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Article

# Effect of Pesticide Addition Sequence on the Preparation of Phytosanitary Spray Solutions

*Efeito da Sequência de Adição de Agrotóxicos no Preparo de Caldas Fitossanitárias*

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ABSTRACT - The addition of adjuvants to herbicide solutions is aimed at preserving or enhancing the biological effect of treatment. However, it is commonly performed without knowledge of the physicochemical interactions between products. This study aimed to assess the effects of different addition sequences of the herbicide aminopyralid + fluroxypyr and adjuvants in the preparation of phytosanitary spray solutions on the surface tension and contact angle. Two experiments were carried out with herbicide doses of 1 and 2 L ha$^{-1}$ associated with the adjuvants mineral oil (MO), silicone-polyether copolymer (SIL), and a mixture of phosphatidylcholine (lectin) and propionic acid (LEC), all at a proportion of 0.3% v v$^{-1}$. The application rate was 150 L ha$^{-1}$. Surface tension was measured by the pendant droplet method. Contact angle was measured on the adaxial and abaxial surfaces of leaves of the pasture weed *Senna obtusifolia* and parafilm. Preparation sequence did not change the contact angle on any of the analyzed surfaces at a dose of 1 L ha$^{-1}$ of herbicide. For the dose of 2 L ha$^{-1}$, the adjuvants SIL and LEC showed a higher spreading when previously added to the herbicide. MO resulted in a higher spreading when added after the herbicide, with higher surface coverage. Therefore, the preparation sequence influences the dispersion of phytosanitary spray solutions on targets.

**Keywords:** adjuvants, preparation sequence, *Senna obtusifolia*.

*RESUMO - A adição de adjuvantes às caldas herbicidas visa preservar ou aumentar o efeito biológico do tratamento, porém é comumente realizada sem conhecimento das interações físico-químicas entre os produtos. Assim, objetivou-se neste trabalho avaliar os efeitos sobre a tensão superficial e o ângulo de contato decorrentes de diferentes sequências de adição do herbicida aminopiralide + fluroxipir e adjuvantes no preparo de caldas fitossanitárias. Foram realizados dois experimentos, com a dosagem de 1 e 2 L ha$^{-1}$ do herbicida, associados aos adjuvantes óleo mineral (OM), copolímero de poliéter e silicone (SIL), mistura de fosfatidicolina e ácido propiônico (LEC), todos na proporção de 0,3% v v$^{-1}$. A taxa de aplicação considerada foi de 150 L ha$^{-1}$. Mediu-se a tensão superficial pelo método da gota pendente. O ângulo de contato foi medido nas superfícies adaxial e abaxial de folhas da planta daninha de pastagens Senna obtusifolia e em parafilme. Verificou-se que a ordem de preparo não alterou o ângulo de contato em nenhuma das superfícies analisadas na dosagem de 1 L ha$^{-1}$ do herbicida. Para a dosagem de 2 L ha$^{-1}$, os adjuvantes SIL e LEC apresentaram maior espalhamento quando adicionados previamente ao herbicida. O OM resultou em maior espalhamento quando adicionado após o herbicida, com maior cobertura da superfície. Portanto, a sequência de preparo das caldas fitossanitárias influencia no espalhamento destas sobre os alvos.*

**Palavras-chave:** adjuvantes, ordem de preparo, *Senna obtusifolia*.

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## INTRODUCTION

Product addition sequence to the sprayer tank during the preparation of spray solution with herbicides and adjuvants is important to avoid possible problems with phytointoxication, treatment ineffectiveness or damages to the sprayer equipment due to potential incompatibilities (Cessa et al., 2013).

Agricultural adjuvants are compounds added to formulations or spray solutions directly into the sprayer tank to modify their physicochemical properties. These compounds may contribute to the compatibility of products in the sprayer tank and improve the performance of agricultural applications, influencing the viscosity, surface tension, contact angle, pH, electrical conductivity, and retention and droplet deposition (Prado et al., 2016; Cunha et al., 2017). Each adjuvant has specific properties aimed at acting in increased permeability and absorption of molecules, retention of spray solution, surface coverage, reduction of foam, adequacy of droplets for the dispersion of spray solution on targets, among others (Oliveira et al., 2013; Decaro Junior et al., 2015; Decaro et al., 2016).

