

Mechanisms for adjuvancy in agrochemicals, and their role in formulation

Dr David Calvert
iFormulate Limited

www.iformulate.biz

David@iformulate.biz

Programme

- Adjuvants
 - Definitions
 - Functions
 - Suppliers
 - Mechanisms
- Spraying
 - Process
 - Problems
 - Formulation Options
 - Drift
 - Spray retention and Spreading

Adjuvants: Definitions

- Various definitions, e.g. UK Crop Protection Directorate:
 - *"a substance other than water which is **not in itself a pesticide** but which enhances or is intended to **enhance the effectiveness** of the pesticide with which it is used"*
- An adjuvant can be built into the formulation or a separate tank-mix additive for the spray tank.



Adjuvants: Definitions

- International Society for Agrochemical Adjuvants (ISAA):
 - “An adjuvant is a substance **without significant pesticide properties**, added to a agricultural composition to aid or modify the activity of this chemical” where the **function of the adjuvant** can be emission reduction, wetting of the target plant, make-up of the drop deposit (for example humectancy and solubility), increased uptake of the pesticide into the target, improved rainfastness, reduced antagonist effect, **overcoming compatibility problems and/or foam reduction.**”
- ASTM Definition:
 - “adjuvant is a material added to a tank mix to **aid or modify the action of an agrichemical**, or the **physical characteristics of the mixture.**”
 - ASTM E1519 “Standard Terminology Relating to Agricultural Tank Mix Adjuvants”

Classification of Adjuvants

Activator Adjuvants

- Enhance the AI activity
 - Surfactants
 - Oil Adjuvants
 - Crop Oil Concentrates
 - Fertilizers?

Utility Adjuvants

- Modify the physical properties of the spray liquid
 - Spreaders
 - Drift control
 - Stickers
 - Water conditioners
 - Humectants
 - Foaming Agents
 - UV absorbents

What About Formulants, Safeners and Synergists?

- **(Co-)Formulants**
 - Material added during (formulation) manufacture of the agrochemical to provide a specific function, or to improve its performance or stability
 - A formulants **may** have an **adjuvancy** function (i.e. to improve the product performance **when it is used**)
 - A formulant **may also** provide the product with the desired properties **before use** (stability, compatibility, handling etc)
- **Safeners**
 - Used to protect crops from damage by herbicides. Usually have a specific biological mode of action. May be added to formulation
- **Synergists**
 - Components of pesticide treatment that enhances efficacy of AI by a specific biological mechanism, usually inhibiting detoxifying enzymes
- **Tank Adjuvants**
 - A material **added to the tank mix** to aid or modify the action of an agrochemical or the physical characteristics of a mixture

CATEGORIES AND FUNCTIONS OF ADJUVANTS

Main Functions of Adjuvants (from UK Pesticide Guide 2016)

- Acidifier (3)
- Activator (3)
- Adjuvant (17)
- Anti-Drift Agent (9)
- Anti-Transpirant (9)
- Buffering Agent (1)
- Carrier, Cationic Surfactant, Coating Agent, Compatability Agent, Deposition Agent (0)
- Drift Retardant (4)
- **Extender (21)**
- Fertilizer (1)
- Fogging Agent (0)
- Mineral Oil (11)
- Non-ionic Surfactant (9)
- Penetrant (13)
- **Spreader (67)**
- **Sticker (47)**
- Surfactant (2)
- UV Screen (9)
- Vegetable Oil (18)
- Water Conditioner (4)
- **Wetter (99)**

Some adjuvants listed in numerous categories.
Numbers are total listed in each category

EPA Adjuvant Examples

Acidifying Agents

Buffering Agents

Anti-foam Agents

Defoaming Agents

Anti-transpirants

Dyes and Brighteners

Compatibility Agents

Crop Oil Concentrates

Oil Surfactants

Deposition Agents

Drift Reduction Agents

Foam Markers

Feeding Stimulants

Herbicide Safeners

Spreaders

Extenders

Adhesive Agents

Suspension Agents

Gelling Agents

Synergists

Wetting Agents

Emulsifiers

Dispersing Agents

Penetrants

Tank and Equipment Cleaners

Neutralisers

Water Absorbents

Water Softeners.

