Polyglycerolester as Sticker Penetrant Adjuvants

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SUMMARY

The effect of adjuvants on the biological efficacy of agrochemical sprays is related to improving the surface activity of pesticide formulations. By improving adhesion and retention of spray solution droplets the uptake of the active ingredients through the cuticular waxes is increased.
Today new adjuvants also need to comply with eco-toxicological, safety and sustainability criteria. This paper presents a new class of benign adjuvants based on polyglycerolesters to improve the efficacy of pesticide formulations for tank-mix and in-can applications. Polyglycerolesters are natural derived and biodegradable. The performance of adjuvants based on polyglycerolester, hydrophilic and hydrophobic, and their influence on adhesion, retention, foliar uptake and drift control is presented. Field results confirm the enhancement of the biological efficacy of pesticides. The paper demonstrates that safe and environmentally friendly adjuvants are already available for formulator and consumer acceptance.

INTRODUCTION

Polyglycerolesters and their derivatives have been used in various industrial applications such as emulsifiers in food and personal care products. Since polyglycerolesters are produced from renewable natural oils and fatty acids, they are safe and ecological friendly products. Their acceptance for food use in many countries makes them particularly interesting as tank mix additives or for application in water based agrichemical formulations and also in oil based formulations such as OD and ECs. Their high surface activity makes them suitable for use as emulsifiers, dispersants or spreading agents in pesticide formulation [1].
Furthermore they have a positive impact on droplet adhesion and retention of the tank mix spray to the waxy leaf surface [2]. Depending on the structure polyglycerolesters can be hydrophilic or hydrophobic, thus either freely miscible with water or in oil based systems.
Surprisingly, specially designed hydrophobic polyglycerolester adjuvants can be used for both lipophilic, and also for hydrophilic active ingredients, yielding excellent adjuvant performance. Furthermore they reduce the amount of driftable fines of the pesticide spray.
BREAK-THRU® SP is a new class comprising hydrophilic and hydrophobic polyglycerol-esters based adjuvants, low foaming, low viscous and easy-to-handle. BREAK-THRU® SP 131 is hydrophilic (water miscible), BREAK-THRU® SP 133 is hydrophobic, emulsifiable in water as well as soluble in many solvents. SP means sticker and penetrant which are the main performance properties for both products. This paper describes the impact on adhesion and retention, penetration of oils and active ingredients and the influence on spray drift.

BREAK-THRU® SP - Adjuvants based on Polyglycerolesters

Chemistry of polyglycerolesters

Polyglycerolester are usually synthesized in a two-step process as illustrated in Figure 1 to 3. Step one is the condensation of glycerol which can lead to a broad range of chemical species, varying in oligomer distribution (broad or narrow) and isomer distribution yielding linear, branched and cyclic molecules.

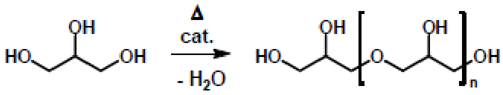

Figure 1: Condensation of glycerol

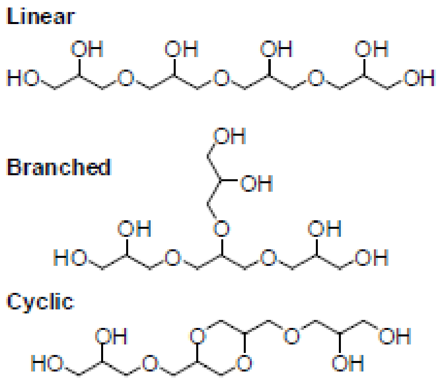

Figure 2: Isomer distribution of Polyglycerol

Different types of fatty acids, varying in chain lengths (linear, branched) can be attached through the esterification of the polyglycerols (Figure 3).

