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PHYSICAL CHARACTERISTICS OF OILY SPRAYING LIQUIDS AND DROPLETS FORMED ON COFFEE LEAVES AND GLASS SURFACES

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ABSTRACT: The physical characteristics of a spray liquid are important in getting a good droplet formation and control efficiency over a particular target. As a function of these characteristics, it is possible to decipher which is the best adjuvant based on the respective concentration used during the spray. Therefore, ten spraying liquids were prepared, which varied in concentrations of pesticide lufenuron + profenofos, mineral oil, water and manganese sulfate. Pendant droplets formed from these mixtures were measured to examine their impact on surface tension. Droplets were applied to the surface of coffee leaves and the surface tension, contact angle formed and the leaf area wetted by the droplet, were measured. A smooth glass surface was taken as a comparative to the coffee leaves. The highest concentrations of oil resulted in lower surface tension, smaller contact angles of droplets on leaf surfaces and larger areas wetted by the droplets. Both surfaces showed hydrophilic behavior.

KEYWORDS: surface tension, contact angle, wetted area, oil

CARACTERÍSTICAS FÍSICAS DE CALDAS OLEOSAS E DE GOTAS FORMADAS EM SUPERFÍCIE DE FOLHAS DE CAFÉ E DE VIDRO

RESUMO: As características físicas da calda de pulverização são importantes para que haja boa formação de gotas e eficiência de controle sobre determinado alvo. Em função dessas características, pode-se decidir sobre qual o melhor adjuvante, em sua respectiva concentração, poderá ser utilizado durante a pulverização. Para tanto, foram preparadas dez caldas fitossanitárias em que variaram as concentrações do inseticida lufenuron + profenofós, óleo mineral, água e sulfato de manganês. Gotas pendentes formadas a partir dessas misturas foram medidas em sua tensão superficial. Aplicaram-se gotas sobre a superfície de folhas de café e foram medidos a tensão superficial, o ângulo de contato formado e a área da folha molhada pela gota. Uma superfície lisa de vidro foi tomada como comparativo às folhas de café. As maiores concentrações de óleo resultaram em menores valores de tensão superficial, menores ângulos de contato de gotas com a superfície foliar e maiores áreas molhadas pelas gotas. Ambas as superfícies mostraram-se hidrofílicas.

PALAVRAS-CHAVE: tensão superficial, ângulo de contato, área molhada, óleo.

INTRODUCTION

Applications of plant protection products in liquid form are characterized by the elaboration of a mixture involving a vehicle-diluted pesticide and, in some cases, an adjuvant, to allow droplets to be produced from this mixture by spraying. In Brazil, the predominant vehicle used to dilute pesticides is water, due to its easy availability and low cost. In some cases, such as in the application of ultra low volume (ULV), the water vehicle is reduced and partially replaced by an oil-based adjuvant. There are also situations in which the vehicle is composed almost exclusively of oil, as is the case of applications of low oily volume (MONTEIRO, 2006).

Varying the volume of application reflects in a larger or smaller vehicle usage within the spraying liquid. By using a reduced volume, it is necessary to make use of an adjuvant in the

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mixture, while high volumes can bring problems inherent to the vehicle, such as hardness and high surface tension in water (IOST, 2008; PRADO et al., 2011).

When using water as a vehicle, the surface tension of the liquid or solution is the main property that is affected by surfactant adjuvants, as it is understood that there is a force that attracts surface molecules to the center of the liquid body (IOST, 2008).

Once hydrophobic (or lipophilic), a surface shows no affinity with the volume of spray that reaches it, thus concentrating the volume into droplets at a high contact angle and leading to a decrease in the retention of spraying liquid (XU et al., 2011). It is considered a hydrophilic surface when deposited droplets form contact angles of less than 90°, while a hydrophobic surface forms angles above 90° and may reach values above 160° in the case of the super hydrophobic (Tang et al., 2008).

MINGUELA & CUNHA (2010) mentions that by increasing the sprayed volume, an improvement in surface coverage is obtained. However, in aiming to remedy the problem of low coverage, growers are increasing the application volume beyond the point of runoff, resulting in a huge waste of spraying liquid that could be avoided through the correct use of an adjuvant.

Cited as a positive effect of adjuvants usage, is the improvement in wettability of hydrophobic surfaces, such as leaves and fruit with wax or pest integuments (XU et al., 2011). The coverage provided is more uniform due to the better distribution of the applied liquid, which is very important in the case of pesticides with contact mode of action. Another advantage occurs when spraying hairy leaf surfaces, on which hairs normally leave the droplets suspended, as the use of an adjuvant can improve the spreading, allowing the liquid to reach the target of the leaf surface. This effect is also replicated in facilitating the penetration of spraying liquid between several grooves, hyphae of fungi, mites webs, etc. (KISSMANN, 1998).

