as fine layers at both e.s.w. Three glass slides were placed on the mass of grains to ensure that the intended application rate was achieved. After treatment, depositions on the grains and glass slides were analyzed by gas chromatography. Mix viscosity (1.82 mPa s) was 82 % higher than water viscosity; conversely, surface tension in the mix (35.47 mN $m^{-1}$) corresponded to 49 % of the water surface tension value. The droplets spectrum was influenced by the fluid's physical properties. For water, e.s.w. and coefficient of variation (c.v.) reached values of 0.425 m and 9 %, respectively; for the mix, however, the e.s.w. and c.v. values were 0.60 m and 5 %, respectively. Deposits of both insecticides at the 0.60 m e.s.w. were significantly higher ($P < 0.05$) than deposits at the 0.425 m e.s.w., both on grains and glass slides. The results obtained demonstrate the great influence of emulsifiable concentrate formulations on the physical properties of the fluid, spray characteristics, and insecticide deposits on stored grains.

*Key words:* 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

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insecticide application method is perhaps more important than biological efficiency studies, since 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 producers income in jeopardy. Several studies have demonstrated the influence of agricultural adjuvants on the physical properties of the fluid, its volumetric distribution pattern, and droplets spectrum; however, little information is available about the effect of the insecticide formulation on the above-mentioned parameters. 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, droplets spectrum, and insecticide depositions on stored corn and wheat grains.

## Material and methods

These application technology studies were conducted at the Laboratory for the Evaluation of Phytosanitary Product Applications, of Departamento de Engenharia Rural of Escola Superior de Agricultura "Luiz de Queiroz" (ESALQ/USP). The insecticide deposition determinations were performed at the Pesticide Residue and Chromatographic Analysis Laboratory of Departamento de Entomologia, Fitopatologia e Zoologia Agrícola of Escola Superior de Agricultura "Luiz de Queiroz" (ESALQ/USP), in Piracicaba, SP, Brazil.

In order to determine the fluid's physical properties (surface tension and viscosity), the mix was prepared at a concentration of 0.4 % of the commercial product Sumigranplus® EC. Surface tension was determined by the burette method, according to the NBR 13241 standard for surface tension determination in agrochemicals (ABNT, 1994). Viscosity was determined with a Brookfield, model LVDV-III Ultra viscometer at 26 $^{o}$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 5682/1-1981 (E) standard (ISO, 1981). Clean water and an insecticidal mix (0.4 % Sumigranplus® EC) 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. Droplets 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 cards of water-sensitive paper (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 cards were collected and analyzed using a computerized image analysis system, Gotas, version 1.0 (Embrapa Meio Ambiente, São Paulo, Brazil).

A plastic tarp was placed between the rails and the grains were uniformly spread as a fine layer onto a plastic tarp. The swath widths where the grains were spread were established based on the nozzle's transversal volumetric distribution study performed previously. In order 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. Fenitrothion and esfenvalerate were applied so as to produce theoretical concentrations of 10 and 0.5 mg $kg^{-1}$, respectively. The commercial product Sumigranplus® EC (500 g of the a.i. fenitrothion + 25 g of the a.i. esfenvalerate/liter) was used. During application, the mobile system was moved along the material to be treated. 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 six experimental plots, and two insecticides were analyzed, totaling twenty-four subplots. The samples were analyzed by gas-phase chromatography, with a Thermo Electron Corporation, model Finnigan Trace Ultra gas chromatograph, equipped with an electron capture detector (ECD, $Ni^{63}$). 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.

## Results

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, since according to the WHO (1976), 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 (c.v.) of 40.9 and 34 %, respectively. From Figure 1, 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 c.v. for total swath width was higher than the 7 % limit established by the prEN 12761-2 international standard (ECS, 1997). In order to obtain an insecticidal mix distribution as uniform as possible, and considering that in Brazil a c.v.