Some Adjuvant Suppliers*

Amega, Clayton, Petro-Lube, Agrovista, De Sangosse, Intracrop, Helena, United Agri, Headland, Microcide, Taminco, Certis, Barclay, Interagro, Nufarm, Pan Agriculture, BASF, Plant Solutions, Koppert, Greenaway, Syngenta, PP Products, AgChem Access, Akzo Nobel, Croda, Dow, AgroSciences, Adjuvant Plus Inc, Brandt Consolidated, Clariant International, Lamberti SpA, Momentive Performance Materials, Solvay SA, Tanatex Chemicals BV, Borregaard, Aceto Agricultural Corp, Adjuvants Unlimited, Agmarket Results, Albaugh Inc, Ashland Inc, Chemorse, Compliance Services Int., Ensafe, Ethox, Evonik Corporation, Exacto Inc., ExcelAg Corp, Exponent, Exxon Mobil Chemical, Fina Americas, Garrco Products, Glysortia, Huntsman Corp, Kalo, Keller and Heckman, Kincannon and Reed, KRS Inc, Landis International, Lonza Agro Ingredients, Oleon, Oro Agri, Oxiteno, Precision Laboratories, Rosens, Royal Chemical, Sipcam Advan, Spring Trading Company, Stepan Company, Stillmeadow Inc., Technology Sciences Group, Tide International USA Inc, United Suppliers, Vive Crop Protection, Wilbur-Ellis Company, Winfield Solutions, Miller Chemical, Max Systems LLC, J.R. Simplot, BioSafe Systems, WinField, Borregaard

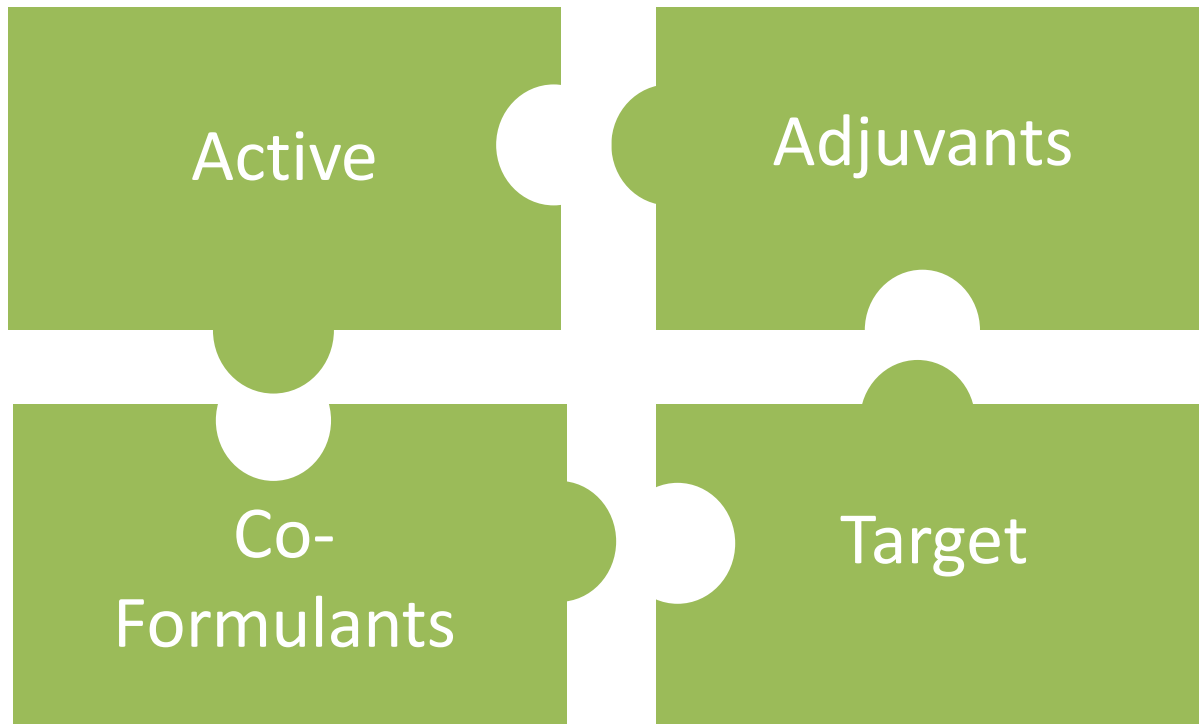
*Not fully comprehensive

Adjuvant and Formulants: General Comments on Market Needs

- No obvious gaps in adjuvant function but current solutions are always capable of being improved
- Major pesticide suppliers are continually developing new “in-formulation” adjuvant solutions
 - Often these are not apparent as they do not appear on a label
 - Main need is for performance at **lower adjuvant concentrations** – leaving more room in formulation and potentially lower costs
 - Available “room” within the formulation is a major issue – multifunctionality is an advantage
 - Criteria are mostly obvious: Biological performance, environmental or human safety and acceptability, cost:performance ratio
- Tank adjuvants also remain an area of development
 - The drivers are essentially similar although the room within the formulation is not an issue