Therefore, this work aimed to detect variations in the physical characteristics of spraying liquid surface tension by using different concentrations of oil adjuvant, and the interaction of the droplets produced on the target surface through the contact angle formed.

MATERIAL AND METHODS

In the laboratory of Núcleo de Estudos e Desenvolvimento em Tecnologia de Aplicação – NEDTA, belonging to the Department of Plant Protection, Campus UNESP Jaboticabal – SP, ten different spraying liquids were prepared. The compositions of these spraying liquids varied according to the amount of insecticide profenofos (50%) + lufenuron (5%) (Curyom ® 550 EC) (55% ai g.L^{-1}), mineral oil Argenfrut ®, manganese sulfate (31% of Mn^{2+}) and water (Table 1). A control T11 spraying liquid, composed of distilled water in Milli-Q equipment was taken to compare the results.

TABLE 1. Constituent proportions presented in spraying liquids used in the assessments of the experiment and control of spraying liquid composed of water.

Composition	Spraying liquids (T1-T10) and control (T11)										
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11
Inseticide (% v/v)	4	2.67	2	0.4	0.2	1.74	1.2	0.87	0.4	0.2	-
Mineral oil (% v/v)	25	16.7	12.5	2.5	1.25	10	10	10	0.5	0.25	-
Water (% v/v)	70.7	80.3	85.2	96.8	98.2	86.3	86.8	87.1	98.1	98.56	100
$MnSO_4$ (g.L^{-1})	3	3	3	3	3	20	20	20	10	10	-

These different spraying liquids were analyzed on their physical characteristics when in contact with the adaxial surface of coffee leaves and in contact with a comparatively smooth glass surface. Physiologically active coffee leaves were collected with the use of surgical gloves to avoid contact of skin oils with leaves.

Assessment of the results

The surface tension of the spraying liquids utilized in the experiment, as well as the contact angle and the area wetted by the applied droplets on the surface of coffee leaves and smooth glass, were assessed using a tensiometer equipment, Contact Angle System model OCA 15 EC/B, from Dataphysics enterprise. The tensiometer was equipped with a CCD high speed, high definition camera, which captures droplet formation with the aid of SCA20 software used for the automation of the equipment and handling of images obtained on a computer.

For the surface tension analysis, pendant droplets were formed at the end of a needle (0.52 mm in external diameter) attached to a Hamilton® syringe (graduated until 5 µL of volume) which in turn was attached to the tensiometer. For each spraying liquid, five pendant droplets were formed and analyzed by the software according to the Young-Laplace equation. Surface tension values expressed as $mN.m^{-1}$ unit (Figure 1A) were then obtained.

For the analysis of contact angle and leaf area wetted by droplets, the collected coffee leaves were cut into rectangles of about 5 cm^2. These were set in a press in such a way so their adaxial surfaces were facing upward, before droplets of each spraying liquid were deposited (Figure 1B). Images were captured every second for 180 seconds. On the smooth surface of glass, the variables of contact angle and wetted area were also determined in relation to the application of droplets.

An automatic device applied to the tensiometer determined movements on the syringe plunger that dispensed droplets both on the coffee leaves and the glass surface, so as to allow for the analysis of the contact angle and wetted area. Once the whole droplet volume was dispensed on the surfaces, the syringe was rapidly retracted from the camera focus so the contact angle measurement could begin.

For the contact angle analysis, droplets were dispensed in the fixed volume of 3 µL, while for surface tension analysis pendant droplets of 4 µL was used. These volumes were selected in the experiment to provide better quality droplet images by the software camera, without influencing the spraying liquid's characteristics. For all variables, values for the average of 180s (average), values for the first 5 seconds (5s) and for the total 180 seconds (180s) were obtained and compared.

