

Multifunctional Additives for Performance Enhancement of Oil-based Formulations



The key selling points for newer formulation technologies include improved handling, optimized adhesion, spreading and up-take and an overall better environmental profile. The basic components of an agricultural oil dispersion formulation are the solvent or oil phase and the dispersed solid phase. These basic components may include active ingredients, petroleum or naturally derived solvents, safeners, rheology modifiers, emulsifiers, dispersants and other co-formulants that help deliver the desired attributes of the product.

KEY BENEFITS DERIVED FROM OIL-BASED FORMULATIONS

In oil-based formulations the oil can act as an adjuvant by interacting with the cuticle, they provide better contact to the hydrophobic surface by spreading over the cuticle wax and better bio-efficacy by penetration into it. Penetration into leaves is one of the most essential steps for biological performance. The cuticle wax is the limiting barrier of the leaf for the transport of the active ingredients, this barrier can be significantly lowered by oils. Therefore, when the oils come in contact with the cuticle, this leads to a swelling of the cuticle waxes becoming more permeable and therefore the active ingredient can better penetrate into the interior of the leaf. Due to these properties, oils increase the biological efficacy of the formulation.

By inducing bigger droplets of the tank mix spray oils can also reduce drift. Thus, they improve the environmental performance by reducing drift pollution in its surroundings during the spraying process, and due to the increased performance of the active

Majority of pesticides are formulated and applied in aqueous form. Some pesticides, however, exhibit limited water solubility. Alternatively, mineral and vegetable oils serve as the carriers to deliver these actives to plants or pests. Oils are excellent carriers for water insoluble or sensitive active ingredients. Oil dispersions (OD) are one type of liquid formulation and are defined as stable suspensions of active ingredients in a water-immiscible fluid which may contain other dissolved active ingredients and is intended for dilution with water before use.

ingredient less chemicals can be sprayed. MSO are particularly recognized to have the above described anti-drift properties. But also, other oils show a similar performance. It is believed that the mechanism that leads to lamella break-up when oils are being used.

EVONIK'S APPROACH TO ENHANCE THE PERFORMANCE OF OIL-BASED FORMULATIONS

The performance of oils can be improved by additives so called oil enhancers (OE). Added in small quantities to OD formulations such oil enhancers reduce the surface tension of oils which improves the spreading of the oils on a hydrophobic leaf surfaces providing and even better contact to the waxy cuticle.

Evonik additives for oil dispersions are in the market for many years and known as BREAK-THRU® OE additives designed to improve the performance of oil-based crop protection formulations. BREAK-THRU® OE additives are based on organo-modified siloxane chemistry which combines the advantages of silicone with oleochemicals. They work by lowering the surface tension of oils and solvents, thus enabling

Oil dispersion formulations have recently become more important in current formulation research and application. For examples OD formulations are applied for sugar beet, rice, maize or cereals. Oils like methylated seed oil (MSO) are used in many formulations like emulsion concentrates (EC) and oil dispersions. The long-term outlook is likely to see a growth in these formulation technologies as they offer new solutions and come with multiple advantages.

faster and more complete leaf coverage and penetration into the plant. Added in small amounts, they enhance the efficacy of oil-based pesticides formulations. As oil preferences and compositions vary globally, the BREAK-THRU® OE comprise a series of products designed for a broad spectrum of oils from vegetable to mineral based formulation types. These products are suitable for use in EC, EW, SE, and OD crop protection formulations. Moreover, Evonik BREAK-THRU® OE increase the performance of such sustainable formulations.

It is essential for the OE to be soluble in the solvent in order to prevent the solid particles to clump together into a floc and improve the overall stability given that the active ingredient is insoluble in water and suspended for a length of time. The table 1 shows the difference of the solubility of three different BREAK-THRU® OE products with various solvents required for their incorporation in the formulation. For every kind of oil Evonik offers a dedicated BREAK-THRU® OE product.

Solvent	BREAK-THRU® OE 440	BREAK-THRU® OE 444	BREAK-THRU® OE 446
Methylated Rapeseed Oil / Methyl Soyate	✓	✓	✓
Paraffinic Oil		✓	
Mineral Oil	✓	✓	✓
Vegetable Oil (Soya, Sunflower, Rapeseed)	✓		
Water			✓

✓ Recommended

✓ Soluble

Table 1. Solubility of BREAK-THRU® OE Product Range at 5 %-wt %

WHAT MAKES OUR BREAK-THRU® OIL ENHANCERS DISTINCT?

BREAK-THRU® OE enables by its' multifunctional mode of action an increase in performance of sustainable formulations and allows to reduce the applied amount of oil volumes that further supports sustainability.