Thus, surface tension is the force on fluid surfaces, and its reduction in the spray solution provides a higher spreading capacity of droplets (Silva et al., 2006). Thus, this property interferes with the amount of herbicide retained on the leaf surface and, together with leaf chemical composition, how this interaction occurs (Prado et al., 2016). Adjuvants differ significantly from each other in reducing the surface tension and contact angle, factors relevant to droplet formation and target coverage, which should be carefully considered for an appropriate selection (Li et al., 2016).

Considering the lack of information on the technology of pesticide application in pastures, this study aims at contributing to the decision-making of farmers regarding the most appropriate combination between adjuvants and herbicide, as well as the correct product addition sequence to the phytosanitary spray solution since it is possible that adjuvant addition alternation interferes with the surface tension and, consequently, droplet spreading on leaf surfaces.

Thus, this study aimed to assess the effects of different addition sequences of the herbicide aminopyralid + fluroxypyr and adjuvants in the preparation of phytosanitary spray solutions and their influence on the surface tension and contact angle.

## MATERIAL AND METHODS

The study of effects of the addition sequence of herbicides and adjuvants on the preparation of spray solution was carried out in 2016 in a completely randomized design with four replications, arranged in a 2 × 3 + 1 factorial scheme. Interaction factors consisted of two treatments related to the preparation sequence of the spray solution (herbicide + adjuvant and adjuvant + herbicide) and three adjuvants, with water as the control (Table 1).

The herbicide used in the experiment was aminopyralid + fluroxypyr (Dominum® 40.0 g a.e. $L^{-1}$ + 80 g a.e. $L^{-1}$, SL, Dow AgroSciences), belonging to the groups pyridinecarboxylic and pyridinyloxyalkanoic acids, respectively, with registration for *Senna obtusifolia* in pastures. This herbicide was associated with three adjuvants: 1 – aliphatic hydrocarbons (mineral oil: Nimbus®, 428.0 g a.i. $L^{-1}$, EC, Syngenta); 2 – organosiliconate (silicone-polyether copolymer: Silwet®, 1,000 g a.i. $L^{-1}$); and 3 – mixture of phosphatidylcholine (lectin) and propionic acid (LI-700®, 712.88 g a.i. $L^{-1}$, CE, De SANGOSSE Agroquímica). Each adjuvant was added to the spray solution at a proportion of 0.3% v $v^{-1}$, alternately to the herbicide (Table 1), as recommended in the herbicide leaflet. A concentration equivalent to the application rate of 150 L $ha^{-1}$ was used as a basis.

Two experiments were performed: one at a dose of 1 L $ha^{-1}$ of commercial herbicide (experiment I) and the other at a dose of 2 L $ha^{-1}$ of herbicide (experiment II), considering the control of *S. obtusifolia* and other broadleaf weed species present in the pasture (Table 1).

Experiments were also performed to determine the physicochemical characteristics of the phytosanitary spray solutions, in which the surface tension and contact angle were assessed. The equipment used was the Contact Angle System OCA 15-Plus (Dataphysics®) equipped with a high speed and definition digital camera and the software SCA20® for automation and processing of the obtained images.

***Table 1*** - Treatments for the assessments of surface tension and contact angle of both experiments, with the respective preparation sequences

| Treatment | Experiment I[(1)] | Experiment II[(2)] |
|---|---|---|
| | Preparation sequence | Preparation sequence |
| 1 | Control | Control |
| 2 | HERB[(3)] + MO[(3)] | HERB + MO |
| 3 | HERB + [3]SIL | HERB + SIL |
| 4 | HERB + [3]LEC | HERB + LEC |
| 5 | MO + HERB | MO + HERB |
| 6 | SIL + HERB | SIL + HERB |
| 7 | LEC + HERB | LEC + HERB |

[(1)] Experiment I – dose of 1 L c.p. $ha^{-1}$ of aminopyralid + fluroxypyr; [(2)] Experiment II – dose of 2 L c.p. $ha^{-1}$ of aminopyralid + fluroxypyr; [(3)] Abbreviations: HERB = aminopyralid + fluroxypyr; MO = mineral oil; SIL = silicone-polyether copolymer; LEC = mixture of phosphatidylcholine (lectin) and propionic acid.