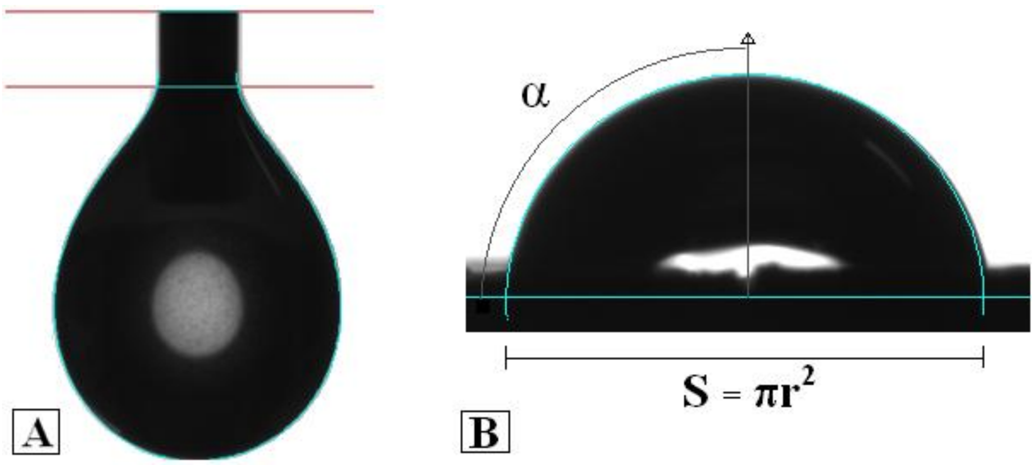

FIGURE 1. Obtained images in the tensiometer equipment. A. Formation of a 4 µL pendant droplet to be read on its surface tension. B. Aspect of 3 µL deposited droplet to be read on its contact angle and wetted area on a coffee leaf surface.

Experimental design

The analysis followed a randomized factorial design 11 x 3, representing 11 treatments (spraying liquids) in three different times (5s, average and 180s) with five replicates, for surface tension, contact angle and wetted area variables, measured separately. The means of the variables were subjected to analysis of variance and compared using the multiple comparisons Tukey test to the level of 5% probability.

The variables data was subjected to Pearson's linear correlation analysis in order to verify correlation between surface tension and contact angle and between surface tension and wetted area on both the coffee leaf and smooth glass surfaces.

RESULTS AND DISCUSSION

Surface tension

Significant differences were found among the treatments and for the interaction between the factors for the surface tension values obtained on the tensiometer. Pendant droplets of the ten different spraying liquids all showed to be different from the control with water. The surface tensions were significantly lower compared to water with the lower values in the highest concentrations of mineral oil mix, considering an average of 180 values, during 180 seconds (Table 2).

TABLE 2. Values in $mN.m^{-1}$ of droplets surface tension from the different spraying liquids at different moments of measurement.

Spraying liquids (% oil)	Average	5s	180s
T1 (25%)	30.59 defg AB[1]	31.82 e A	29.38 de B
T2 (16.7%)	29.02 g B	30.69 e A	27.99 e B
T3 (12.5%)	32.06 cde A	32.77 de A	31.29 bcd A
T4 (2.5%)	31.82 cdef B	33.95 cd A	30.83 cd B
T5 (1.25%)	32.44 bcd B	38.79 b A	31.01 cd B
T6 (10%)	31.61 cdef A	32.1 de A	31.20 bcd A
T7 (10%)	30.34 efg AB	30.99 e A	29.24 de B
T8 (10%)	29.96 fg AB	31.07 e A	28.59 e B
T9 (0.5%)	33.07 bc B	35.32 c A	32.02 bc B
T10 (0.25%)	34.26 b B	39.36 b A	33.12 b B
T11 (water)	76.39 a A	75.61 a A	76.43 a A
MSD[2]	2.08		
MSD[3]	1.50		
180s	34.64 c		
Average	35.60 b		
5s	37.50 a		
MSD[2]	0.55		
CV	2.78		

[1]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test ($p>0.05$). Minimum significant difference for columns[2] and lines[3].

At 5s, the lowest surface tension values were those with the highest concentrations of oil in the mixture. By decreasing the oil proportion and increasing water concentration, the surface tension value increased significantly (Table 2). At 180s, the treatments showed the same behavior.

In comparing dynamic surface tension over the 180 evaluated seconds, significant differences were found to that at 5s; the surface tension of the spraying liquids containing adjuvant were higher compared to the average value, which in turn was greater than the values at 180s (Table 2). This variation of surface tension at180s is a function of energy balance among solid, liquid and gas interfaces tending to the equilibrium of forces. The use of adjuvant significantly affected this balance, resulting in lower surface tension values for the spraying liquids, which could not be observed for the pendant droplets with water at 180s. The spraying liquids with the largest concentration of water were significantly different from the others, presenting higher surface tension values (Table 2).