MECHANISMS

The Right Combination



Adjuvants: Mechanisms

Multiple Mechanisms: Complex Topic

- **Enhancing spray performance, wetting, coverage and initial adhesion**
 - Stickers, spreader – stickers, foaming agents, drift control agents
- **Enhancing uptake by leaf** → mechanism depends on physicochemical properties of the AI)
 - May minimise potential loss mechanisms, e.g. rainfastness of foliar fungicides,
 - For systemic herbicides, fungicides, insecticides (i.e. which are delivered within the plant) enhanced uptake (penetration) and translocation can reduce wash-off and loss of activity
 - Surfactants, crop oil concentrates, water conditioners

“Different surfactants do different things to different agrochemicals on different target species” Stock and Holloway 1993 (not that much has changed!)

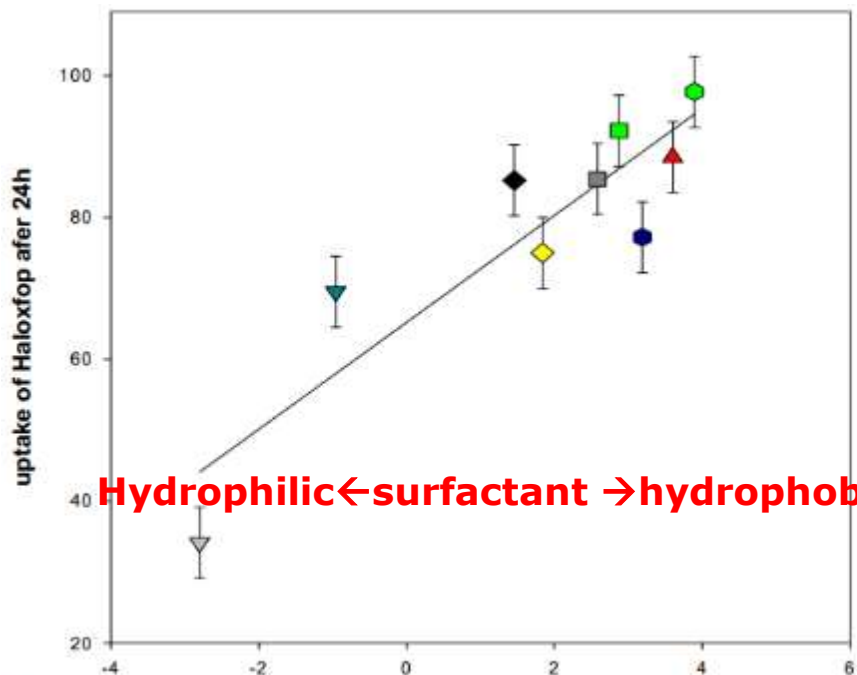
Adjuvants: Mechanisms

Comparison of uptake data:

