Sustainable Surfactants for Crop Protection Solutions

EVONIK
Leading Beyond Chemistry

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The agricultural market is under increasing pressure as consumers ask for food containing lower, or no amounts of residual chemicals, but at the same time growers need to prevent the development of pathogens and pests resistant to active ingredients. Regulators demand less agrochemical input and some chemical pesticides have already been phased-out.

Well-known in the agrochemical market, Surfactants are used in formulations and as tank mix adjuvants. The benefits of adjuvants are important in plant protection products from pesticide formulation to storage, tank-mix dilution, spraying, targeting and finally acting on the pest. In water-based formulations, their main task is to decrease surface tension resulting in better wetting of the dispersed particle in water and more stable formulations. In oil-based formulations, emulsification properties support the quality of the emulsion ensuring higher stability and lower droplet size. In tank mix dilutions for all kinds of formulations, surfactants prolong physical stability as they reduce the surface tension of water. Targeted delivery is the main purpose of surfactants during spraying, which enhances efficacy and decreases the active amount needed. Targeted delivery is achieved by: 1) reducing driftable particles 2) enhancing adhesion and retention of spray droplets on the plant. 3) Improving uptake and penetration of active ingredients, and 4) increasing rain fastness.

However, regulatory pressure is rising with additives like NPE based solutions phased-out globally. With the agrochemical market demanding innovative, more sustainable additives, Evonik has developed benign surfactants which enable a more environmentally friendly plant protection.

New adjuvants that comply with eco-toxicological, safety and sustainability criteria provide solutions to support the plant protection industry. Evonik is introducing sustainable and biodegradable adjuvants in the following four classes: Wetting agents and multifunctional additives based on biodegradable trisiloxanes, polyglycerolester and sophorolipids.

Due to their chemistry, the way these novel surfactants work is different. Roughly speaking, the lower the surface tension of spray droplets the better adhesion and retention on the leaf. Water with 72 mN/m gives a strong bounce off of spray droplets. Trisiloxanes help to reach the lowest surface tensions and Evonik has developed readily biodegradable trisiloxanes based on a unique patented technology. The reduction of water surface tension down to 21 mN/m facilitates the best adhesion and retention of droplets on very difficult to wet surfaces. Due to their special phase behavior in water, they provide superspreading of water, solutions and dispersions to ensure the best coverage of contact actives on surfaces thanks to the contact angle of 0°. This also enables the highest biological efficacy. In contrast to other superspreading trisiloxanes, these biodegradable trisiloxanes have no ecotoxolocial classification and are not dangerous goods for transportation.

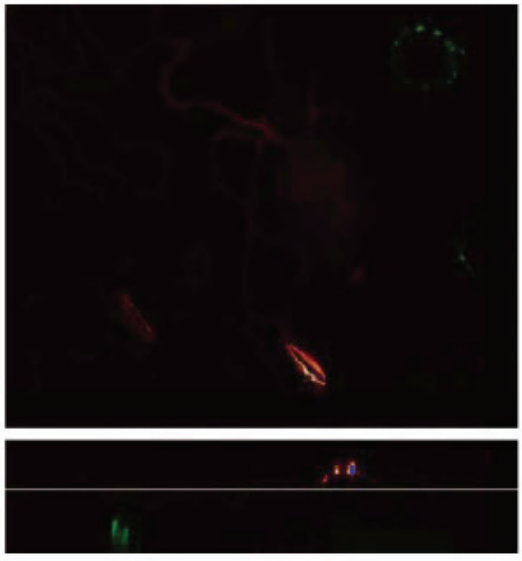
BREAK-THRU® S 301 is soluble in water and many oils, so it can be used in all kinds of liquid formulations and as a tank mix adjuvant to give excellent adhesion and retention of spray droplets. Commercially available products with living microbial actives rarely contain surface-active molecules, and alongside the low wetting and low dispersing properties of solid formulations in water, can often provide low and inconsistent field performance. BREAK-THRU® S 301 can be used as a carrier liquid in dispersion concentrates for increased shelf life of living microbial products. As a tank mix additive, BREAK-THRU® S 301 leads to a better dispersion of microbial actives in the spray solution, and to excellent wetting in the application, helping increase the efficacy of microbial-based pesticides.