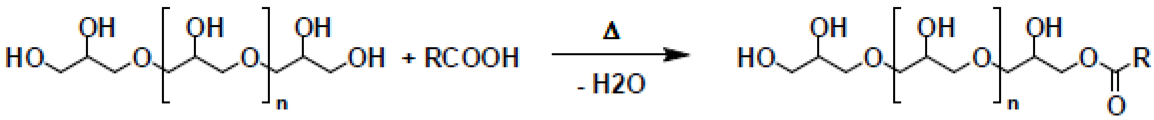

Figure 3: Esterification of polyglycerol

By adjusting the polyglycerol distribution, the degree of substitution, and the type of fatty acid group, the properties of the final product can be taylor-made.
In addition to emulsification and dispersing properties, these polyglycerolesters provide a positive impact on spreading of water and oils, improve retention, and exhibit anti-drift-performance.

Droplet adhesion and retention of agrichemical sprays

Droplet adhesion and retention of pesticide spray are impacted by the properties of the leave surface. Further factors affecting the droplet adhesion and retention are droplet size and spray velocity. The surface tension of the spray droplet is known to correlate well with retention of the droplets, too [4]. When added into water or oils BREAK-THRU® SP 131 and

BREAK-THRU® SP 133 reduce significantly the surface tension, so the physico-chemical interaction of the sprays with the surface [5] leads to better adhesion and improved retention (Figure 4).

Figure 4: Example of retention of a spray droplet with BREAK-THRU® SP 131 (spread droplet on the left side of the leaf) on rapeseed leaf compared to pure water droplets (right side of the leaf)

Determination of adhesion on Avocado and Spinach

The impact on adhesion of BREAK-THRU® SP 131 and BREAK-THRU® 133 was evaluated with the moderately difficult-to-wet adaxial spinach leaf surface and on the very waxy difficult-to-wet surface of mature abaxial avocado foliage. Mono-sized droplets of ca. 500 micrometer diameter where produced with an impulse-jet drop generator and a fall distance of 97 cm to the leaf surface. Blankophore® P dye (1%w/v) was added dropwise onto the adaxial surface of spinach seedling leaves and the abaxial surface of mature avocado leaves mounted at 0-, 22,5° or 45° inclinations from the horizontal. Adhesion was quantified (under UV light) by observing the fate of 10 replicate droplets impacted onto each of five replicate leaves which were excised from different spinach plants or avocado branches. Adhesion is expressed as a percentage of droplets applied which adhere at first impact (no bounce or shatter), (Table 1).

Table 1: Adhesion as % droplets applied of spray droplets (500 micrometer diameter) to avocado and spinach foliage oriented at different leaf angles.

Adjuvant at 0.1 % w/v	Avocado (abaxial)		Spinach (adaxial)		
	0°	22,5°	0°	22,5°	45°
BREAK-THRU® SP 131	77	11	100	100	100
BREAK-THRU® SP 133	66	22	100	100	100

The results confirm that the hydrophilic BREAK-THRU® SP 131 and the hydrophobic BREAK-THRU® SP 133 promote very good adhesion (100%) on moderately- difficult-to-wet spinach leaves. They are also acceptable on the very waxy and difficult-to-wet abaxial leaf surface of mature avocado foliage.
Overall, one can conclude that both polyglycerolester blends are good “sticker” adjuvants for difficult-to-wet targets.

Determination of spray retention on whole plants

As shown in Table 2, spray retention with several treatment blends containing the tartrazine food grade dye (8 g/L) on spinach plants raised in a controlled environment was determined using a moving head track sprayer. Treatments were applied at 100 L/ha through a spraying systems air induction flat fan even spray nozzle operated at 250 kPa, with flow of 0.56 L/min.

After spraying, leaves were sampled and washed immediately with deionized water. The tartrazine dye recovered in each wash was quantified by spectrophotometry. Surface coverage was determined using a Leaf Area meter. Spray retained on leaves was determined as spray volume/leaf area and calculated as a percentage of volume per area applied (100 L/ha).
The retention is presented in Table 2 as volume retained per area of leaf, as a % of total theoretical deposit and as dose per area.