This reduction of surface tension value was due to the presence of mineral oil adjuvant that is based on molecules with apolar (hydrophobic) and polar (hydrophilic) linking sites, concurrently (SILVA et al., 2003). The same author explains that, once in contact with water, the adjuvant molecules are arranged in formation, as the polar portion of these arrangements are positioned with water molecules, while the apolar portion borders the other molecules. Thus, there is a linkage between molecules that are chemically distinct, leading to a homogeneous solution. This arrangement of polar and apolar phases consist of micelles, which are formed in a minimum concentration of these molecules, referred to as the critical micellar concentration (CMC).

A value of CMC is intrinsic to each adjuvant formulation, which can be determined by varying the concentration mix with another liquid and measuring the values of surface tension. Thus, the CMC is obtained when increases in the adjuvant concentration stop resulting in decreases of the solution surface tension (IOST, 2008).

The water used in the experiment under conditions of temperature and relative humidity during the analysis showed a mean surface tension value of 76.39 $mN.m^{-1}$, close to the value of 72.74 $mN.m^{-1}$ for pure water at 20^{o}C.

Foliar surface

Contact angle

Significant differences in the contact angle of droplets were found among the treatments and in the interaction between the factors of spraying liquid and time of measurement. The treatment control with water produced the biggest contact angle with foliar surface. Then, the oil concentrations of 0.25, 12.5, 25 and 10% (T6), in descending order, resulted in lower contact angle with the leaves, but without significant differences among them (Table 3). The lowest means of contact angles related to the concentrations of 10 (T8), 10 (T7), 2.5 and 16.7%, with no significant difference between them. The average value of contact angle of droplets composed by water was 73.85 degrees, which characterizes the coffee leaves as hydrophilic ($<90^{o}$).

In general, there is a slight variation between the angle of the droplets at different concentrations of oil and insecticide. However, there is an increment in the angle values with higher volumes of the water vehicle mixed into the spraying liquid.

In a field situation of spraying, in which the sprayed droplets form a high contact angle, confining the deposited volume in a small area on the leaves surface, there is the necessity for a high application volume of spraying liquid, so that the leaves are efficiently covered with the droplets. Nevertheless, the use of a suitable adjuvant in the correct concentration is required, leading to a better spreading of droplets on the surface of the leaves.

In the case of hydrophobic leaf surfaces, the success of a spray is compromised due to the problem of droplets that ricochet and scatter from the leaves, soon after coming into contact with them. Even the droplets that remain on the leaf may form very high contact angles, as the droplets are confined to a small wetted area. This behavior of droplets leads to erroneous agricultural practices when using high-volume application (KOCH; ENSIKAT, 2008; KIRKWOOD, 1999; FERREIRA et al., 2012).

TABLE 3. Degree values of contact angle formed by droplets applied on adaxial coffee leaves surface, using the different spraying liquids at different moments of measurement.

Spraying liquids (% Oil)	Average	5s	180s
T1 (25%)	40.94 bc AB[1]	46.01 bc A	38.26 bc B
T2 (16.7%)	30.59 d B	41.54 cd A	25.52 d B
T3 (12.5%)	42.01 bc AB	46.98 bc A	38.80 bc B
T4 (2.5%)	30.19 d B	39.19 cd A	26.31 d B
T5 (1.25%)	32.82 cd B	54.53 b A	26.39 d B
T6 (10%)	36.14 bcd AB	43.07 cd A	33.66 bcd B
T7 (10%)	29.33 d AB	35.50 d A	26.75 d B
T8 (10%)	28.54 d B	37.28 cd A	24.59 d B
T9 (0.5%)	33.30 cd B	45.90 bc A	29.29 cd B
T10 (0.25%)	44.84 b B	55.07 b A	39.52 b B
T11 (water)	73.85 a B	86.92 a A	67.20 a B
MSD[2]	9.89		
MSD[3]	7.14		
180s	34.21 c		
Average	38.43 b		
5s	48.36 a		
MSD[2]	2.15		
CV	11.79		

[1]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test ($p>0.05$). Minimum significant difference for columns[2] and lines[3].

At 5s and 180s after droplets application, there was a greater contact angle with the treatment composed of water, followed by treatment with least oil and pesticide concentration (Table 3). Similarly to the previous item, explaining about surface tension, there were significant differences between the contact angles at the three time variables, so that the droplets were conducted at a gradual dynamic spreading, reaching the smallest angle at the 180s, intermediate on the average and the highest at 5s (Table 3).

TANG et al. (2008) studying the SILWET surfactant L-77 ®, showed that under increasing concentrations of this product, the contact angle of deposited droplets on dry and wet surfaces decreased rapidly and significantly in the first seconds. The smallest contact angles occurred at the highest concentration while in the absence of the surfactant, high angles formed on both surfaces.