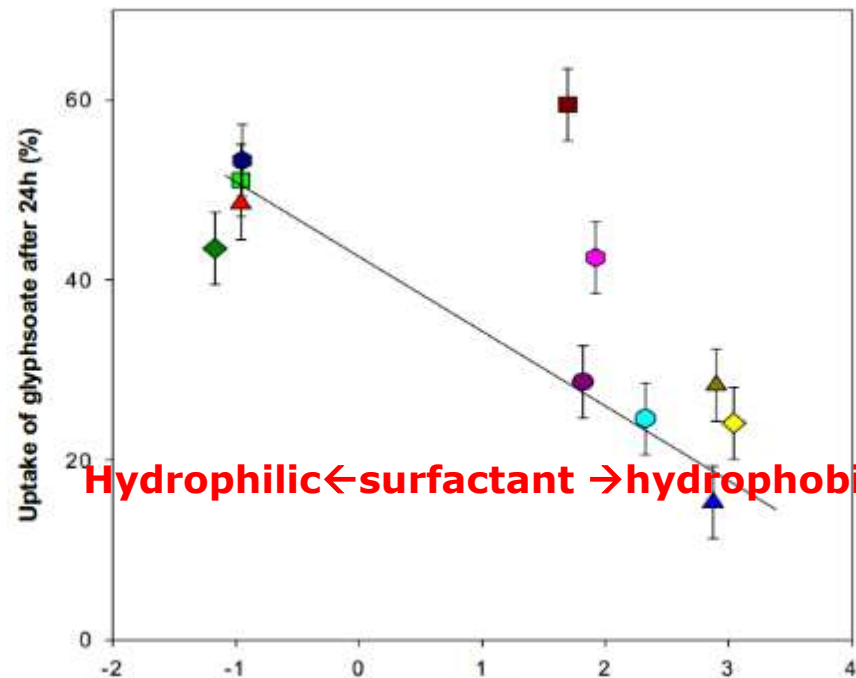
Glyphosate (hydrophilic) and Haloxyfop-methyl (hydrophobic)

Source: Croda technical presentation, H.Rieffe 2008

Haloxyfop-methyl (hydrophobic)

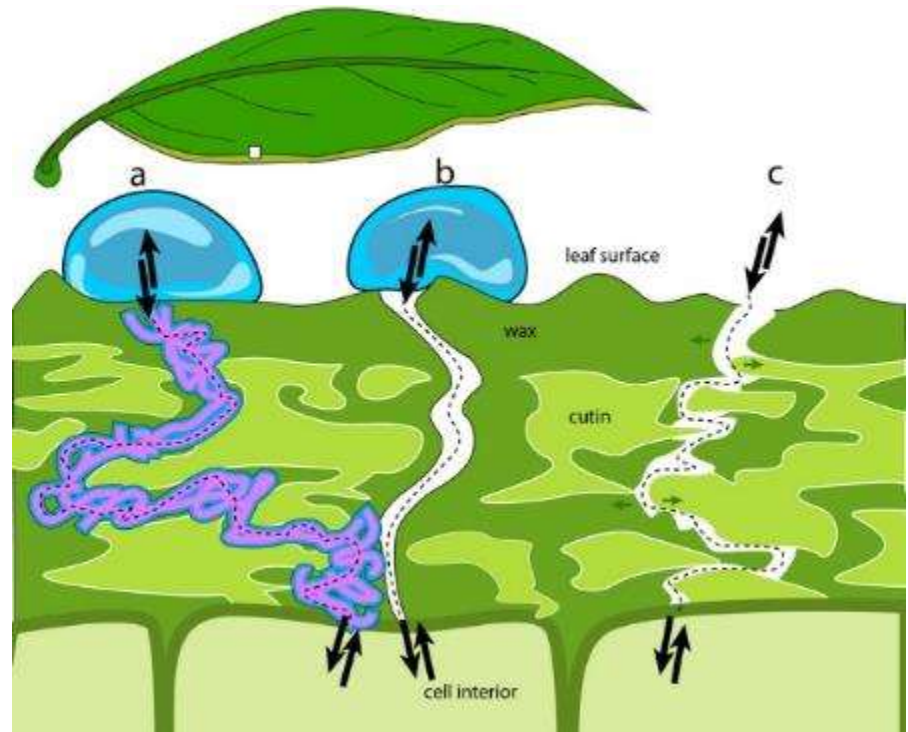


Glyphosate (hydrophilic)



