Preparation of a Chlorantraniliprole–Thiamethoxam Ultralow-Volume Spray and Application in the Control of *Spodoptera frugiperda*

Kun Wei, Weiming Xu,* Qin Liu, Liyun Yang, and Zhuo Chen*

Cite This: ACS Omega 2020, 5, 19293–19303

**1. INTRODUCTION**

*Spodoptera frugiperda* (J. E. Smith) is a typical global pest. It is a polyphagous insect of the lepidoptera order, originating from the tropical and subtropical regions of the Americas.\(^1\)\(^2\) It is one of the top 10 plant pests in the world as rated by the International Center for Agricultural and Biosciences (CABI), and it can harm food and cash crops.\(^3\)\(^4\) It has strong migratory ability, fast propagation, and an abundance of host plants and it is difficult to prevent and control.\(^5\) In April 2019, *S. frugiperda* was found to damage corn in Guizhou Province, China.\(^6\) By July, the province’s crop area affected by *S. frugiperda* was over 21,000 ha.

Internationally employed methods to control *S. frugiperda* are the use of genetically modified technology, biological control, biopesticides, and chemical pesticides. In 2008, Siebert et al. found that the feeding amount of *S. frugiperda* on Cry1F-Bt transgenic corn is 1.3 and the larval infection rate is 0–0.6%, while the feeding amount on common corn is 7.9 and the larval infection rate is 2.5–4.4%. This shows that transgenic corn can greatly reduce the feeding of *S. frugiperda* on leaves and can thus reduce the damage to plants.\(^7\) In 2010, Negrisoli et al. studied the control effect of nematodes (*Heterorhabditis indica*) mixed with insecticide on *S. frugiperda*. The results showed that the combination of *H. indica* and lufenuron (0.15 L/ha) can improve the efficacy—the control effect of the mixture on *S. frugiperda* adults is 62.5% and that on larvae is 57.5%.\(^8\) In 2011, Hardke et al. studied the control effect of nine insecticides on *S. frugiperda*. The results showed that all nine insecticides have a certain control effect on *S. frugiperda*, but chlorantraniliprole and spinetoram are the better options.\(^9\)

Generally, the most economical and effective method for controlling *S. frugiperda* is the use of chemical pesticides.\(^10\) The Ministry of Agriculture and Rural Affairs of the People’s Republic of China released a list of recommended pesticides, which includes indoxacarb, chlorantraniliprole, \(\lambda\)-cyhalothrin, and so forth, on June 3, 2019, for controlling *S. frugiperda*.\(^11\) The current common preparations of these pesticides are emulsifiable concentrates and suspension concentrates. In practical applications, they are applied by traditional pesticide...
application machinery, such as backpack sprayers and tractors.\textsuperscript{12} Pesticides cannot be sprayed over a large area in a short time; thus, when pests with strong migration capacity such as \textit{S. frugiperda} are concentrated in outbreaks, they cannot be controlled in a small area. In America, the blind use of pesticides has caused a serious resistance of \textit{S. frugiperda}, which has resulted in great difficulties in subsequent studies.\textsuperscript{13,14}

Plant protection unmanned aerial vehicles (UAVs) are an agricultural UAV that provides plant protection operations, such as spraying pesticides for agricultural and forestry plants.\textsuperscript{15} Such UAVs are a modern pesticide application machinery with high work efficiency, superior control effects, and wide-ranging adaptability.\textsuperscript{16,17} With the progress of urbanization in China, unified and professional control of agricultural pests and diseases has become increasingly popular. The use of UAVs for plant protection has become one of the hot topics in the development of modern agriculture in China.\textsuperscript{18} The plant protection UAVs have extensive adaptability, are not restricted by crop growth, and can be used for low-altitude and low-volume spraying operations.\textsuperscript{19} They have the irreplaceable advantage of ground machineries.\textsuperscript{20} The research results of Qin et al. showed that both the insecticidal efficacy and the persistence period of pesticides sprayed by drones for plant protection were greater than those achieved with a hand lance operated from a stretcher-mounted sprayer.\textsuperscript{21} This indicates that UAVs have a low-volume and highly concentrated spray pattern that can enhance the duration of efficacy. However, given the operation characteristics of the plant protection UAVs, the requirements for pesticide formulations, such as low droplet drift and uniform distribution, are increased.\textsuperscript{22}