One of the key features of BREAK-THRU® OE is improving the penetration by cuticle interaction with the waxy leaf layers. A clear illustration of figure 1 shows the penetration of Rhodamine B as a mimic for a lipophilic active into a bean leaf analyzed by confocal laser scanning microscopy (CLSM). The difference of a formulation with and without BREAK-THRU® OE is demonstrated in the penetration of the lipophilic substances (simulating the oil) into epidermal cells. The picture on the right clearly shows the enhanced up-take in leaf facilitated by the additive.

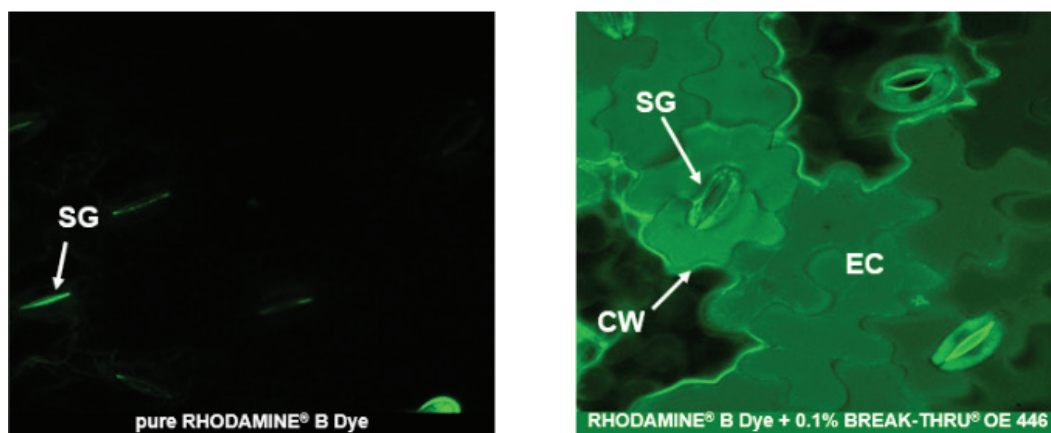


Figure 1. CLSM study of penetration of the pseudo-lipophilic pesticide mimic (Rhodamine B) into bean leaves, horizontal sections: 10 µm below surface, 4 hours after application. CW: Epidermal Cell Wall, EC: Epidermal Cell, SG: Stomatal Guard Cell.

Left photo without BREAK-THRU® OE; right photo with BREAK-THRU® OE.

In addition, BREAK-THRU® OE increases the leaf coverage of oils by enhancing the spreading property. **Figure 2** shows the spreading effect of 1 droplet of 10 µL samples on a potato leaf after 2 minutes of spraying. An undisputed difference is apparent between the two sections. On the right section, the droplets on the leaf coverage is spread out using the paraffinic oil with 1% of BREAK-THRU® OE, while on the left section, the covered leaf area on potato leaf is much smaller.

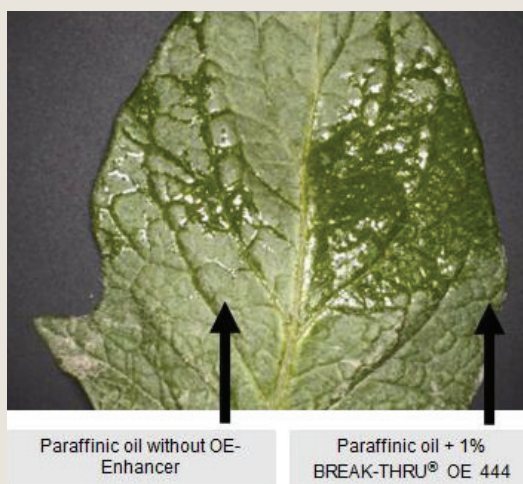


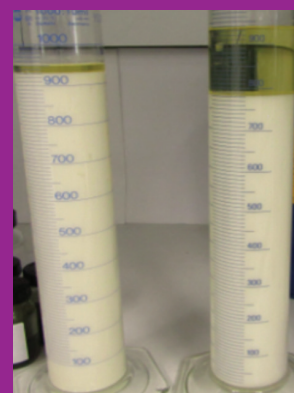
Figure 2. Spreading of a paraffinic oil-based formulation with and without BREAK-THRU® OE 444 on a potato leaf.

Another attribute the usage of BREAK-THRU® OE adds to the OD formulations, is preventing phase separation and improving its stabilization, as OD tend to separate over time. **Figure 3** illustrates how BREAK-THRU® OE 440 significantly reduces syneresis of a Nicosulfuron 45 g/L OD formulation based on sunflower oil, left tube Nicosulfuron OD formulation with BREAK-THRU® OE 440 (Formulation 1) and the right tube a market standard formulation without BREAK-THRU® OE 440. The formulation including the oil enhancers is more stable showing a much lower tendency for phase separation.