In a study involving a microemulsion mixed with water, TAMHANE et al. (2012) found smaller contact angles formed by droplets (30.4 to 26.7^{o}), when compared to water droplets (122.3°), on a hydrophobic surface. Visually, as shown in Figure 2, it was found that in this study, droplets behavior was similar to that described by other authors using other adjuvants.

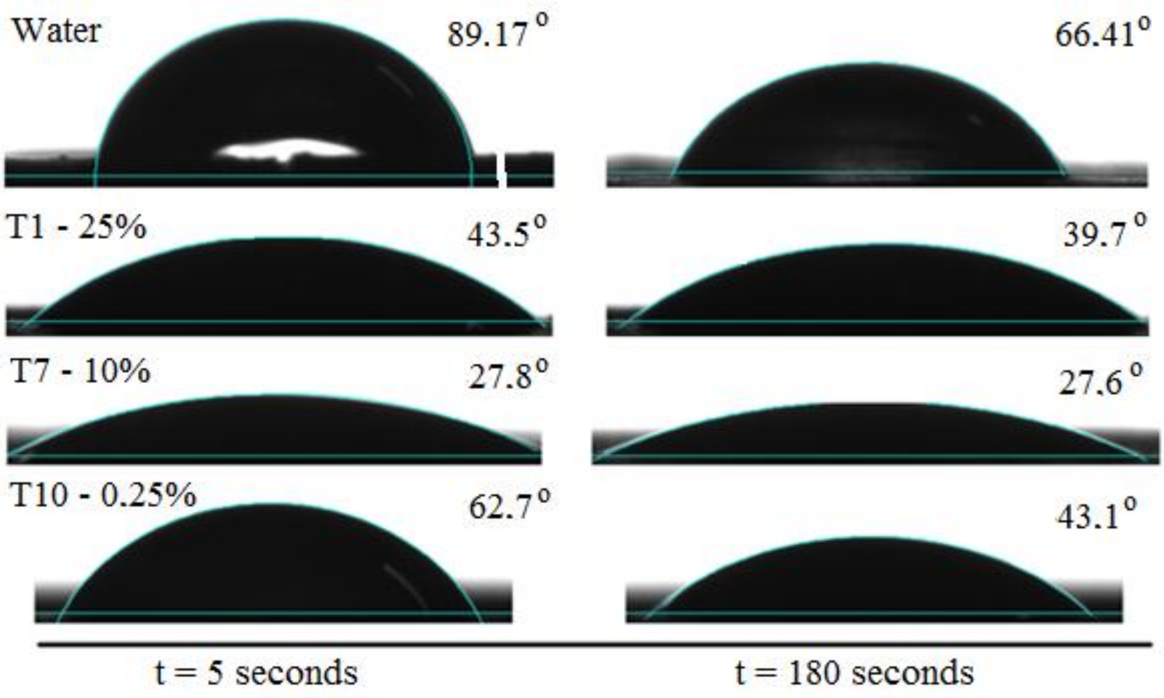

FIGURE 2. Values of contact angle formed by droplets applied on the surface of coffee leaves physiological active, using four spraying liquids on its respective oil concentration at the moments of 5 and 180 seconds.

The relationship between the variables of surface tension and contact angle of droplets on coffee leaves is strongly positive, according to Pearson's linear coefficient of correlation, which was 0.87. Thus, any decrease on the surface tension of the spraying liquid results in a direct reduction in contact angles of droplets formed on the coffee leaf surface.

Wetted area

The values of wetted area by droplets expressed in mm^2 did not differ significantly among the treatments and the times of measurement (Table 4). This variable is positively correlated with the contact angle variable, since the smaller the angle, the greater the wetted area.

The highest volumes of water in a mixture of spraying liquids leads to higher contact angles, and therefore smaller wetted areas on the leaf surfaces (Table 4). Similar information was found by XU et al. (2011) in a study involving four adjuvants and five concentrations, showing that values of wetted area for the adjuvants increases under higher concentrations.

The evaluation showed that the dynamics of the wet area, considering all the spraying liquids, have showed no significant difference among the timeframes of 5s, 180s and average value. Under laboratory conditions, even monitoring the temperature and relative humidity during the 180 seconds of analysis, part of the volume of the droplet applied on the leaf surface evaporated. Thus, the reading may have been underestimated by the apparatus according to method and time adopted.

XU et al. (2011) demonstrated in a study that the use of adjuvants can considerably improve the homogeneity of the spray and consequently increase the wetted area on the target surface in question, making it possible to adopt smaller spraying liquid volumes, resulting in economic and environmental benefits. The author also points out that, depending on the morphological variations of leaf surfaces and the mixture used in the spraying liquid, there are also variations in the behavior of deposited droplet, in such a way that each situation must be analyzed in order provide a better spray efficiency.