Ultralow-volume (ULV) sprays are an oily pesticide formulation made by dissolving the active ingredient into a solvent with a high boiling point, added with adjuvants.\textsuperscript{23} They are not diluted with water during use and are sprayed directly using aviation settings or ground equipment. As such, it is an ideal pesticide formulation suitable for spraying using plant protection UAVs at low volume.\textsuperscript{24,25} Mulrooney et al. studied the effect of a pesticide formulation that contains the malathion control effect of ULV sprays (1.17 L/ha) and conventional sprays (46.8 L/ha) on \textit{Anthonomus grandis} grandis. The ULV spray treatments resulted in a 70\% mortality rate of \textit{A. grandis} grandis throughout the 48 h test period, whereas the conventional spray mortality steadily decreased from 71\% at 4 h after treatment to 12\% at 48 h after treatment.\textsuperscript{26} Wills et al. studied the control effect of different spraying doses on pitted morningglory, velvetleaf, and barnyard grass after adding adjuvants to an imazethapyr preparation. The control of all species was similar at spray volumes of 9.4 and 94 L/ha.\textsuperscript{27}

The use of ULV sprays with high-efficiency pesticide application machineries, such as plant protection UAVs, can effectively reduce the amount of pesticides while ensuring a suitable control effect. China’s Ministry of Agriculture announced the “Action Plan for Zero Growth in Pesticide Use by 2020” in 2015, which encourages the use of advanced application techniques, such as low-volume sprays, to improve pesticide utilization and to reduce the use of pesticides.\textsuperscript{28,29}

Chlorantraniliprole is widely used to control lepidopteran pests.\textsuperscript{30} It can activate ryanodine receptors in insect muscles, causing muscular dysfunction and paralysis, eventually resulting in death.\textsuperscript{31} The mode of action is highly selective and has no cross-resistance with other insecticides.\textsuperscript{32} Thiamethoxam has also been used to control lepidopteran insects, such as \textit{Pyrausta nubilalis} (Lepidoptera: Pyrididae) and \textit{Helicoverpa armigera} (Lepidoptera: Noctuidae), in China and other regions.\textsuperscript{33} In an insect’s body, thiamethoxam binds to nicotinic acetylcholine receptors, blocking the normal conduction of the central nervous system of the insect and causing its paralysis and death.\textsuperscript{34} The compound application of pesticides with different action mechanisms can prolong the service life of pesticides and can reduce the generation of resistance.

In this study, we selected chlorantraniliprole and thiamethoxam as active ingredients to prepare ULV sprays. The preparation process is shown in Figure 1. Corn leaves were used to study the wetting spreading, deposition, rain wash resistance, and infiltration performance of the prepared ULV sprays. The preparation process is shown in Figure 1. Corn leaves were used to study the wetting spreading, deposition, rain wash resistance, and infiltration performance of the prepared ULV sprays.
sprays. Samples with better performance were selected and then sprayed using plant protection UAVs to test the control effect on *S. frugiperda* larvae.

### 2. RESULTS AND DISCUSSION

#### 2.1. Screening of the Stable Drug Storage System.

Solvent selection is a key for the development of ULV sprays. The main technical performance indicators of the preparation, such as volatility and stability, all depend on the variety and characteristics of the solvent. Therefore, a reasonable combination of organic solvents must be screened out. In this work, the solvent combination and dosage are shown in Table 1.

There are strict standards for the use of solvents in pesticide formulations. For example, in China, the use limit of acetonitrile is 1% and the use limit of N,N-dimethylformamide (DMF) is 2%. In the screening of solvents, we found that the solubility of the two active ingredients using a single solvent is very poor. When DMF is used alone, the two active ingredients are basically insoluble; when N-methyl-2-pyrrolidinone (NMP) is used alone, the two active ingredients are partially dissolved. Therefore, we use a combination of solvents to dissolve chlorantraniliprole and thiamethoxam. The solubility of the different combinations of solvents was different. As shown in Table 2, the best combination was 5% NMP + 8% Cyc.

#### Table 2. Selection of the Type and Dosage of the Adjuvant

| anionic surfactants | nonionic surfactants | dosage (%) | dosage (%) | state       |
|---------------------|----------------------|------------|------------|-------------|
| LAS-30              | AEO-5                | 8          | 9          | emulsification |
| LABSA               | TW-60                | 5          | 7          | transparent homogeneous |
| AESA                | XL-70                | 9          | 8          | stratified   |
| OEP-70              | LEP-10               | 8          | 8          | emulsification |

"LAS-30: sulfate surfactant; LABSA: sulfonate surfactant; AESA: phosphonate surfactant; OEP-70: carbonyl surfactant; AEO-5: fatty alcohol polyoxyethylene ether surfactant; TW-60: fatty acid ester ether surfactant; XL-70: isomerized alcohol ether surfactant; and LEP-10: polyether and block polyether surfactant.

An adjuvant must be added to form a transparent and homogeneous ULV spray. The adjuvant can improve the physical and chemical properties of ULV sprays and can also increase their efficacy. The screening results of the adjuvants highlighted that sulfonate assistant linear alkylbenzene sulfonic acid (LABSA) mixed with polysorbate series adjuvants (TW-20, -40, etc.) showed superior cold storage stability, as shown in Table 2.