Table 2: Comparison of adjuvants in the retention of sprays on spinach foliage

Rate L/ha	Adjuvant 0,1 % w/v	Retention microliter/cm^2	Retention %	Retention[1] microgramm/cm^2
100	BREAK-THRU® SP 131	0.65	65.4	6.5
100	BREAK-THRU® SP 133	0.68	68.2	6.8

[1]As normalized dose (at 1 kg/100 L/ha application rate)

Spinach is a good representation of moderately difficult-to-wet crop and weed species which benefit from the use of "sticker" adjuvants, and as such the data confirm that the BREAK-THRU® SP 131 and BREAK-THRU® SP 133 polyglycerolester blends shows high adhesion and retention similar or even better compared to trisiloxanes.

The effect of adjuvants on dye penetration into wheat and bean leaves

The cuticular waxes on a leaf form a transport-limiting barrier. The following study showed that this barrier could be penetrated significantly better by both BREAK-THRU® SP products. A simple trial indicated the increase of penetration. A 10 µL droplet of rapeseed methyl ester (RME) containing BREAK-THRU® SP (1wt.%) placed on a rapeseed leaf leads to cuticular penetration of the RME within 4 minutes (Figure 5). Without the adjuvant the penetration time increases up to 60 minutes.

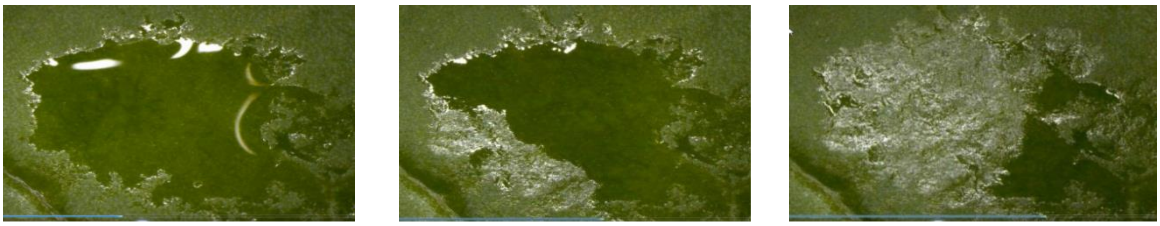

Figure 5: RME penetration which contains 1% BREAK-THRU® SP between 4 minutes, 30 x magnification.

BREAK-THRU® SP lower the surface tension of RME as shown in Figure 6.

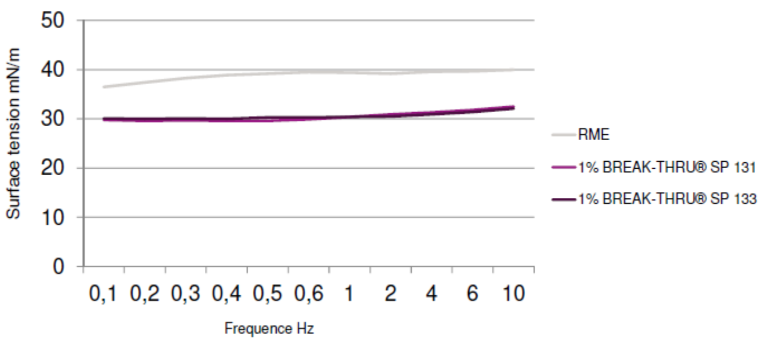

Figure 6: Surface activity measured by bubble pressure tensiometer.

Lowering the surface tension is a precondition for improved spreading and diffusion of active ingredients on and into waxy layers.

The effect of adjuvants on uptake

Fluorescent compounds (dyes) of low molecular weight and different hydrophily were chosen to represent active ingredients [6]. In this study the quantitative dye uptake was measured as follows.

Dye treatments (20 x 0.24 µL drops applied at 100 L/ha dose) were applied to leaves (three reps) in vivo and harvested 24 HAT (hours after treatment).

As dye Oregon® green 488 was used in aqueous acetone (3+2) solution at 0.5 mg/ml, and Rhodamine® B diluted in double distilled water at 0.5 mg/ml. The treated plants were leafs of bean (Vicia faba) and wheat (Triticum aestivum).

At harvest, leaf surfaces were washed with 50% aqueous acetone (2x4 ml) and dye recoveries were quantified using a spectrophotometer (Shimadzu 1240, 570 nm wavelength). The uptake was determined as the amount of applied dye not recovered in surface wash-offs (Table 3).