TABLE 4. Values in mm^2 of wetted area by droplets formed with the different spraying liquids applied on the adaxial coffee leaf surfaces at different moments of measurement.

Spraying liquids (% oil)	Average	5s	180s
T1 (25%)	9.64 a A[1]	8.29 a A	7.87 a A
T2 (16.7%)	10.40 a A	9.43 a A	9.74 a A
T3 (12.5%)	11.58 a A	8.61 a A	11.58 a A
T4 (2.5%)	9.43 a A	9.41 a A	8.74 a A
T5 (1.25%)	10.12 a A	8.96 a A	10.44 a A
T6 (10%)	9.31 a A	8.04 a A	9.66 a A
T7 (10%)	10.42 a A	10.28 a A	10.18 a A
T8 (10%)	11.42 a A	9.40 a A	11.32 a A
T9 (0.5%)	9.14 a A	8.05 a A	9.27 a A
T10 (0,25%)	8.42 a A	7.85 a A	8.49 a A
T11 (water)	7.04 a A	7.25 a A	6.93 a A
MSD[2]	5.31		
MSD[3]	3.83		
180s	9.47 a		
Average	9.48 a		
5s	8.69 a		
MSD[2]	1.16		
CV	27.71		

[1]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test (p> 0.05). Minimum significant difference for columns[2] and lines[3].

The differences found in this experiment between the ten spraying liquids and water allow us to determine, in field conditions, the amount of droplets required for each spraying liquid to cover the surface of a coffee leaf. Comparing the average wetted area of 1,420 mm^2 by droplets of water with the wetted area of 863 mm^2 by treatment with 12.5% of oil, it would be necessary for there to be 40% less droplets for the latter to completely recover the same coffee leaf surface. This fact demonstrates a safe number of droplets and, consequently a safe mix of pesticide and water, leading to lower environmental contamination and waste.

According to BAUER et al. (2008), spray nozzles JA-2, working at a pressure of 400 kPa, produce droplets with a Volume Median diameter (VMD) of 153 µm, with a diameter that separates half of the spray volume loaded into droplets, so it was possible to formulate comparisons with the values of the wetted area in this work.

If a spraying liquid with 12.5% of oil is sprayed by JA-2 nozzles, in the same pressure of 400 kPa and same VMD, an application volume can be adopted with 40% lower liquid compared to the spray with water and 27.3% lower than spraying with the lowest concentration of oil, resulting in an operational gain in economy in agricultural activity (CUNHA et al., 2011).

The use of oil-based adjuvants provides a formation of sprayed droplets with a more uniform size and with less risk of drift due to the protection afforded to them (YAMAUTI et al., 2012). Thus, with the use of a mineral oil in a mixture of spraying liquid, it is possible to utilize spray nozzles capable of producing droplets with a smaller VMD without major losses due to unfavorable weather conditions.

Therefore, by using a spraying liquid with 12.5% mineral oil, in addition to the reduction of 40% in application volume of treatment water, to a same coffee leaf surface, we can obtain greater reductions in volume. Greater leaf coverage may be obtained by using a spray nozzle that produces droplets of smaller size (ZAIDAN et al., 2012).

According to Pearson's coefficient of -0.64 in the relationship between the variables of surface tension and wetted area by droplets on coffee leaves, there was a negative correlation. Another negative correlation was found between the variables of contact angle and wetted area (-

0.75). Thus, the use of mineral oil at sufficient quantity to reduce the surface tension of the spraying liquid consequently reduces the contact angle and increases the wetted area of coffee leaves by applied droplets.

Smooth surface of glass

Contact angle

On the smooth surface of glass, taken as a comparison to the coffee leaves, significant differences between the means of contact angles of droplets of spraying liquids were only observed at 5s, as the treatments with 25, 12.5 and 10% (T6) of oil differed significantly from the other treatments (Table 5).

As with the coffee leaves, the droplets contact angle gradually decreased throughout the 180 seconds evaluated. Consequently, at 5s of measurement the mean of contact angle was significantly higher than the average, which in turn was higher compared to 180s (Table 5).

TABLE 5. Degree values of contact angle formed by droplets applied on a smooth surface of glass, using the different spraying liquids at different moments of measurement.