In the cold-storage stability test, the samples containing the anionic adjuvant LABSA and the nonionic adjuvant polysorbate series (TW-20, -40, etc.) were stored at 0 °C for 1 h without precipitation or being layered. After 7 days of continuous storage, it formed a yellowish, transparent, homogeneous liquid with certain fluidity. After being allowed to stand at 20 °C for 3 h, the samples returned to its original state. Therefore, LABSA and polysorbate series (TW-20, -40, etc.) were selected to prepare the ULV sprays. The ULV sprays (samples 1–5) used in this study are shown in Table 3. The reference product used was dilution of the 40% chlorantraniliprole–thiamethoxam water-dispersible granule (Syngenta Nantong Crop Protection Co., Ltd., China), which was recorded as sample 6. A total of 0.5 g of the reference sample was weighed and 1.5 L of water was added to dilute for subsequent testing.

#### 2.2. Application Evaluation.

Compared to smooth crop leaves, the fluff on the corn leaves makes it easier for the droplets of the pesticide formulation to rebound and splash, making it more difficult to wet and spread of the droplets on the corn leaves. Compared to conventional application devices, the plant protection UAVs spray pesticide preparation droplets that have a large initial velocity and a smaller size and that are more likely to be lost, resulting in waste of the pesticide. Therefore, the wetting and spreading on the leaves of the pesticide droplets sprayed using the plant protection UAVs is a key to the successful application of pesticides and to improving the utilization rate of pesticides.

##### 2.2.1. Surface Tension

Interfacial chemistry indicates that if the surface tension of the liquid is lower than that of the solid surface, the liquid can be completely wetted on the solid surface. The test results in Figure 3 show that the surface tension of each sample was smaller than the critical surface tension of the corn leaves, indicating that the pesticide droplets could completely wet the leaf surface. Significant difference analysis was performed on the surface tension measurement results of six samples and the results are shown in Figure 2. The surface tension of the reference product was 35.83 ± 0.15 mN/m, which was the largest among the samples, and the surface tension of the five ULV sprays was significantly different from the reference product. The surface tension of sample 3, containing TW-60 in the ULV spray, was the smallest—that is, 32.50 ± 0.10 mN/m.

##### 2.2.2. Contact Angle

The contact angle is generally usually used to characterize the wetting and spreading properties of droplets. A contact angle of 90° can be used as the boundary between wetting and nonwetting. At more than 90° contact angle, the droplet has poor wettability and easily rolls off of the leaves. At less than 90° contact angle, the droplets may wet and spread over the leaves. The contact angle of the different samples on the corn leaves as a function of time is shown in Figure 3. The results in Figure 3 show that the contact angle of the five prepared ULV sprays on the corn leaves is smaller than that of the reference product and their spreading speed is higher. Young’s equation (eq 1) describes the relationship

### Table 3. Composition of the ULV Sprays in This Study (1% Chlorantraniliprole + 1% Thiamethoxam)

| sample | organic solvents | anionic surfactant | nonionic surfactant | oily solvent | filler   |
|--------|------------------|--------------------|---------------------|-------------|---------|
| 1      | NMP              | Cyc                | LABSA               | TW-20       | methyl oleate | chlorinated paraffin |
| 2      | NMP              | Cyc                | LABSA               | TW-40       | methyl oleate | chlorinated paraffin |
| 3      | NMP              | Cyc                | LABSA               | TW-60       | methyl oleate | chlorinated paraffin |
| 4      | NMP              | Cyc                | LABSA               | TW-80       | methyl oleate | chlorinated paraffin |
| 5      | NMP              | Cyc                | LABSA               | TW-85       | methyl oleate | chlorinated paraffin |
between surface tension and contact angle. According to the description of the Young’s equation, the smaller the surface tension, the smaller the contact angle. This corresponds to the test results of the surface tension and contact angle of each sample. In the surface tension test shown in Section 2.2.1, the surface tension of sample 3 was 32.5 mN/m, which was the smallest of the six samples. The initial contact angle on the corn leaves was 31° and the static contact angle was 19°, which were also the smallest. The surface tension of the reference product was 35.83 mN/m, which was the biggest of the six samples. The initial contact angle on the corn leaves was 46° and the static contact angle was 25°, which were also the biggest. The initial contact angle and static contact angle of the other samples on the corn leaves also decreased as their surface tension decreased.

\[ \gamma^* = \gamma^l + \gamma^s \cos \theta \]  

(1)

