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Application Report

Surfactant Additives for Pesticide Formulations

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Surfactant Additives for Pesticide Formulations – Effects on Both Spray Atomization and Substrate Wettability

Abstract

Optimizing the application of pesticides, herbicides, and fungicides by spraying techniques – either on the small scale or in the case of large agricultural application – depends on some fundamental surface science. For example the interfacial tension determines (for any given amount of pressure and nozzle configuration) the size of the formed droplets of pesticide.

Reducing the size of spray droplets down to a certain point (typically 100 μm, wherein spray drift becomes a problem in large scale applications) means more uniform application of the pesticide to crops. This means lowering surface tension through the addition of surfactants. To make matters more complicated, it is not just the equilibrium surface tension of the formulation that needs to be considered in choosing surfactants to use, because spraying is a dynamic process. One needs to consider not only what surface tension a surfactant can ultimately impart on a formulation, but also how quickly the surfactant is capable of lowering the surface tension of freshly formed surface.

Spray droplets are dynamic surface, not at equilibrium conditions – a fact that also has implications on wetting (the second function of surfactants in a pesticide formulation) once the spray hits its target surface (generally the leaves of the crop). The data and methods we share here are the result of a recent investigation in our labs and others aimed at finding a good surfactant additive for one of our customers pesticide formulations considering both spraying and wetting aspects. The main goal is to share the techniques, not to promote either of the surfactants mentioned in the work, or to necessarily show an ultimate solution.

Background

The base pesticide formulation was initially found to have an equilibrium surface tension of 55.3 mN/m and had issues with large droplet size with its intended sprayer and nozzle apparatus according to droplet size testing performed on a VisiSizer S100 (Oxford Lasers, Ltd.). Specifically, only 29% of the droplets produced where found to be under the 350 μm "medium" drop size definition used by the American Society of Agricultural Engineers (ASAE) Standard S-572: Spray Nozzle Classification by Droplet Spectra. The formulation was also found to show unacceptable levels of "run off" on some of the more waxy leaf types in our customer's independent wetting tests.

These two factors (drop size and wettability) have to be improved, in order to optimize the effectiveness of the pesticide.

Methods

The KRÜSS Bubble Pressure Tensiometer BP2 was used to investigate the surface tension effects of adding Agrosurf SSP (sodium dioctylsulphosuccinate anionic surfactant in glycol) and Agrosurf NEC38 (a non-ionic alcohol ethoxylate) separately at 0.5% wt to our customer's pesticide formulation.

As a result of the wetting issues, we also employed time-resolved sessile drop contact angle by means of the KRÜSS DSA100 to study the effects of the two added surfactants on spreading wetting on the surface of Parafilm®. And, we further devised a test for "run off" based on tilted surfaces, which are schematically depicted below. Parafilm® is a common wrap material used for a variety of purposes in laboratories, and is often used as a standard model for a waxy leaf surface, due to its high contact angle with water (about 120°). The contact angle for water on waxy leaf surfaces varies by type from about 90° to about 150° in extreme cases, but in general 120° is an upper median – making Parafilm® very suitable as a model.