The BREAK-THRU® SP 131and BREAK-THRU® SP 133 increased the uptake of the Rhodamine® B dye which is a pseudo-lipophilic pesticide mimic and the uptake of the hydrophilic pesticide mimic Oregon® Green in both species.

Table 3: % Uptake of dye into bean and wheat leaves at 24 HAT influenced significant by BREAK-THRU® SP

Adjuvant	**Bean**	**Wheat**	**Adjuvant**	**Bean**	**Wheat**
Rhodamine® B	12.8	6.4	Oregon® Green	6.6	0.7
+ 0.1% BT SP 131	39.8	45.1	+ 0.1% BT SP 131	17.7	8.2
+ 0.1% BT SP 133	28.3	33.1	+ 0.1% BT SP 133	15.8	7.5

In order to visualize the mode of action for penetration and uptake by BREAK-THRU® SP confocal laser scanning microscopy (CLSM) was chosen. The same dyes being used in the uptake study were also used for this CLSM study.

The adjuvants were blended with the dyes immediately prior to use and were applied with a micro-syringe- as 10 x 0.24 µL droplets to approximately- 1 cm^2 area on the adaxial surface of a leaf.

The CLSM study (Figures 6 to 9) show images of horizontal- and vertical cross-sections of qualitative dye uptake of the wheat and bean leaves.

Without adjuvants, dye solutions did not spread at all. With adjuvant BREAK-THRU® SP present, the spreading of droplets applied to the leaf surface varied but it is clearly visible that the polyglycerolester based products increased penetration of the pseudo-lipophilic pesticide mimic Rhodamine® B into the bean and wheat leaves as compared to the dye only. The same outcome is confirmed for the uptake of the hydrophilic Oregon® green dye into bean and wheat leaves as compared to the dye alone.

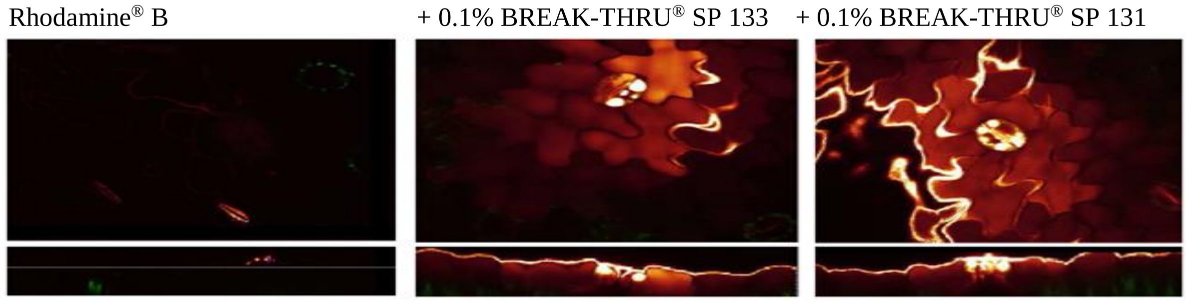

Figure 6: CLSM study of BREAK-THRU® SP penetration of the pseudo-lipophilic pesticide mimic (Rhodamine® B) into bean leaves. [2 HAT 63 x mag.]

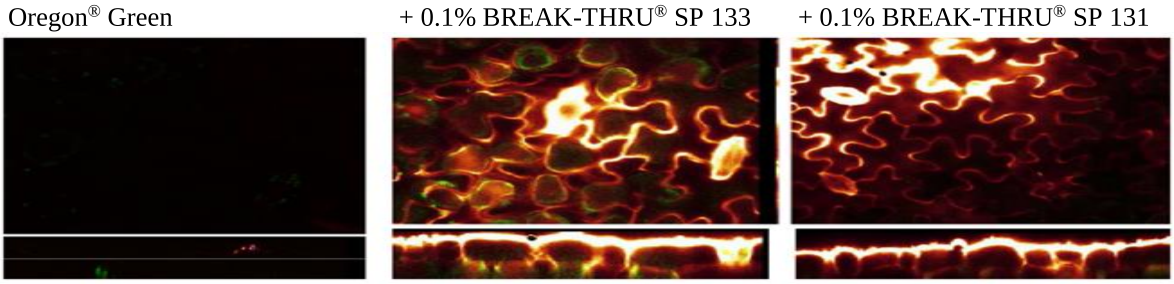

Figure 7: CLSM study of BREAK-THRU® SP penetration of the hydrophilic pesticide mimic (Oregon® Green) into bean leaves. [2 HAT 63 x mag.]