The Leaf Cuticle

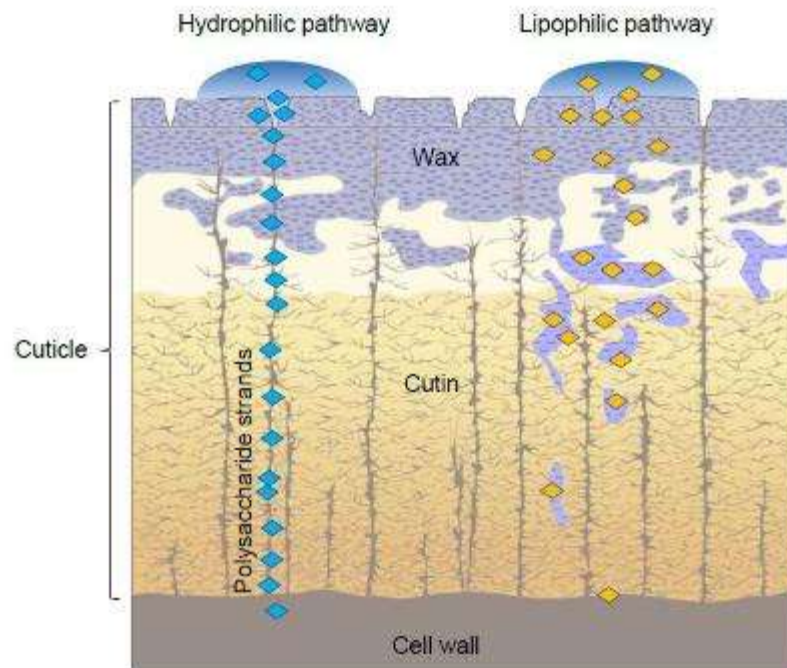
- Wax
 - Long Hydrocarbon Chains
 - Lipophilic
- Cutin
 - Intermediate length (C16-C18) hydrocarbon fatty acids
 - Lipophilic but contains some free carboxyl and hydroxyl groups that ionise in water
- Pectin
 - Polymers of galacturonic acid
 - Forms strands that are hydrophilic



<https://asknature.org/strategy/leaf-cuticle-allows-select-chemicals-to-pass/#.WMfhgTvyhPY>

Delivery Pathways

- Lipophilic pathway (orange diamonds) helped by compounds that have a plasticising effect
- Hydrophilic route across polysaccharide strands
- Hygroscopic substances (humectants) hydrate droplet deposit by attracting water from atmosphere
 - AI uptake via hydrophilic route
 - So what are properties of adjuvant for glyphosate?



E. Asmus and M. Riederer – University of Wurzburg

SPRAYING

Formulation Spray – Key Steps in the ‘Biodelivery’ Process

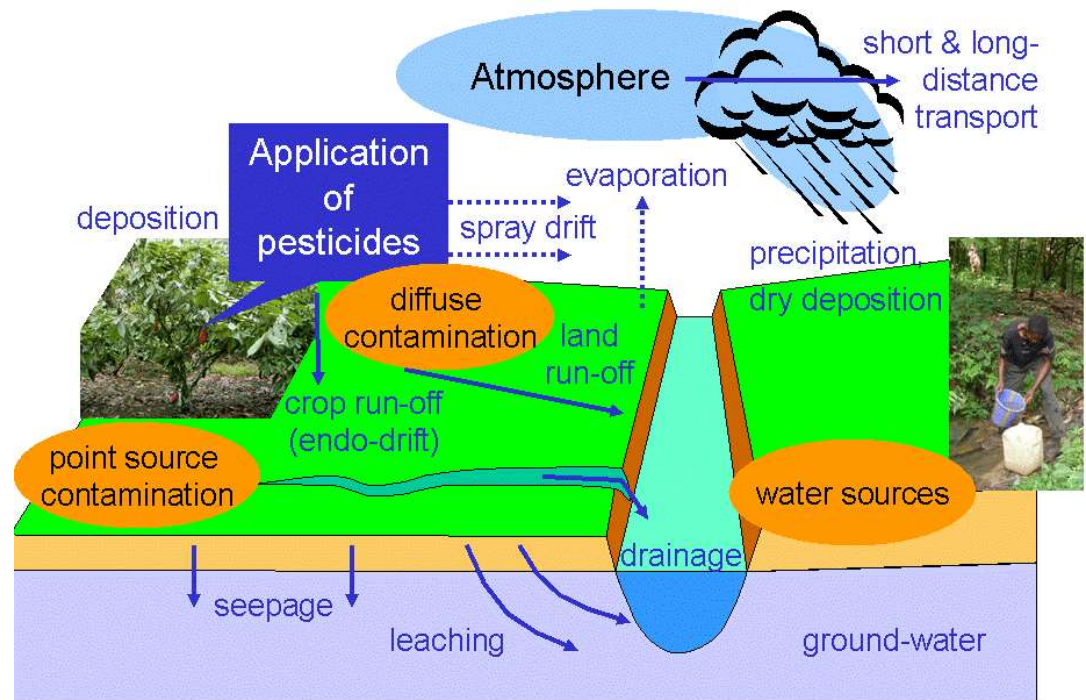
(for the case of plant mobile active ingredients)