Spraying liquids (% oil)	Average	5s	180s
T1 (25%)	6.11 a A[1]	10.10 cd A	4.55 a A
T2 (16.7%)	10.61 a A	16.06 abcd A	6.93 a A
T3 (12.5%)	5.14 a A	11.81 bcd A	2.79 a A
T4 (2.5%)	19.18 a AB	28.33 a A	13.22 a B
T5 (1.25%)	15.07 a AB	22.73 abcd A	9.48 a B
T6 (10%)	9.35 a AB	18.08 abcd A	5.02 a B
T7 (10%)	6.97 a A	9.57 d A	7.44 a A
T8 (10%)	10.23 a A	16.04 abcd A	7.79 a A
T9 (0.5%)	18.67 a AB	27.32 ab A	12.10 a A
T10 (0.25%)	18.60 a AB	25.84 abc A	13.63 a B
T11 (water)	15.76 a A	17.07 abcd A	12.56 a A
MSD[2]	15.87		
MSD[3]	11.47		
180s	8.68 c		
Average	12.33 b		
5s	18.45 a		
MSD[2]	1.51		
CV	58.16		

[1]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test ($p > 0.05$). Minimum significant difference for columns[2] and lines[3].

Once droplets of water formed angles with values of 17.07 ° and 12.56 °, at 5 and 180s, the smooth glass surface was characterized as pronouncedly hydrophilic. The influence of an adjuvant added to the spraying liquid is not as intense, as the spreading of droplets occurs naturally and the contact angles are small. After applying the droplet onto the hydrophilic smooth surface of glass, the surface tension is not enough to confine the droplet to a small area. Gradually, the interface forces overcome the inertia of the molecules, causing spreading and reductions in angle values.

Gradual action is characteristic of mineral or vegetable oil-based adjuvants, decreasing the spraying liquid surface tension as concentration increases. However, IOST & RAETANO (2010) studied the behavior of surfactants LI-700, Pronto 3 and UNO at both the recommended and double the recommended dose. This author found no significant reduction in the value of the contact angle of droplets from the adjuvants in comparison with the control treatment using water. Nevertheless, using the surfactant Silwet L-77 and Supersil, the contact angle reached zero. Thus, it is understood that, for each adjuvant, there is an optimum concentration as a mixture in the spraying liquid for a particular purpose.

The different concentrations of mineral oil reflected in visible changes, as seem in photos taken during the dynamic analysis of contact angle formed by droplets at 5 and 180s (Figure 3).

According to Pearson's linear correlation analysis, there was a slight positive correlation between the contact angle of droplets and the surface tension value on the glass surface, expressed by the coeficient 0.23. This positive relationship was also found for coffee leaves, although the correlation was far more strong than that found for the glass surface. Thus, surface tension reductions provided by the mineral oil resulted in tiny decreases on the contact angle of droplets applied on the glass surface.

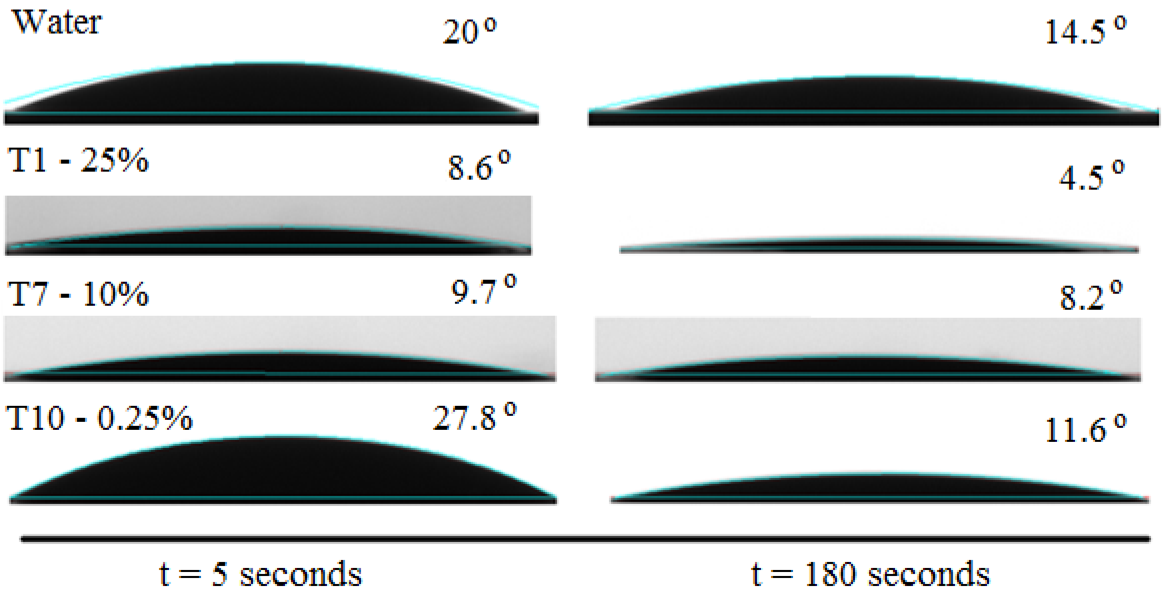

FIGURE 3. Values of contact angle formed by droplets applied on the smooth surface of glass, using four spraying liquids on its respective oil concentration at the moments of 5 and 180 seconds.