2.2.3. Wetting Time. The canvas used in the wetting force test was a hydrophobic solid. By measuring the time during which the canvas sheet settled in the liquid, the wetting property of the liquid was intuitively displayed. Values are expressed as the mean ± standard deviation. The results in Table 4 indicate that the five ULV sprays developed in this study had superior wetting behavior, sinking almost immediately after immersion in the liquid. They were able to quickly settle to the bottom of the beaker, far superior to the reference product (more than 900 s). Sample 3, containing TW-60, had the shortest wetting time of only 4.33 ± 0.32 s. This result was consistent with the surface tension and contact angle results. The measurement results of the surface tension, contact angle, and wetting time show that the ULV sprays developed by this research have superior wetting and spreading properties. The ULV sprays have shorter wetting time, smaller initial contact angle, and faster spreading rates relative to the

Figure 2. Surface tensions of the different samples. 1—6 means different samples. Different letters on the top of the columns indicate significant differences between mean. Means followed by the same letter are not significant at the 5% significance level by the LSD test (LSD = 0.05). Bars indicate standard error of the mean.

Figure 3. Contact angles of the different samples on the corn leaves. (a) Change in the contact angle in 0–10 s and (b) droplet shape during spreading (0–10 s).
Table 4. Wetting Time and Penetration Time for the Different Samples

| sample | wetting time (s) | penetration time (s) |
|--------|-----------------|---------------------|
| 1      | 6.10 ± 0.40     | 9.13 ± 0.26         |
| 2      | 6.20 ± 0.36     | 8.31 ± 0.34         |
| 3      | 4.33 ± 0.32     | 6.37 ± 0.31         |
| 4      | 5.55 ± 0.41     | 6.88 ± 0.37         |
| 5      | 6.50 ± 0.43     | 8.59 ± 0.40         |
| 6      | 924.02 ± 5.26   | 926.97 ± 5.34       |

“Wetting time is the time from the loading of the canvas to the start of sinking; penetration time is the time when the canvas begins to fall to the bottom of the beaker. Sample 1 contains TW-20; sample 2 contains TW-40; sample 3 contains TW-60; sample 4 contains TW-80; sample 5 contains TW-85; and sample 6 is the reference product. Different letters indicate significant differences between means. Means followed by the same letter are not significant at the 5% significance level by the LSD test (LSD = 0.05).

Figure 4. Maximum retention of the diﬀerent samples on the corn leaves. 1–6 means diﬀerent samples. Different letters on the top of the columns indicate signiﬁcant diﬀerences between means. Means followed by the same letter are not signiﬁcant at the 5% signiﬁcance level by the LSD test (LSD = 0.05). Bars indicate the standard error of the mean.

2.2.5. Volatility. The plant protection UAVs generally work at a certain height when applying pesticides. If the droplets are easily volatilized, their size decreases during the sedimentation of the droplets and take a long time to deposit on the crop leaves. This then causes a reduction in the deposition of pesticides and even phytotoxicity. Therefore, in a pesticide formulation for plant protection UAVs, the volatility of the preparation signiﬁcantly inﬂuences its control eﬀect. The measurement results of the volatility rate of the six samples and the analysis of the signiﬁcant difference between the test results are shown in Figure 5. We can see that the volatilization of the ULV sprays was much smaller than that of the reference product. The volatilization of the ULV sprays was 3–5%, whereas that of the reference product was over 26%. This result is due to the low volatility of the organic solvents used in the ULV sprays, and chlorinated parafﬁn can also effectively suppress evaporation. The dispersion medium of the reference product was water and its evaporation rate was large. In the process of droplet settling onto the crop leaves, the volume of the droplets will decrease because of rapid evaporation. If it is in a high-temperature environment, the droplets will even disappear. Thus, the droplets of the ULV sprays can effectively reduce the size reduction during the sedimentation process and can be deposited on crop leaves.

2.2.6. Rain Wash Resistance Performance. The disease and pests of Chinese corn primarily emerge in the summer rainy season, and environmental factors, such as rainfall, greatly influence the control eﬀect of pesticides. If it rains within a short time after spraying a pesticide, the pesticide is washed away by the rain, which reduces the control eﬀect and causes environmental pollution. Superior rain wash resistance performance can improve the adaptability of pesticide preparations to the environment and can extend their period of validity.

Figure 6 shows that for thiamethoxam, the residual amount of sample 3 was up to 27.83 ± 1.61 μg/kg and that of the reference product.
reference product was 0. For chlorantraniliprole, the maximum residue in sample 5 was $31.40 \pm 1.33 \, \mu g/kg$ and that in the reference product was $30.16 \pm 3.45 \, \mu g/kg$. The solubility of thiamethoxam in water is large. After half an hour of drying, all of the water in the reference product (WG) had evaporated. Given the lack of solvent protection, the remaining active ingredients were exposed to the air, coupled with the large water solubility of thiamethoxam. This condition allowed the excess water to easily wash away all of the thiamethoxam on the leaves without any residue. Given the low volatilization rate of the ULV sprays, the evaporation of the droplets was extremely small and the solvent was not completely evaporated within half an hour. Therefore, some of the pesticides were washed away by a large amount of water with the preparation but could still deposit a part on the leaves; thus, the final residual amount was not significantly different from the reference product. In summary, the ULV sprays have superior rain wash resistance performance on the leaves.