Surface tension was determined by the pendant droplet method, in which the image of the formed droplet at the tip of a syringe is captured by high speed and resolution CCD camera (30 frames per second) and sent for processing in equipment that analyzes the droplet format by axis asymmetry. The calculation of surface tension is based on the Yang-Laplace equation, considering the deformation of the droplets emitted at each sampling (Ferreira et al., 2013). The measurement of surface tension was performed for 60 s after droplet formation, considering moments 5, 15, and 30 s for assessment.

Contact angle was assessed on three different surfaces: two natural (adaxial and abaxial surface of *S. obtusifolia* leaves) and an artificial surface (parafilm: a resistant mixture of plastic paraffin with paper, waterproof, marketed as Parafilm M®). Plants of *S. obtusifolia* were cultivated in pots containing substrate composed of soil, sand, and animal manure (3:3:1) in a greenhouse for 60 days for leaf collection. Fully developed leaves were collected, and longitudinal rectangles of approximately 5 × 1 cm were sectioned. These sections were arranged horizontally on stretchers to reduce undulations that hamper contact angle readings. Images were assessed every second for one minute after the deposition of each droplet on the surfaces. The angle was assessed considering 5, 15, and 30 seconds after the droplet was deposited on the surface.

The results were submitted to analysis of variance by the F-test and treatment means were compared by the Tukey's test (p>0.05) using the software Asistat 7.7 Beta® (Silva and Azevedo, 2016).

## RESULTS AND DISCUSSION

The study of characteristics of surface tension and contact angle as a function of the preparation sequence of the addition of herbicide and adjuvant to the spray solutions showed no differences for the variable surface tension. However, the contact angle showed significant differences, denoting the interference of preparation sequence on the spray solution characteristics and its interaction with the surfaces on which the droplets are deposited.

For surface tension, even in the absence of differences for the factor preparation sequence, differences were observed between treatments (herbicides and adjuvants) and between treatments and control (water) (Table 2). Despite the difference between adjuvants, the addition sequence of these products in the sprayer tank did not interfere with the surface tension when the used dose was 1 L $ha^{-1}$ of herbicide.

The adjuvant composed of the mixture of phosphatidylcholine (lectin) and propionic acid (LEC) and that of mineral oil (MO) led to higher surface tension values (Table 2). The addition of MO resulted in a higher tension value at all times assessed in experiment I (1 L $ha^{-1}$ of herbicide) and did not differ for LEC in experiment II (2 L $ha^{-1}$ of aminopyralid + fluroxypyr). It was possibly due to the bi-fold dose of herbicide in the second experiment, which implied a higher amount of adjuvants in the spray solution since they already compose the herbicide formulation itself. Thus, MO addition in herbicide spray solutions may have reached the critical micelle concentration, not leading to a decrease in the contact angle since the increasing concentration of OM in phytosanitary spray solutions presents a limit of surface tension decrease (Decaro Júnior et al., 2015).

Regarding the organosiliconate adjuvant (SIL), lower surface tension values were verified at the three analyzed moments, as well as in both experiments (Table 2). Surface tension values

***Table 2*** **-** Means of surface tension (mN $m^{-1}$) of treatments at 5, 15, and 30 seconds after droplet formation, F-values, and coefficients of variation (CV%) for experiments I and II