Figure 8: CLSM study of BREAK-THRU® SP of the pseudo-lipophilic pesticide mimic (Rhodamine® B) into wheat leaves. [16 HAT 25 x mag.]

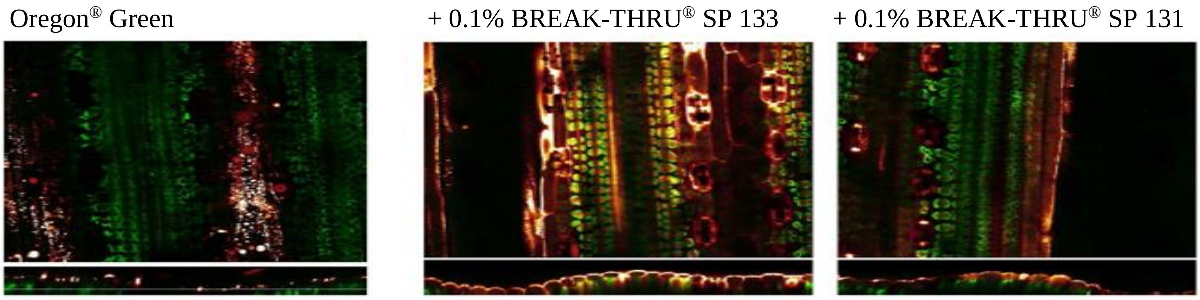

Figure 9: Increased rate of penetration of hydrophilic pesticide mimic (Oregon® Green) into wheat leaves. [16 HAT 25 x mag.]

The uptake results and the confocal images substantiate the premise that both polygylcerolester adjuvants improve and accelerate the penetration of actives into the plants. CLSM also confirms the measured uptake shown in Table 3. The more active penetrated into the leaf surface, the higher the biological efficacy of the crop protectant.
The BREAK-THRU® SP adjuvants are enhancers of penetration of active ingredients.

The effect of adjuvants on drift control results

Off target movement of spray solutions, known as drift, poses certain risks to people`s health, environment or nearby crops. Especially droplets < 150 microns are prone to spray drift, and these driftable fines must be reduced by the equipment (nozzles) and the formulation of agrochemical sprays. The effect on driftable fines by the polyglycerolester adjuvants was analyzed with a high speed video [7]. Trials were carried out with 0.1wt. % dose of the adjuvants.
It was found that an early breakup of a spray lamella leads to a significant reduction of driftable spray droplets as shown in Figure 10. The study of the spray pattern in Figure 11 shows that BREAK-THRU® SP 133, through its hydrophobic nature, increases the droplet size and thus reduces spray drift up to 60 %.