BREAK-THRU® SD 260 is developed specifically for use in WP – formulations for chemical pesticides or for biopesticides. The product is the first water soluble, solid trisiloxane to provide humectant properties, and to offer excellent wetting properties as it includes BREAK-TRHU® S 301. The addition of 1 - 5% w/w BREAK-THRU® SD 260 to the powder or granules of biopesticides significantly increases the surfactant properties of the final tank-mix dilution. At a concentration of 0.1 w/w-% it reduces the surface tension of water to 22 mN/m and the humectant property supports the field efficacy of the microbes.

Unique readily biodegradable adjuvants based on polyglycerol esters and sophorolipids fulfill modern requirements for all types of plant protection products and consist of a natural carbon source. They reduce the surface tension of water down to 30-35 mN/m. Incoming droplets solutions with such surface tensions normally show a strong and fast receding effect from the contact line, often leading to bounce off and loss of spray droplets. The new action is based on the interaction of the hydrophobic emulsified droplets with the cuticle leading to a so called 'pinning effect' preventing the droplet receding from the contact line of the water droplets. These droplets also stick to the surface so retention is excellent. It's well-known that polyglycerol esters and sophorolipids lead to a swelling of the cuticle wax which improves the penetration through the cuticle. This facilitates the uptake of lipophilic and hydrophilic active ingredients through the cuticle and epidermal cells (see **Figure 1** and **Figure 2**). This physico chemical interaction of the bio-based molecules with the cuticle wax can be shown nicely with confocal laser scanning microscopy as reported previously [Haensel, et. al. (2015) Polyglycerolester as Sticker Penetrant Adjuvant]. For systemics and contact active ingredients these products are well suited, and due to their hydrolytic stability these surfactants can be used for water-based and oil-based formulations.

Figure 1. CLSM study of BREAK-THRU® SP 133 penetration of the pseudo-lipohilic pesticide mimic (RHODAMINE® B) into bean leaves [2 HAT 63 x mag.]. Near-surface horizontal and vertical cross-sections

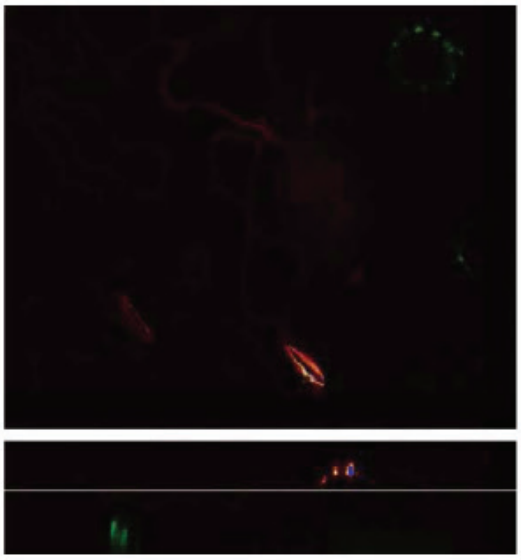
a) pure RHODAMINE® B Dye



+ 0.1% BREAK-THRU® SP 133

Figure 2. CLSM study of BREAK-THRU® SP 133 penetration of the hydrophilic pesticide mimic (Oregon® Green) into bean leaves [2 HAT 63 x mag.] Near-surface horizontal and vertical cross-sections

b) pure Oregon® Green



+ 0.1% BREAK-THRU® SP 133

BREAK-THRU® SP 133 has a natural carbon content of 93%, is readily biodegradable and comes without a hazardous label. Its raw materials glycerol and fatty acids are derived from different vegetable oils. This polyglycerol ester-based product also provides excellent adhesion and retention of difficult to wet target species. Wind tunnel trials at the University of Nebraska have shown that BREAK-THRU® SP 133 reduces the amount of driftable particles due to an increase of the spray droplet size: the expanding water film is broken up directly after the nozzle, which induces bigger droplets that are less prone to drift. Less driftable droplets means not only a higher field efficacy, but also less harm to the environment.