| Factor | Variable | Surface tension (mN $m^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Experiment I(1) | | | Experiment II(2) | | |
| | | 5 s | 15 s | 30 s | 5 s | 15 s | 30 s |
| Preparation sequence | Herb.(3) + Adj. | 30.95 a | 30.57 a | 30.27 a | 29.55 a | 28.63 a | 28.19 a |
| | Adj.(3) + Herb. | 30.18 a | 29.85 a | 29.60 a | 29.45 a | 28.99 a | 28.85 a |
| LSD | | 1.59 | 1.52 | 1.52 | 0.80 | 0.96 | 1.08 |
| Adjuvants | MO(3) | 35.75 a | 34.94 a | 34.26 a | 32.54 a | 31.18 a | 30.61 a |
| | SIL(3) | 24.97 c | 25.19 c | 25.22 c | 24.08 b | 23.87 b | 24.01 b |
| | LEC(3) | 30.98 b | 30.50 b | 30.34 b | 31.89 a | 31.39 a | 30.94 a |
| LSD | | 2.36 | 2.25 | 2.26 | 1.19 | 1.42 | 1.61 |
| ANOVA | | | | | | | |
| | | Calculated F-values (Experiment I) | | | Calculated F-values (Experiment II) | | |
| Preparation sequence | | 1.02ns | 0.95ns | 0.84ns | 0.06ns | 0.61ns | 1.57ns |
| Adjuvants | | 66.29** | 59.35** | 51.00** | 197.03** | 114.69** | 74.55** |
| Preparation sequence vs. adjuvants | | 2.10ns | 1.88ns | 1.15ns | 2.24ns | 0.34ns | 0.25ns |
| Treatments vs. control | | 1988.9** | 2213.1** | 2056.3** | 8153.4** | 5893.9** | 4305.5** |
| CV (%) | | 5.07 | 4.88 | 4.96 | 2.63 | 3.19 | 3.66 |

Means followed by the same letter in the columns do not differ from each other by the Tukey's test ($p>0.05$). ns Not significant; * Significant at 5% probability; ** Significant at 1% probability. (1) Experiment I – dose of 1 L c.p. $ha^{-1}$ of aminopyralid + fluroxypyr; (2) Experiment II – dose of 2 L c.p. $ha^{-1}$ of aminopyralid + fluroxypyr; (3) Abbreviations: MO = mineral oil; SIL = silicone-polyether copolymer; LEC = mixture of phosphatidylcholine (lectin) and propionic acid; Herb. = herbicide; Adj. = adjuvant.

for SIL lower than those of other adjuvants have been observed in other studies, corroborating the results found here (Iost and Raetano, 2010). This lower value is due to the organosiliconate formulation, which, due to its high surfactant power, rapidly reduces the surface tension of aqueous solutions, overcoming the effects generated by hydrocarbon adjuvants (Prado et al., 2016).

Water, a predominant component in the spray solution, has a high surface tension, which implies low spreading of droplets when deposited on the plant. It interferes with product efficacy since the area covered by droplets and the amount of liquid present directly affect the evaporation and absorption rates of the deposited spray solutions (Yu et al., 2009; Decaro Junior et al., 2014).

The presence of additives is frequent in formulations of agricultural pesticides, including surfactants with a high frequency and importance to reduce surface tension (Iost and Raetano, 2010). Formulations influence development costs, manufacturing process, contents of commercial products, and application given their influence on leaf surface wetting, product retention on the treated surface, liquid absorption by leaf surface, and product activation to maintain the expected biological effect (Cunha and Alves, 2009; Maciel et al., 2010; Decaro Junior et al., 2015; Calore et al., 2015). The better understanding of the effects of surface tension brings possibilities of a better use of adjuvants for pesticide formulation, prepared spray solutions, and applications directly in the field.

Regarding the contact angle (θ°), the values found for the analyzed factors were lower than those of control in both experiments (I and II) on all surfaces (Table 3), which means that droplets formed from water spread less than those arising from phytosanitary spray solutions composed by adjuvants (Decaro Junior et al., 2015). The use of adjuvants in spray solutions increases the wetted area by the droplet on both sides of soybean leaves due to the effect of adjuvants on the interaction between the droplet and leaf surfaces (Gimenes et al., 2013).

The adjuvant SIL presented lower values of contact angle on all surfaces and in both doses. The organosiliconate adjuvant (SIL) is classified as a spreader-sticker, which, when associated with phytosanitary spray solutions, provides a higher contact of the droplet with the surface due to its surfactant action.