Our simple run-off test with the tilting table of the DSA100 involved inclining the Parafilm® surface incrementally in 10° increments from 10° to 60° and applying 20 drops of each formulation to fresh areas of each surface. Drops were each approximately 2 μl and were dropped to the surface from 1 cm above.
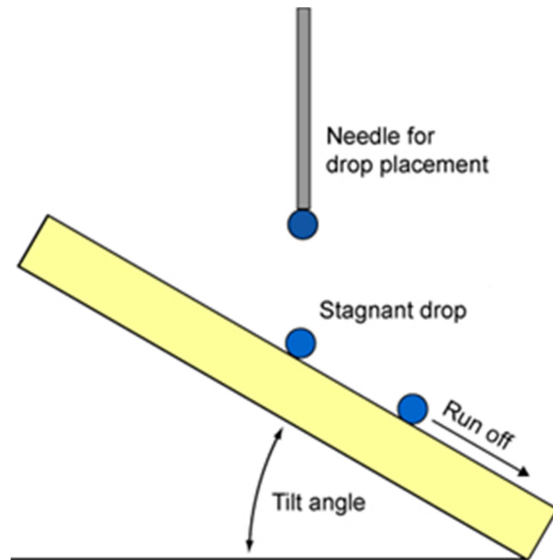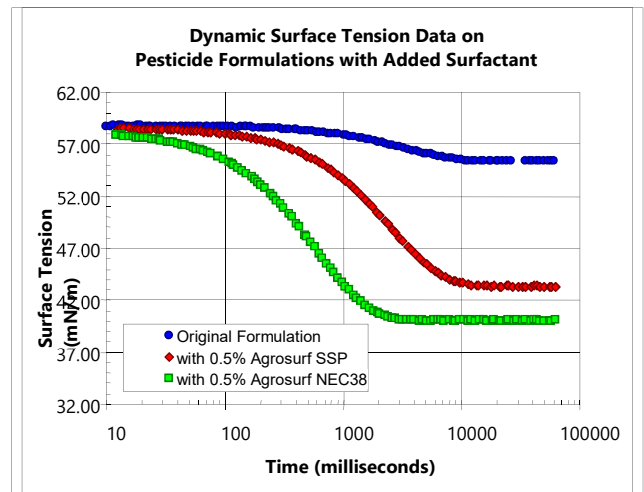

We were looking for one simple thing – whether the drop ran down the sample from where we dropped it or whether it stuck to the surface where it landed.

Results

Dynamic surface tension measurement

The results of dynamic surface testing on the customer's original formulation and the formulations with 0.5 wt% added surfactant are shown graphically below.

Each of the formulations shows a surface tension around 58 mN/m in the 10 millisecond range of surface age. The original formulation only decreases in surface tension to its 55.3 mN/m equilibrium surface tension as indicated previously. The formulation with 0.5% Agrosurf SSP decreases to an equilbrium surface tension of 43.3 mN/m and the formulation with 0.5% Agrosurf NEC38 decreases to an equilibrium surface tension of 40.1 mN/m and does so more quickly.

The key aspect for spray droplet size effect, however, is a rapid decrease in surface tension after initial surface formation – generally thought to be dependent on the surface tension within the first 250 milliseconds after surface formation. Neither of these surfactants are truly excellent surface tension reducers in that time scale. However, you will note the 0.5% Agrosurf NEC 38 formulation has a surface tension which is 7.7 mN/m lower than that of the original formulation at 250 milliseconds of surface age, whereas the 0.5% Agrosurf SPS formulation has a surface tension which is only 1.7 mN/m lower than that of the original formulation at 250 milliseconds.

The table below shows percentages of drops (as determined using the VisiSizer S100) in each ASAE Standard S-572 general category for each formulation.

Category	ASAE Definition	Original Formula	With 0.5% Agrosurf SSP	With 0.5% Agrosurf NEC38
	μm	Percentage of Droplets		
(VF) – Very Fine	< 150	0%	1%	1%
(F) – Fine	150-250	7%	12%	21%
(M) - Medium	250-350	22%	25%	38%
(C) - Coarse	350-400	38%	33%	24%
(VC) -Very Coarse	450-550	28%	22%	10%
(XC) – Extreme	> 550	9%	7%	6%

You can add the first three rows of each column to conclude that the percentages of droplets under 350 μm are 29% for the original formula, 38% with 0.5% Agrosurf SSP and 60% with 0.5% Agrosurf NEC38. Our customer is currently seeking further decreases in droplet size based on dynamic surface tension data – which is far easier and cheaper to evaluate first as compared to studying every possible formulation for droplet size analysis. The goal is to get the surface tension even lower in the first 250 milliseconds to have more than 85% of the droplets be 350 μm or less in diameter.

Contact angle measurement

The graph below shows time-resolved contact angle data for drops of each formulation placed on a Parafilm® surface using a KRÜSS Drop Shape Analyzer – DSA100 at a rate of 20 contact angles per second.