2.2.7. Penetration Performance Measurement. *S. frugiperda* is a pest that feeds on crop leaves. If pesticides have superior permeability properties, they can rapidly accumulate on the leaves and crops in increased volumes; when pests, such as *S. frugiperda*, gnaw on the leaves, they ingest pesticides and thus experience the insecticidal effects of the pesticides. The pesticides thiamethoxam and chlorantraniliprole exhibit these properties. Figure 7 visually shows the change in the brightness of the leaves in the ultraviolet environment with time after application.

The higher the optical density, the brighter the picture and the more the pesticides accumulate in the leaves. The maximum optical density of the ULV sprays was larger than that of the reference product. No significant difference was found in the optical density of the six samples at 72 h; however, they showed different changes. The optical density of the corn leaves treated with the ULV sprays initially increased with time, peaked at 12 h, and then decreased with time. However, the optical density of the corn leaves treated with the reference product reached its maximum at 3 h and then decreased with time. Figure 7 demonstrates this change.

Such a situation may be due to their different evaporation rates. The dispersion medium of the reference product (water-dispersible granules) is water, and the rapid evaporation of moisture allowed the pesticides to enter the interior of the leaves quickly. However, after the water had completely evaporated, the pesticides can no longer enter inside the leaves. Therefore, the maximum optical density (the first test time point) appeared after 3 h of treatment. After that, as the time increased, the optical density gradually decreased, showing a curve that the optical density decreased with time. In the ULV sprays, given that solvents with a low volatilization rate were used and added chlorinated paraffin, their evaporation is very slow and the pesticide penetration is slow. However, in the process of ULV spray evaporation, the pesticides were able to gradually accumulate in the leaves over time. Thus, the highest optical density of the ULV sprays was greater than that of the reference product. In the first 12 h after the treatment, a curve showed the increase in optical density with time. The maximum optical density appears after 12 h of treatment. After 12 h of treatment, the dispersion medium of ULV sprays has completely evaporated, and the pesticides cannot continue...
to enter the leaves, showing a curve of optical density decreasing with time. Turner believes that organic solvents have a certain solubility in the waxy layer of plant leaves.47 The solvents in ULV sprays dissolve the waxy layer on the surface of the leaves, allowing increased pesticides to enter the leaves. This mechanism is also the reason for the high permeability of ULV sprays. After the drug enters the interior of the leaves, the pesticide preparation can no longer affect pesticide conduction. Thus, the optical density of the six samples at 72 h after dosing was not much different.

2.2.8. Evaluation of the Efficacy Trial. On the basis of the measurement results of the wettability and deposition performances, sample 3 (which contains TW-60) was selected for the efficacy trial. The control effect of the ULV spray was measured by investigating the number of S. frugiperda larvae changes in the corn field before and after pesticide application. The results are shown in Table 5 and Figure 8.

The efficacy trial shows that spraying a chlorantraniliprole and thiamethoxam ULV spray using plant protection UAVs has a remarkable control effect on S. frugiperda larvae. The decrease rate reached 81.31 ± 2.41%, and the control effect was 83.01 ± 2.80% in treatment sprayed with 3 L/ha. This value was better than that of the reference product, 40% chlorantraniliprole–thiamethoxam water-dispersible granules (decrease rate 67.39 ± 2.87%, control effect 70.35 ± 2.61%). The significant difference in the efficacy trial results was analyzed. The results show that the prepared ULV spray and the reference product had significant differences in their decrease rates of and control effects on S. frugiperda larvae, meaning that the ULV spray had a satisfactory control effect on S. frugiperda larvae.

We developed a series of ULV sprays suitable for plant protection UAV spraying to control S. frugiperda larvae. The results show that the wetting, deposition, rain wash resistance, and penetration performances of the ULV sprays were greater than those of the reference product (40% chlorantraniliprole–thiamethoxam water-dispersible granules). The wetting time of the ULV sprays was much smaller than that of the reference product, and the surface tension was smaller than the critical surface tension of the corn leaves. The contact angle on the corn leaves was less than 19°, and the spreading speed was fast. Through the measurements of the rain wash resistance, maximum retention, and penetration behavior, we found that the amount of the ULV sprays deposited on the corn leaves was larger than that of the reference product. Therefore, these ULV sprays can effectively improve the utilization rate of pesticides and can prolong the duration of pesticides. An efficacy trial was carried out by spraying a sample containing TW-60 using the plant protection UAV XAV P-30. We found

| Table 5. Efficacy Trial Results of the Different Preparations in Controlling S. frugiperda Larvae† |
|---|
| sample | M1 (pcs) | M2 (pcs) | N1 (pcs) | N2 (pcs) | 7 days after application |
|---|
| block control | 10 | 11 | 10 | 11 | decrease rate (%) | average (%) | control efficacy (%) | average (%) |
| reference product | 10 | 11 | 13 | 4 | 69.23 | 67.39 ± 2.87b | 72.03 | 70.35 ± 2.61b |
| ULV spray | 10 | 11 | 12 | 2 | 83.33 | 81.31 ± 2.41a | 84.85 | 83.01 ± 2.80a |