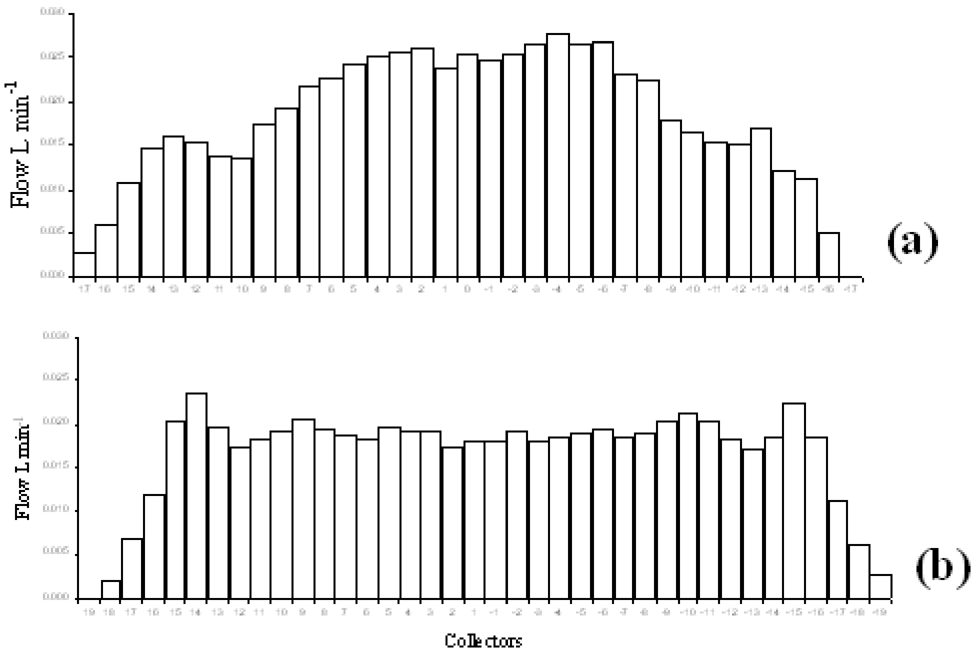


**Figure 1.** Transversal volumetric distribution pattern of a TJ-60 8002EVS nozzle using clean water (a) and insecticidal mix (b).

of up to 10 % is acceptable, we determined effective swath width and c.v. values of 0.425 m and 8.9 % for water and 0.6 m and 5.1 % for the mix, respectively. Under these conditions, 65.4 and 71.6 % of the water and mix volumes sprayed were collected within their corresponding effective swath widths. 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.

Tables 2, 3, and 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 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 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, where corn and wheat were not significantly different ($P > 0.05$) (Table 2).

**Table 1**. Droplet analysis for a TJ-60 8002EVS nozzle.

| | | Position of water-sensitive paper on effective swath width | | |
|---|---|---|---|---|
| Test fluid | Parameter | Left | Center | Right |
| Clean water | Volume (L $ha^{-1}$) | 153.5 ± 17.9 | 87.1 ± 13.9 | 127.8 ± 18.6 |
| | Density (nº $cm^{-2}$) | 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 (mm) | 378.7 ± 14.6 | 320.4 ± 14.8 | 362.8 ± 15.5 |
| | NMD (mm) | 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 (nº $cm^{-2}$) | 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 (mm) | 362.4 ± 9.2 | 370.4 ± 15.5 | 384.5 ± 32.6 |
| | NMD (mm) | 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 |

VMD: Volumetric mean diameter

NMD: Numeric mean diameter.

**Table 2.** Means and standard errors of insecticide depositions on grains and glass slides for different grain species and swath widths.

| | Grain species | |
|---|---|---|
| Effective swath width | 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 |

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.

| Insecticide | Grain species: Corn | Grain species: 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 |

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 4.** Means and standard errors of insecticide depositions on grains and glass slides for different insecticides and swath widths.

| Effective swath width | Insecticide: Esfenvalerate | Insecticide: 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 |

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 ($P < 0.05$).

## 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, either by means of the tank agitators or the pressure received as the fluid passes through the spray tip's orifice, will not change its 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 (Butler Ellis and Tuck, 1999). The nozzle model studied is a continuous deposition type, and is only used 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 (Le Patourel 1992, Jermannaud and Pochon 1994, Acda et al. 1994) have demonstrated that great insecticide deposition variation occurs in stored grains.

Pesticide sprays are generally classified based on droplet size, with particular reference to VMD or $D_{0.5}$, i.e., volumetric mean diameter (Matthews, 2000). 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, since 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 (Lefebvre, 1989). 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. (1997) demonstrated that emulsions cause a rapid fluid sheet disintegration with the formation of large droplets. 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 physico-chemical 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. 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. 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. Finally, the results herein reported demonstrate the influence of the emulsifiable concentrate formulation on the fluid's physical properties, volumetric distribution, droplets spectrum, and insecticide deposition on stored corn and wheat grains. Consequently, evaluations of technical characteristics of agricultural nozzles using clean water as test fluid are only useful 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 based on such data.

## Acknowledgements

We thank the Programa de Estudante-Convênio de Pós-Graduação (PEC-PG) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the doctoral scholarship awarded to the first author.

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