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Leaf Spray Deposit

- Getting the formulation to the leaf
- Main issue?
 - Spray Drift



By Roy Bateman at English Wikipedia, CC BY-SA 3.0,
<https://commons.wikimedia.org/w/index.php?curid=11923365>

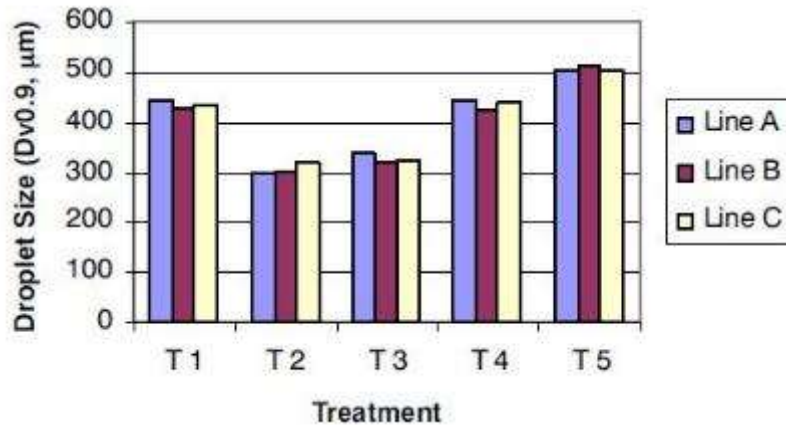
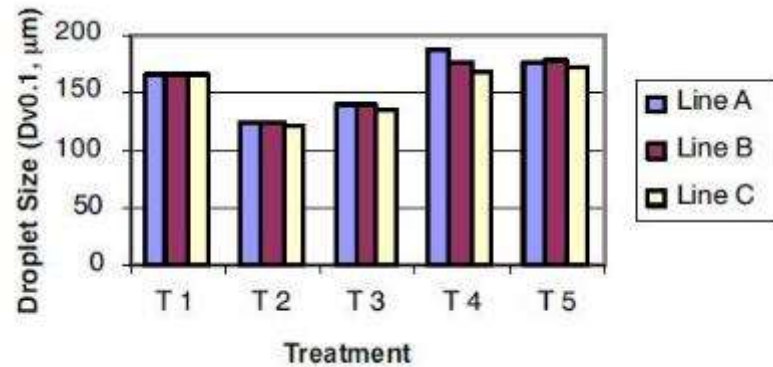
Causes of Spray Drift

- Wind velocity at spray nozzle height
- Atmospheric conditions
- Wrong nozzles or pressure choice
- Vehicle speed
- Boom height
- Equipment maintenance/setting

Preventing Drift

- Check weather conditions
- Keep spray boom low
- Spray angles and height
- Coarsest possible spray quality
- Reduce pressure and forward speed
- Formulation!!!

Increasing Droplet Size*



Treatment	Adjuvant	Company
T1	Array	Rosen's Inc
T2	EC Blank Only	Exxon/Stepan
T3	In-Place	Wilbur-Ellis Inc
T4	Vector	Rosen's Inc
T5	Control	GarrCo Products Inc

*Y. Lan et al; Spray Drift Mitigation with Spray Mix Adjuvants; Applied Engineering in Agriculture Vol 24 (1): 5-10; 2008

Chemistry of Anti-Drift Products

- Water soluble synthetic polymers
- Polyacrylamides
- Polyvinylpolymers
- Gums/Thickeners
- Surfactants

Anti-Drift Products

- Intracrop Driftless
 - “Unique Polymeric Material which decreases the number of small fine driftable droplets”
 - <http://www.intracrop.co.uk/anti-drift.php>
- Brandt 38-F[®]
 - Liquid 32% active polyacrylamide
 - <http://www.brandt.co/categories/adjuvants-and-application-aids/>
- Helena Chemical StrikeZone[®] DF
 - Blend of non-ionic polymers
 - <http://www.helenachemical.com/upl/downloads/products/strike-zone-df-flyer.pdf>

Formulation Spray – Key Steps in the ‘Biodelivery’ Process

(for the case of plant mobile active ingredients)