†M1 and M2 are the number of insects before and after application in the block control area, respectively; N1 and N2 are the number of insects before and after application in the treatment area, respectively. Different letters indicate significant differences between means. Means followed by the same letter are not significant at the 5% significance level by the LSD test (LSD = 0.05). Bars indicate the standard error of the mean.

Figure 8. (a) Number of S. frugiperda larvae before and after application. (b) Decrease rate and control efficacy of different treatments on S. frugiperda larvae. Different letters on the top of the columns indicate significant differences between means. Means followed by the same letter are not significant at the 5% significance level by the LSD test (LSD = 0.05). Bars indicate the standard error of the mean.
that the control effect against S. frugiperda larvae reached 83.01%.

In conclusion, the ULV sprays developed in this paper offer a formulation suitable for the application of plant protection UAVs, which can effectively exert their characteristics. This research provides reference for the development of pesticide formulations suitable for plant protection UAVs.

3. MATERIALS AND METHODS

3.1. Materials. Unless otherwise noted, all chemicals were purchased from commercial suppliers and were used without further purification. Chlorantraniliprole (95%), thiamethoxam (97.2%), chlorinated paraffin, and methyl oleate were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd., China. The anionic surfactant and nonionic surfactant were purchased from BASF SE, Germany. Dimethyl sulfoxide (DMSO) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. NMP and cyclohexanone (Cyc) were purchased from Chengdu Jinshan Chemical Reagent Co., Ltd., China. Methanol anhydrous (MT) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd., China. 40% chlorantraniliprole–thiamethoxam water-dispersible granules were purchased from Syngenta Nantong Crop Protection Co., Ltd., China.

3.2. Screening of the Stable Drug Storage System. 3.2.1. Screening of the Organic Solvents. First, 0.2 g of the active ingredient (0.1 g of chlorantraniliprole and 0.1 g of thiamethoxam) was placed in a 5 mL centrifuge tube and different organic solvents were added. Afterward, the samples were subjected to heating and ultrasonic vibration, and we studied the combination and dosage of the organic solvents used to completely dissolve the active ingredients in the centrifuge tubes. Because the organic solvent increases its volatility after heating up, we set the heating temperature so as not to exceed 35 °C and the ultrasonic time so as not to exceed 20 min.

3.2.2. Screening of the Adjuvants. On the basis of the work mentioned in Section 3.2.1, we added different anionic surfactants and nonionic surfactants to the solution. After the two adjuvants are completely dissolved in the solution, methyl oleate and filler are added and stirred. After the components are thoroughly mixed, samples were let to stand at room temperature and their status was observed. Through this method, we screened out a combination of adjuvants that allowed the system to present a single transparent and stable state. In the selection of adjuvants, the anionic surfactants were sulfonate, phosphate, and sulphate, whereas the nonionic surfactants were polysorbate series, alkylpolyoxyethylene ether, isoalcohol ether, and block polyether. The stability of the preparation was evaluated by its cold storage stability.

3.2.3. Preparation of the ULV Spray. First, chlorantraniliprole and thiamethoxam were placed in a 250 mL beaker at room temperature, sequentially added with organic solvents, and then stirred at 200 rpm for 20 min. After complete dissolution, the anionic surfactant was added while stirring until the solution was clear. Then, the nonionic surfactant was added and stirred at 250 rpm for 15 min. After the mixture was evenly mixed, the oily solvent and filler were sequentially added, and the mixture was stirred at 300 rpm for 20 min. The resulting pale yellow, single transparent, homogeneous liquid was the ULV spray, containing chlorantraniliprole and thiamethoxam.

3.2.4. Cold Storage Stability. Approximately 20 mL of each sample was transferred into a 50 mL glass-cover measuring cylinder. The cork was sealed with sealing film. Each sample was then placed in a 0 °C refrigerator for 1 h. They were checked every 15 min for solid precipitation or stratification. Subsequently, the samples were placed in a 0 °C refrigerator for 7 days. The state of the preparation after allowing to stand at room temperature (not more than 20 °C) for 3 h was observed.