***Table 3*** **-** F-values and coefficients of variation (CV) applied to means of contact angle (θº) of treatments at 5, 15, and 30 seconds after droplet formation for the experiments I and II

| Adaxial surface | Experiment I[(1)] | | | Experiment II[(2)] | | |
|---|---|---|---|---|---|---|
| | 5 s | 15 s | 30 s | 5 s | 15 s | 30 s |
| Preparation sequence | 2.03ns | 0.67ns | 0.02ns | 16.41** | 5.80* | 7.38* |
| Adjuvants | 499.82** | 440.39** | 298.04** | 199.05** | 175.99** | 94.96** |
| Preparation sequence vs. adjuvants | 2.32ns | 2.59ns | 3.23ns | 15.44** | 10.33** | 11.59** |
| Treatments vs. control | 967.24** | 1287.51** | 1026.48** | 81.06** | 654.36** | 448.18** |
| CV (%) | 8.72 | 8.92 | 10.72 | 11.33 | 12.35 | 17.03 |
| Abaxial surface | | | | | | |
| Preparation sequence | 0.91ns | 0.02ns | 0.09ns | 0.62ns | 2.25ns | 2.17ns |
| Adjuvants | 235.01** | 83.12** | 149.71** | 316.09** | 319.78** | 289.01** |
| Preparation sequence vs. adjuvants | 8.17** | 5.14* | 5.90** | 10.74** | 4.44* | 1.65ns |
| Treatments vs. control | 401.94** | 241.77** | 529.17** | 638.29** | 869.33** | 1043.46** |
| CV (%) | 12.82 | 20.37 | 14.9 | 10.20 | 10.48 | 10.64 |
| Parafilm | | | | | | |
| Preparation sequence | 0.00ns | 0.02ns | 0.07ns | 2.74ns | 14.46** | 15.80** |
| Adjuvants | 332.02** | 239.67** | 277.68** | 41.15** | 39.85** | 48.41** |
| Preparation sequence vs. adjuvants | 3.45ns | 2.02ns | 0.94ns | 10.80** | 9.90** | 12.47** |
| Treatments vs. control | 1283.26** | 1318.90** | 1582.51** | 799.85** | 1208.72** | 1324.64** |
| CV (%) | 5.83 | 6.47 | 6.24 | 5.92 | 5.34 | 5.39 |

ns Not significant;* Significant at 5% probability;** Significant at 1% probability. (1) Experiment I – dose of 1 L c.p. $ha^{-1}$ of aminopyralid + fluroxypyr; (2) Experiment II – dose of 2 L c.p. $ha^{-1}$ of aminopyralid + fluroxypyr.

Surfactants added to the spray solution are often able to reduce surface tension as well as decrease the contact angle of droplets on hydrophobic surfaces (Decaro Júnior et al., 2014). The used organosiliconate adjuvant has a significant spreading effect, losing the droplet shape, with a complete, flat, and parallel spread with the surface (θº = 0), practically immediately after the droplets have been deposited on the leaf surface. In general, the decrease in surface tension of the spray liquid results in a reduction in droplet contact angles (Decaro Júnior et al., 2015).

Although a decrease in contact angle is desirable, droplets become more prone to evaporation before absorption occurs through the epicuticular leaf layer, resulting in possible loss of biological effect. Phytosanitary spray solutions characterized by lower surface tensions led to a larger wet area and increase in the evaporation rate (Cunha et al., 2016).

In experiment I, an interaction was observed between the preparation sequence and adjuvants only for the abaxial surface of *S. obtusifolia* (Table 3). When analyzing the effect of adjuvants on preparation sequence (Table 4), the adjuvant LEC led to lower contact angle values when added after the herbicide at all analyzed times. The adjuvant LEC reduces the surface tension less when compared to the other assessed adjuvants.

***Table 4*** **-** Slicing of the significant interaction of contact angle (θº) of the abaxial surface of leaves of *Senna obtusifolia* for the factors preparation sequence and adjuvants at 5, 15, and 30 seconds after droplet formation with spray solutions at a dose of 1 L $ha^{-1}$ of aminopyralid + fluroxypyr (experiment I)

| Preparation sequence | 5 seconds | | | 15 seconds | | | 30 seconds | | |
|---|---|---|---|---|---|---|---|---|---|
| | MO[(1)] | SIL | LEC | MO | SIL | LEC | MO | SIL | LEC |
| Herb.[(1)] + adj. | 83.49 aA | 0.00 aC | 63.16 bB | 76.19 aA | 0.00 aC | 51.92 bB | 70.11 aA | 0.00 aC | 45.99 bB |
| Adj.[(1)] + herb. | 72.13 aA | 0.00 aB | 83.98 aA | 56.80 bA | 0.00 aB | 69.11 aA | 57.97 bA | 0.00 aB | 61.08 aA |
| LSD columns | 11.97 | | | 16.78 | | | 11.67 | | |
| LSD rows | 14.39 | | | 20.34 | | | 14.15 | | |