Figure 3. Nicosulfuron OD formulation with and without BREAK-THRU® OE 440

OD formulations 1 and 2 were prepared in the lab and tested for their performance in field trials. Formulation 1 and 2 are OD formulations with Nicosulfuron (1) and Rimsulfuron (2) based on sunflower oil with 3% BREAK-THRU® OE 440. As additional ingredients the formulations contain emulsifier, dispersant and rheology modifier.

Syneresis after 6 months at 25 °C



**With
BREAK-THRU® OE 440**

**Without
BREAK-THRU® OE 440**

Formulation 1 and 2:

Formulation 1		
g/L	Ingredient	Function
45	Nicosulfuron	Active
q.s.	Sunflower Oil	Solvent
30.0	BREAK-THRU® OE 440	Oil Enhancer
50.0	BREAK-THRU® DA646	Dispersant
120.0	BREAK-THRU® EM V20	Emulsifier
30.0	TEGIN® OV	Emulsifier
30.0	AEROSIL 200	Thickener

Formulation 2		
g/L	Ingredient	Function
125.0	Rimsulfuron	Active
q.s.	Sunflower Oil	Solvent
30.0	BREAK-THRU® OE 440	Oil Enhancer
50.0	BREAK-THRU® DA646	Dispersant
136.0	BREAK-THRU® EM V20	Emulsifier
34.0	TEGIN® OV	Emulsifier
20.0	AEROSIL 200	Thickener

Formulation 1 was applied in a glass-house trial on POA Pratensis (Kentucky Black Grass) in a dose level of 10 g and 2.5 g of active ingredient/ha in comparison to a commercial OD herbicide formulation. 20 and 30 days after treatment formulation 1 shows enhanced performance in weed control (**Figure 4**).

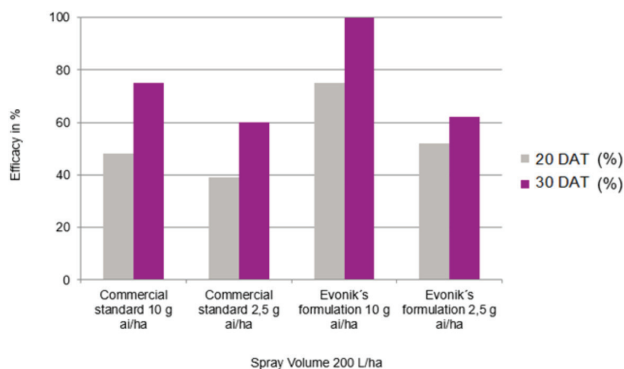


Figure 4. Formulation 1 versus commercial standard OD formulation on POA Pratensis glasshouse trials

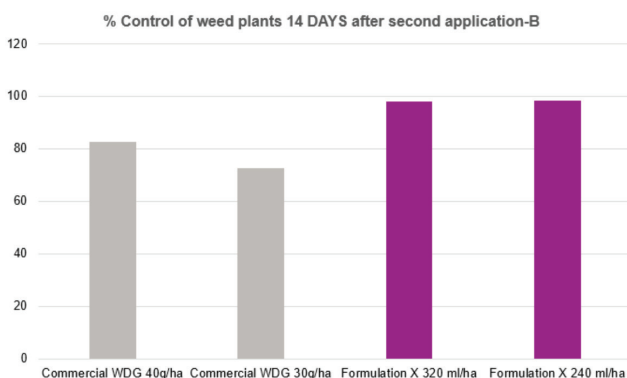


Figure 5. Formulation 2 against WDG formulation commercial standard on weed on potatoes

The results also show that OD in general can outperform the WP formulations with the same active. The OD is therefore a tool to reduce chemical actives and a modern answer to a better environmental impact when using the latter. The oil enhancer even improves this fact. It is essential that the oil enhancer is a good dispersible and soluble in the oil to provide this effect.

Formulation 2 was applied (2 times) in a field trial on potatoes against weed (TTTTT) and compared versus a commercial water dispersible granule formulation. After 14 days formulation 2 shows weed control close to 100% even at reduced treat rate of 240 ml/ha (30 g active ingredient)

In conclusion for actives which are formulated with oils, ranging from mineral to different kind of vegetable oils, the performance can be enhanced by oil enhancers. These kinds of BREAK-THRU® OE additives increase the spreading area of an oil-based formulations on the surface of the leaf and at the same time accelerate the up-take. Thus, use of oil enhancers upgrades the performance of formulations which contain oils. In addition, they stabilize OD formulations and can also reduce crystal growths and agglomeration of actives on the leaf. This leads finally to increased biological efficacy.



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