3.3. Application Evaluation. 3.3.1. Surface Tension Measurement. The surface tension of the samples was measured by the platinum plate method using a tension meter (SFZL-A1, Shanghai Innuo Precision Instruments Co., Ltd., China). Before every measurement, the platinum plate was washed with distilled water and flamed with an alcohol lamp to remove impurities. The tension meter was calibrated on the basis of the surface tension value of distilled water at 25 °C. To ensure the accuracy of the date, each sample was measured three times with a deviation not exceeding ±0.20 mN/m. The reference product used was 40% chlorantraniliprole–thiamethoxam water-dispersible granules (WG, Syngenta Nantong Crop Protection Co., Ltd., China). A total of 0.5 g of the reference sample was weighed and 1.5 L of water was added to dilute for subsequent testing.

3.3.2. Contact Angle Measurement. The contact angle of the different samples on the corn leaves was measured using the contact angle-measuring instrument JC2000D (Powereach Co., Ltd., China). The leaves were collected from corn plants during the flowering stage, which were grown in the greenhouse of Guizhou University. Using a microsampler and a tray, 5 μL of each sample was smoothly deposited onto the corn leaves. The temperature and humidity in the laboratory were maintained as relatively stable during the test. The reference product used was the same as that in Section 3.3.1.

3.3.3. Wetting Time Measurement. The wetting time was measured following the International Standard ISO 8022-1990 and the Chinese National Standard GBT 11983-2008. Approximately, 700 mL of each newly prepared sample was transferred into a 1000 mL beaker. Before measurement, the temperature was maintained at 20 ± 2 °C. A clip was used to keep the cotton piece (untreated 202 canvas) in a vertical position approximately 40 mm below the liquid level. When the lower end of the cotton piece just touched the sample, the stopwatch was started immediately. The timer was stopped when the cotton piece automatically sank. The time recorded by the stopwatch was used as the wetting time of the sample. The same sample was used for 10 repeated measurements, and the average value was considered as the wetting time of that sample. The reference product used was the same as that in Section 3.3.1.

3.3.4. Maximum Retention Measurement. The maximum retention was measured via the immersion method. Fresh corn leaves 2 × 2 cm² in size were cut and weighed (m₁, mg) using an analytical balance (AI204, Mettler Toledo Instruments (Shanghai) Co., Ltd., Switzerland). The leaves were then immersed in each sample for 5 s, and the leaves were weighed (m₂, mg) after removal until no more drops flowed. Each sample was measured three times, and the results were averaged. The reference product used was the same as that in Section 3.3.1, and the corn leaves were the same as that in Section 3.3.2. The maximum retention of each sample on the corn leaves was calculated using eq 2

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3.3.5. Volatility Measurement. The volatility of the different samples was tested by the filter paper method. The filter paper had a diameter of 12.5 mm, and its mass $m_1$ was determined. Approximately, 1.0 mL of each sample was placed onto the filter paper, and the mass $m_2$ was weighed. The droplets were evenly spread on the filter paper, which was then suspended in a drying oven at 30 ± 1 °C for 20 min. The mass $m_3$ was then weighed. The volatility was calculated using eq 3

$$\text{volatility} (\%) = \frac{m_2 - m_3}{m_3 - m_1} \times 100%$$

(3)

3.3.6. Rain Wash Resistance Performance Measurement. The rain wash resistance performance was measured via the method of Andika. The corn leaves were the same as that in Section 3.3.2. As per the typical procedure, 1 g of fresh corn leaves was used, and the upper surface of the leaves was held double-sided up on the glass slide. Approximately, 1 μL of each sample was transferred with a pipette gun and added to the center of the corn leaves. The sample was then allowed to dry for 30 min at room temperature, and deionized water was used from the acid burette to flush the sample from the leaves. The tray angle was 45°, and the vertical distance from the outlet of the burette to the leaves was 2 cm. In the drip process, each leaf was washed three times with 1 mL of water each time. The rate of dropping was 3 drops/s. Five leaves (5 g) were considered a group. The reference product used was the same as that in Section 3.3.1.

For the leaf treatment, the leaves were cut into pieces, washed with 20 mL of methanol anhydrous, and transferred to a centrifuge tube. The leaves were then ultrasonicated for 5 min after shaking and mixing. Then, 0.5 g of Na2SO4 and 0.5 g of NaCl were added to each sample. The mixture was shaken and then ultrasonicated for 3 min. Next, the sample was centrifuged at 4000 rpm for 5 min, filtered, and spin-dried with the solvent. Finally, 2 mL of methanol anhydrous was added to the flask, treated with a filter, and placed in a sample vial. The residual amount on the leaves was determined using high-performance liquid chromatography (HPLC) (Agilent 1260, Agilent Technologies Inc., America). The column used is an Agilent XDB-C18 stainless-steel column (4.6 × 150 mm, 5 μm; Agilent Technologies Inc., America). The retention times of thiamethoxam and chlorantraniliprole were 1.57 and 3.41 min, respectively. The detection conditions are shown in Table 6.2

| injection volume | detection wavelength | flow rate | temperature | mobile phase |
|------------------|----------------------|-----------|-------------|--------------|
| 10 μL            | 230 nm               | 1.0 mL/min| 25 °C       | methanol/water = 70:30 |