Means followed by the same uppercase letter in the row and lowercase letter in the column do not differ from each other by the Tukey's test ($p<0.05$). LSD: least significant difference. (1) Abbreviations: MO = mineral oil; SIL = silicone-polyether copolymer; LEC = mixture of phosphatidylcholine (lectin) and propionic acid; Herb. = herbicide; Adj. = adjuvant.

The adjuvant MO presented lower contact angle values after 15 seconds of droplet deposit on the abaxial leaf surface when it was previously added to the herbicide. It means that the products tend to stabilize the spreading angle, with a more intense effect in the first seconds when the droplets are deposited, just as with surface tension. The addition of SIL led to a contact angle equal to zero degrees, which has also been observed in other studies (Iost and Raetano, 2010). Therefore, the application of high volume pesticides associated with adjuvants that drastically reduce surface tension and hence contact angle should be carefully analyzed as it may cause an increase in production costs, draining losses, and environmental contamination (Prado et al., 2016).

The adjuvants SIL and LEC provided a lower contact angle for the adaxial surface when the herbicide was added after the adjuvants (Table 5). It occurs because the siliconized adjuvant forms a lower contact angle at the highest concentration, while in the absence of this surfactant the angles are small in both surfaces (Tang et al., 2008). Droplet spreading on the artificial surface (parafilm) was similar to that observed on the adaxial leaf surface of *S. obtusifolia* (Table 6) since parafilm has a lipophilic characteristic ($\theta^o > 90^o$) that resembles the adaxial surface of the species used in the experiment (Kissmann, 1998; Iost and Raetano, 2010).

***Table 5 -*** Slicing of the significant interaction of contact angle ($\theta^o$) of the adaxial surface of leaves of *Senna obtusifolia* for the factors preparation sequence and adjuvants at 5, 15, and 30 seconds after droplet formation with spray solutions at a dose of 2 L $ha^{-1}$ of aminopyralid + fluroxypyr (experiment II)

| Preparation sequence | 5 seconds | | | 15 seconds | | | 30 seconds | | |
|---|---|---|---|---|---|---|---|---|---|
| | MO[(1)] | SIL | LEC | MO | SIL | LEC | MO | SIL | LEC |
| Herb.[(1)] + adj. | 57.66 aB | 16.39 aC | 81.86 aA | 53.13 bB | 9.76 aC | 72.27 aA | 50.72 aA | 4.60 aB | 65.40 aA |
| Adj.[(1)] + herb. | 67.26 aA | 0.00 bB | 55.56 bA | 63.22 aA | 0.00 aB | 51.84 bA | 58.85 aA | 0.00 aC | 33.92 bB |
| LSD columns | 9.81 | | | 10.01 | | | 12.35 | | |
| LSD rows | 11.89 | | | 12.14 | | | 14.97 | | |

Means followed by the same uppercase letter in the row and lowercase letter in the column do not differ from each other by the Tukey's test ($p<0.05$). LSD: least significant difference. [(1)] Abbreviations: MO = mineral oil; SIL = silicone-polyether copolymer; LEC = mixture of phosphatidylcholine (lectin) and propionic acid; Herb. = herbicide; Adj. = adjuvant.