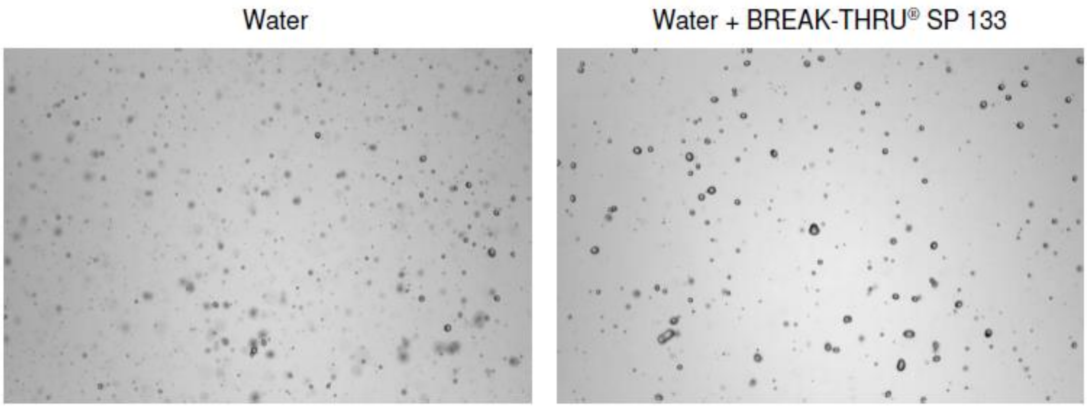

Figure 10: Spray develops from an expanding liquid film. BREAK-THRU® SP 133 is able to trigger an early breakup of the liquid film which leads to bigger droplets and less drift.

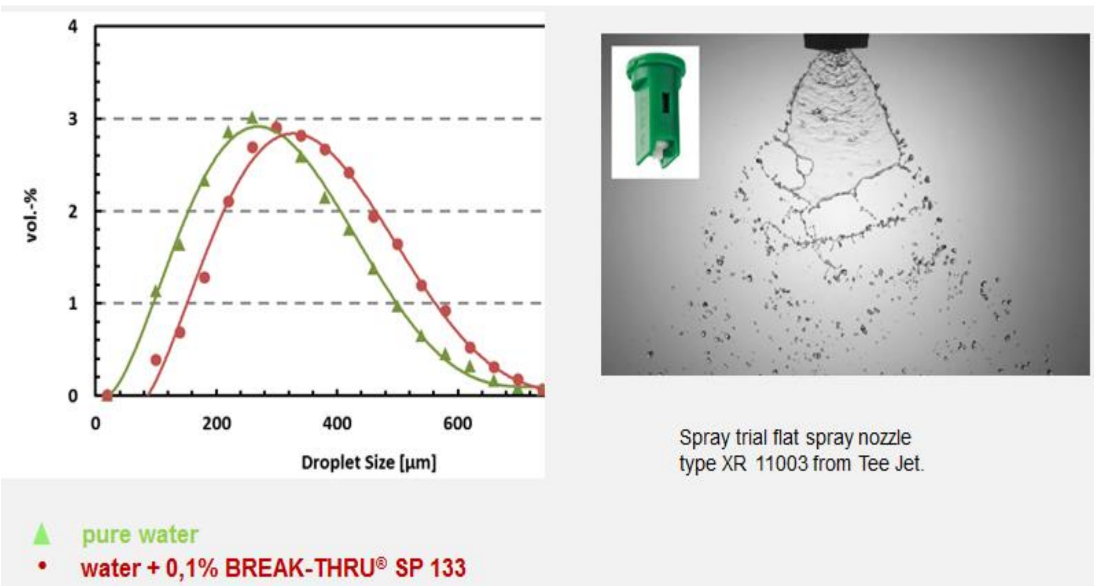

Figure 11: BREAK-THRU® SP 133 increases droplet size.

The effect of adjuvants in field trials

A broad screening including different types of actives and crops was conducted to evaluate the efficacy of BREAK-THRU® SP as adjuvants for herbicides, insecticides and fungicides. In general it can be summarized that the biological efficacy of these adjuvants, at a dose rate for systemic crop protection of 400 ml/ha or 0.1 – 0.25 %, is in the same magnitude of conventional adjuvants. Details are available on request.

CONCLUSIONS

BREAK-THRU® SP 131 and BREAK-THRU® SP 133 are benign adjuvant are derived from mild and green, biodegradable chemistry. Thus labeling is not required.

As demonstrated both adjuvants improve significantly the deposition, adhesion and retention of agrichemical sprays including difficult-to-wet target species. They activate the spreading of water and oils, and they facilitate the uptake of active ingredients through the cuticle and epidermal cell vacuoles. Field trials results confirm their improvement of the biological efficacy of herbicide, insecticide and fungicide plant production products.

Thus BREAK-THRU® SP mean benign alternatives to current conventional adjuvant technologies.

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