3.3.7. Penetration Performance Measurement. Chlorantraniliprole and thiamethoxam both contain a conjugated structure that excites fluorescence exhibition under ultraviolet light. Their concentration in leaves changes with time, thus exhibiting different fluorescence intensities (optical density) in the ultraviolet environment. A gel-imaging system is commonly used to quantify the fluorescence intensity of a stained protein. Therefore, after treating the corn leaves with different samples, pictures of the fluorescence intensity of the leaves were captured under the UV light of the gel-imaging system (JY04S-3E, Beijing JUNYI Electrophoresis Co., Ltd., China). The optical density was calculated using the Image-Pro Plus software to determine the permeability of the samples. The reference product used was the same as that in Section 3.3.1.

Approximately, 50 μL of each sample was added to the middle of the corn leaves using a pipetting gun. At 3, 6, 12, 24, 48, and 72 h after adding the samples, the treated leaves were cut into 2 × 2 cm² pieces. The leaves were thoroughly washed in anhydrous methanol for 20 s, allowed to dry at room temperature, and imaged under the UV light of the gel-imaging system. The Image-Pro Plus software was used to process the picture and to calculate the optical density. Each sample was measured three times, and the average was obtained. The corn leaves used were the same as those in Section 3.3.2.

3.3.8. Efficacy Trial. The efficacy trial was conducted in Daying Village (105°44'10.32" E, 26°54'56.18" N), Zhijin County, Guizhou Province, China, on July 18, 2019. The corn variety used was Zhengda 999, which was in the flowering stage at the time of the test. The height was approximately 1.8 m. The trial object was S. frugiperda larvae.

Three trials were set up, namely, the test product group, the reference product group, and the block control group. The test product was sprayed using the XAG P-30 (XPLANT Co., Ltd., China) UAV. The dose of the test product was 3 L/ha, which was not diluted with water. The reference product used was 40% chlorantraniliprole−thiamethoxam water-dispersible granules, which were sprayed using the knapsack sprayer. The dose of the preparation was 150 g/ha, which was diluted with water to 450 L/ha. The block control group was only sprayed with water using a knapsack sprayer.

The efficacy trial design is shown in Figure 9. Each plot was divided into 10 × 20, and a 5 × 20 m² isolation area was set up between the two plots. The number of S. frugiperda larvae was investigated on the day before and 7 days after application. Among the five sampling points randomly selected in each plot, which was in the shape of an “X”, five corn plants from each point were selected as the survey points. Every trial was repeated four times. The decrease rate and the control effect were calculated using eqs 4 and 5

$$\text{decrease rate} (\%) = \frac{N_1 - N_2}{N_2} \times 100\%$$

(4)

$$\text{control effect} (\%) = \left(1 - \frac{M_1 \times N_3}{M_2 \times N_4}\right) \times 100\%$$

(5)
M1 and M2 are the number of insects before and after application in the block control area, respectively; N1 and N2 are the number of insects before and after application in the treatment area, respectively.

3.4. Statistical Analysis. The least significant difference (LSD) tests were applied to establish the differences between each sample. Data were analyzed using IBM SPSS Statistics 20.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02912.

Characterization data and related chromatograms (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Weiming Xu — State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Center for Research and Development of Fine Chemicals of Guizhou University, Guiyang 550025, People’s Republic of China; orcid.org/0000-0002-5897-8082; Phone: 86-851-88292170; Email: wxmu@zgz.edu.cn; Fax: 86-851-88292170

Zhao Chen — State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Center for Research and Development of Fine Chemicals of Guizhou University, Guiyang 550025, People’s Republic of China; Email: gychenzhuo@aliyun.com

**Authors**

Kun Wei — State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Center for Research and Development of Fine Chemicals of Guizhou University, Guiyang 550025, People’s Republic of China; orcid.org/0000-0002-7648-8708

Qin Liu — State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Center for Research and Development of Fine Chemicals of Guizhou University, Guiyang 550025, People’s Republic of China; orcid.org/0000-0003-0203-4514

Liyun Yang — State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Center for Research and Development of Fine Chemicals of Guizhou University, Guiyang 550025, People’s Republic of China; orcid.org/0000-0002-4218-5977

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c02912

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The research was supported by funding from the National Natural Science Foundation of China (nos. 31760532 and 21262009) and the Support Project of Excellent Scientific and Technological Innovation Talents of Colleges and Universities in Guizhou Province (no. 2013137).

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