Time Resolved Contact Angle Data for Pesticide Formulations on Parafilm
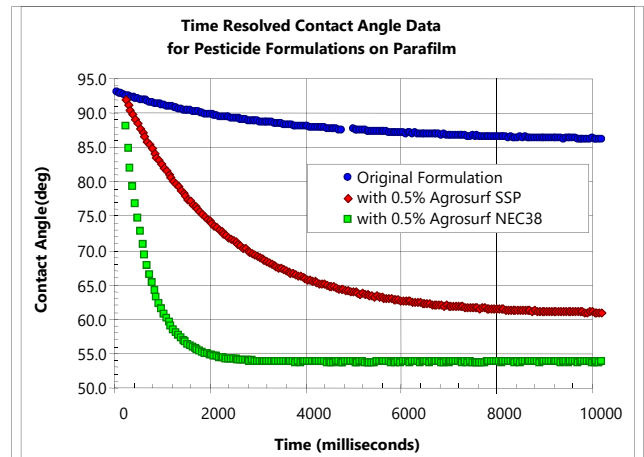
Each of the formulations shows an initial contact angle on the Parafilm® of around 90°. The original formulation only decreases in contact angle to about 86°. The formulation with 0.5% Agrosurf SSP decreases to an equilbrium contact angle of 61° and the formulation with 0.5% Agrosurf NEC38 decreases to an equilibrium contact angle of 54° and does so much more quickly.

As with surface tension in the spraying portion of this application, how rapid the wetting is important. It is actually more valid to compare the equilibrium contact angles, and conclude better wetting for one formulation versus the other, than it is to discuss equilibrium surface tensions as related to droplet formation during spraying – because (barring evaporation) the wetting would be allowed an indefinite period to occur on a flat surface. However, most leaf surfaces are not flat (horizontal), and run-off occurs when wetting does not occur rapidly enough once a drop lands on the surface so that the drop has enough adhesion to the surface to not move (run-off) due to gravitational effects.

For this reason we designed the tilted surface experiment discussed above and at tilt angles of 10°, 20°, 30°, 40°, 50°, and 60°, dropped twenty 2 µl drops of each formulation onto fresh Parafilm® surfaces. The table below shows the number of run-off droplets (20 being the maximum) for each formulation.

Number of Run-Off Drops as a Function of Parafilm Tilt Angle and Formulation Type
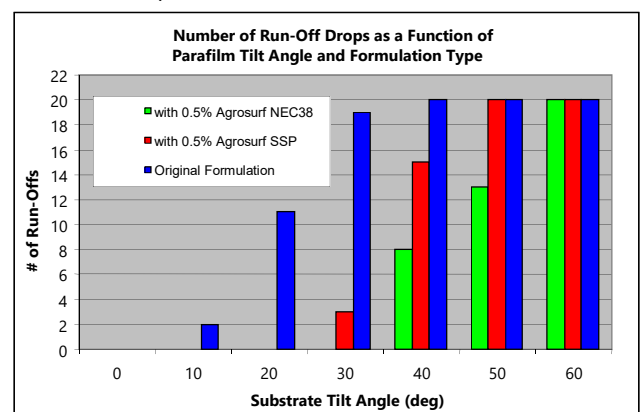
In these data you see that the surfactants tend to prevent drops from running off the tilted model leaf surface. More than half of the drops of the original formulation run off at a 20° tilt angle and all run off at the 40° tilt angle and above. Agrosurf NEC38 is more effective than Agrosurf SSP preventing all run offs at the 30° tilt angle and 60% of run offs (12 drops / 20 drops) at the 40° tilt angle. Agrosurf SSP prevents only 85% of the run-offs (17 drops / 20 drops) at the 30° tilt angle and 25% of the run-offs (5 drops / 20 drops) at the 40° tilt angle. The customer plans to use this technique in search of even better surfactant additives for his pesticides.

Summary

The optimization of pesticide application in terms of spraying and wetting the surfaces of crops involves dynamic surface tension, time-dependent contact angle (spreading), and droplet adhesion on non-horizontal surfaces. Surfactants are commonly added to pesticide formulations to control spray atomization and wetting.

Hopefully this brief note, based on using one example data set from our own experience, gives you insights into methods that can be employed to fundamentally study these important aspects and find the best surfactant additives for your own formulations.

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