***Table 6 -*** Slicing of the significant interaction of contact angle ($\theta^o$) of parafilm for the factors preparation sequence and adjuvants at 5, 15, and 30 seconds after droplet formation with spray solutions at a dose of 1 L $ha^{-1}$ of aminopyralid + fluroxypyr (experiment I)

| Preparation sequence | 5 seconds | | | 15 seconds | | | 30 seconds | | |
|---|---|---|---|---|---|---|---|---|---|
| | MO[(1)] | SIL | LEC | MO | SIL | LEC | MO | SIL | LEC |
| Herb.[(1)] + adj. | 56.50 bB | 50.89 aB | 65.21 aA | 54.82 aA | 48.22 aB | 58.28 aA | 52.05 aA | 45.29 aB | 55.28 aA |
| Adj.[(1)] + herb. | 64.02 aA | 41.69 bB | 59.13 bA | 57.96 aA | 38.04 bC | 50.41 bB | 55.69 aA | 34.24 bC | 47.74 bB |
| LSD columns | 5.62 | | | 4.7 | | | 4.51 | | |
| LSD rows | 6.81 | | | 5.7 | | | 5.47 | | |

Means followed by the same uppercase letter in the row and lowercase letter in the column do not differ from each other by the Tukey's test ($p<0.05$). LSD: least significant difference. [(1)] Abbreviations: MO = mineral oil; SIL = silicone-polyether copolymer; LEC = mixture of phosphatidylcholine (lectin) and propionic acid; Herb. = herbicide; Adj. = adjuvant.

The surface of leaves of *S. obtusifolia* is composed of 93% of polar components on the epicuticular surface and a pH of 6.8, and the presence of non-polar compounds in spray solutions affects surface wetting (Kissmann, 1998). Droplets on hydrophilic surfaces have a larger coverage area and a shorter evaporation time than on hydrophobic surfaces (Yu et al., 2009).

Mineral oil resulted in a higher spreading when added after the herbicide, with higher coverage for all analyzed surfaces (Table 7). However, mineral oil added to spray solutions reduces the evaporation rate on hydrophilic and hydrophobic artificial surfaces but increases it on lipophilic surfaces (Lasmar and Cunha, 2016).

Most of the sprayed droplets come into contact with the adaxial leaf surface, where product absorption rate is higher. The reduced contact angle of droplets with the surface where they are

***Table 7*** **-** Slicing of the significant interaction of contact angle (θ°) of the abaxial surface of leaves of *Senna obtusifolia* for the factors preparation sequence and adjuvants at 5 and 15 seconds after droplet formation with spray solutions at a dose of 2 L $ha^{-1}$ of aminopyralid + fluroxypyr (experiment II)

| Preparation sequence | 5 seconds | | | 15 seconds | | |
|---|---|---|---|---|---|---|
| | MO[(1)] | SIL | LEC | MO | SIL | LEC |
| Herb.[(1)] + adj. | 59.42 bB | 8.20 aC | 80.41 aA | 54.22 bB | 0.00 aC | 70.15 aA |
| Adj.[(1)] + herb. | 78.54 aA | 0.07 aB | 75.63 aA | 68.00 aA | 0.00 aB | 67.33 aA |
| LSD columns | 9.42 | | | 8.76 | | |
| LSD rows | 11.43 | | | 10.62 | | |

Means followed by the same uppercase letter in the row and lowercase letter in the column do not differ from each other by the Tukey's test ($p<0.05$). LSD: least significant difference. [(1)] Abbreviations: MO = mineral oil; SIL = silicone-polyether copolymer; LEC = mixture of phosphatidylcholine (lectin) and propionic acid; Herb. = herbicide; Adj. = adjuvant.

deposited due to adjuvant addition leads to a higher spray solution spreading, providing a larger covered area and increasing the possibility of contact with the desired target or the possibility of product absorption by leaf surface (Cunha et al., 2016).

Regarding the contact angle of experiment I, preparation sequence was different only on the abaxial leaf surface of *S. obtusifolia*, where fewer spray droplets are deposited in conventional applications. Moreover, an alteration was observed for experiment II, in which the adjuvants SIL and ECL showed a higher spreading when added before the herbicide. MO resulted in a higher spreading when added after the herbicide, with a larger surface coverage. The adaxial surface and parafilm had similar contact angle results.

Thus, spray solution preparation sequence did not interfere with the surface tension and contact angle for a dose of 1 L $ha^{-1}$ of herbicide but interfered with for 2 L $ha^{-1}$. Thus, adjuvant addition – SIL and LEC before the herbicide and MO after the herbicide – provides a higher spreading of spray solutions.

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