Wetted area

The means of wetted areas by droplets applied on the smooth glass surface were not significantly different when comparing all the spraying liquids with each other and with water. Similarly, no significant difference was observed when comparing the times of measurement (average time, at 5s and 180s), as well as for the interaction of the factors of spraying liquid and time of measurement (Table 6).

As previously observed for the wetted area by droplets on coffee leaves, losses of droplet volume by evaporation during the 180s of measurement may have also occurred on the smooth glass surface. Even though significant differences were not observed when comparing the means at 5s (15.86 mm2), average time (17.00 mm^2) and at 180s (16.11 mm^2), the latter would probably keep decreasing. This is due to the great spread of droplets on the hidrophilic surface of glass that provides higher liquid surface in contact with the gas interface, leading to losses by evaporation.

The wetted area of 20.46 mm^2, found at a concentration of 25% oil, compared to the area of 11.08 mm^2, found in a concentration of 0.5% oil, shows that it would be necessary to apply 84% more droplets with the lowest concentration on the glass surface, for the same area to be covered. By using the water treatment, 4% more droplets would be required in relation to the spraying liquid with 25% oil to obtain a same wetted area of smooth glass.

TABLE 6. Values in mm^2 of wetted area by droplets formed with the different spraying liquids applied on the smooth glass surface at different moments of measurement.

Spraying liquids (% oil)	Average	5s	180s
T1 (25%)	20.46 a A[1]	17.98 a A	16.53 ab A
T2 (16.7%)	18.89 a A	16.20 a A	19.26 ab A
T3 (12.5%)	18.44 a A	19.19 a A	15.30 ab A
T4 (2.5%)	13.86 a A	11.89 a A	14.40 ab A
T5 (1.25%)	15.75 a A	14.03 a A	16.97 ab A
T6 (10%)	19.20 a A	15.92 a A	20.42 a A
T7 (10%)	17.38 a A	18.04 a A	14.77 ab A
T8 (10%)	18.41 a A	18.36 a A	15.54 ab A
T9 (0.5%)	11.08 a A	9.99 a A	9.65 b A
T10 (0.25%)	13.96 a A	12.92 a A	14.18 ab A
T11 (water)	19.63 a A	19.98 a A	20.19 a A
MSD[2]	10.32		
MSD[3]	7.46		
180s	16.11 a		
Average	17.00 a		
5s	15.86 a		
MSD[2]	1.75		
CV	30.47		

[1]Means followed by the same lower case letter on the column and uppercase letter on the line does not differ by Tukey test ($p > 0.05$). Minimum significant difference for columns[2] andd lines[3].

In analyzing the relationship between the variables, a slight positive correlation was found between the surface tension and wetted area by droplets on the glass surface, according to Pearson's linear correlation analysis with a coefficient of 0.28. Thus, decreases in the surface tension variable were followed by tiny reductions in the variable of wetted area. This differs from the findings of IOST (2008), which demonstrated a negative correlation between these variables when working with different adjuvants on a glass surface.

This difference compared to the negative correlation observed for coffee leaves may be associated with differences between the two surfaces, as glass is far more hydrophilic than coffee leaves.

There was a negative correlation found between the variables of contact angle and wetted area with a coefficient of -0.57. This relationship follows the same but less intense pattern compared to that found for the coffee leaves, in which the smaller variable was the contact angle of droplets on the glass the higher variable was that of variable wetted.

CONCLUSIONS

Mineral oil in a mixture of spraying liquid reduces surface tension of the liquid and increasing concentration decreases surface tension up to a limit, based on the values used in this research. Increasing concentrations of mineral oil in the spraying liquid has resulted in smaller contact angles of droplets on the surface of coffee leaves, which demonstrated hydrophilic characteristic. The smooth glass surface was intensely hydrophilic, so the influence of mineral oil on the contact angle, and thus on the wetted area, was not enough to cause significant differences in the results. This indicates that it is a better idea to have natural surfaces in tests when spreading spraying liquids.

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