BREAK-THRU® SF 420 is a sophorolipid-based surfactant manufactured by the fermentation of rapeseed oil and sugar. This vegetable, not genetically modified feedstock is sourced in Europe. The yeast strain used is also a natural microorganism: Starmerella bombicola. It is a readily biodegradable biosurfactant with dispersing und wetting properties. Due to the special geometrical structure, BREAK-THRU® SF 420 is an excellent dispersant for metal hydroxides like $Cu(OH)^2$ in water which makes it an excellent option for SL and nutrient SC formulations. Due to the more even distribution of, for example, copper spray solution on the foliage, it improves the control by fungicides. However, it was proven to also improve insecticide performance and enhance the activity, the speed of action and the duration of herbicides.

At the same time this multifunctional biosurfactant performs very well as a water soluble, low foaming tank mix surfactant by reducing the surface tension of water down to < 35 mN/m. However, due to the novel mode of action BREAK-THRU® SF 420 provides excellent adhesion and significantly higher retention on very difficult to wet species. After drying the remaining film generates with rainwater a gel layer by a hydration effect of the polymeric sophorolipid. This results in excellent rainfastness (see **Table 1** and **Figure 3**).

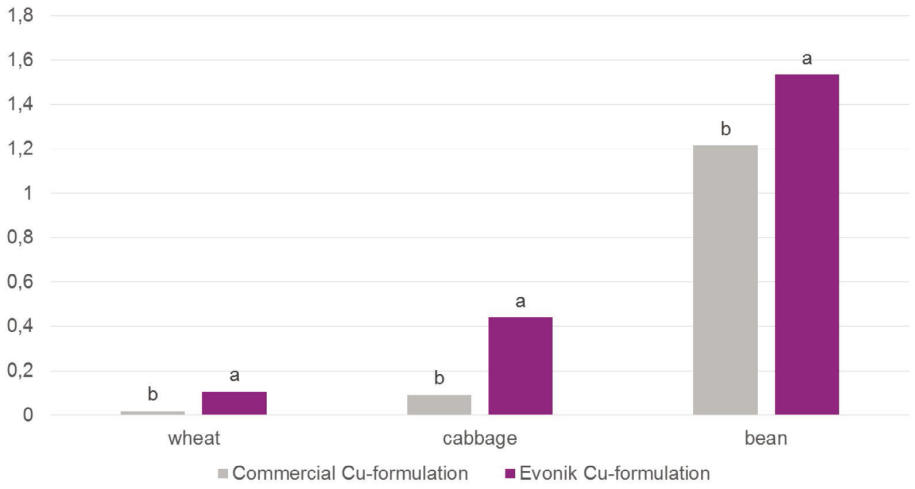


Figure 3. Effect on mean copper deposits (µg/cm^2) retained on wheat, cabbage and bean foliage - Post Rain Analysis

Table 1
Evonik Cu-formulation; Copper hydroxide 383 SC

g/L	Ingredient	Function
383.0	Copper Hydroxide	Active Ingredient
75.0	BREAK-THRU® SF 420	Dispersing and Wetting Agent
3.0	BREAK-THRU® AF 9903	Antifoam
3.3	NaOH (20% solution)	Neutralization
2.5	Xanthan gum	Thickener
50	Propylene Glycol	Antifreeze
q.s.	Water	Solvent

Taken together, all the features of our sustainable multifunctional surfactants help increase the biological efficacy of agrochemicals and biosolutions. This has already been proven in many field trials around the globe. BREAK-THRU additives enable microbials as active ingredients to have the lowest environmental impact, leading to a higher acceptance of these solutions by farmers and addresses the need of consumers for food with lower chemical residuals.

Approvals for organic farming become more important, even for conventional farming, as it demonstrates the superior sustainability of the products. Therefore, the possibility of getting these approvals is a key criteria for Evonik in the development of new additive products. BREAK-THRU® S 301 and BREAK-THRU® SP 133 are already approved for OMRI, and BREAK-THRU® SP 133 is additionally FIbl registered and thereby the first surfactant for the German speaking organic agricultural market.

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