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Spray Retention

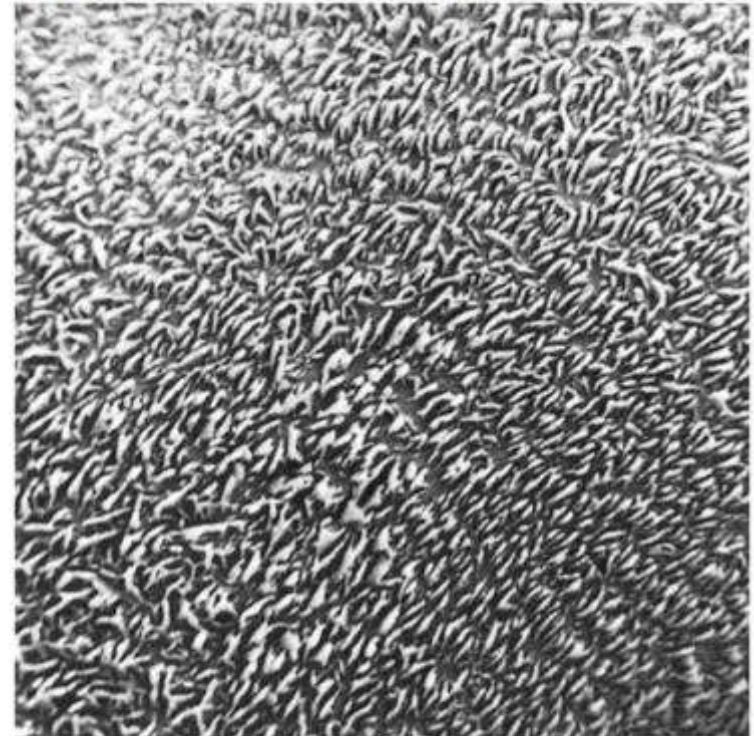
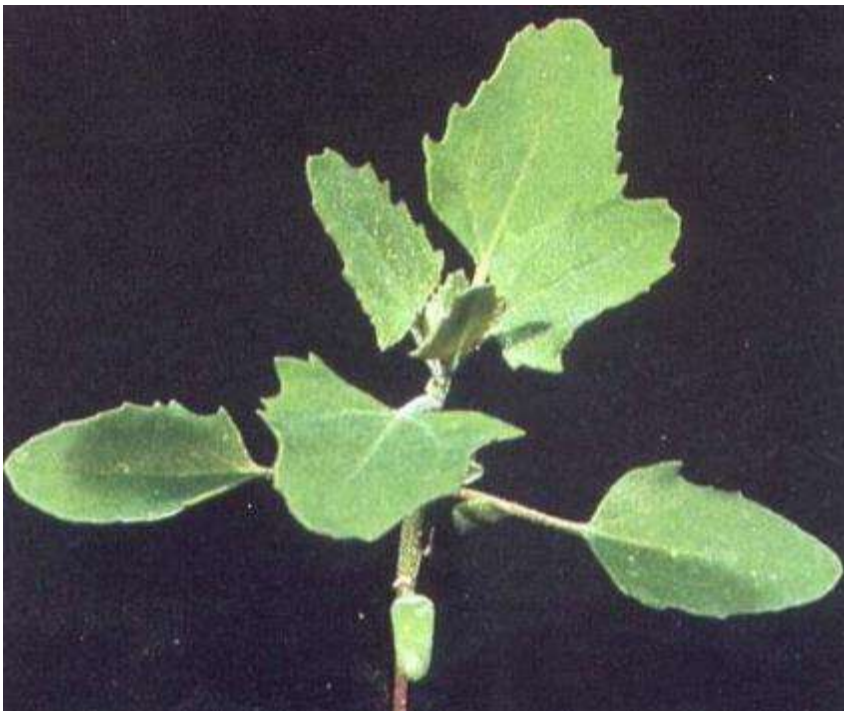
- Surface Properties of Leaf and Dynamic Contact Angle of Droplet on the Leaf
- Dynamic Surface Tension of Spray Solution
- Droplet Velocity and Size
- Adjuvant Type and Concentration of the Spray Volume
- Plant Density and Canopy Structure

Deposit Wetting and Spreading

- Key role for surfactants
 - In-can
 - Tank-mix
- A dynamic process
- Not all leaves are the same

Common Lambsquarters*

Scanning electron microscope – 3500X



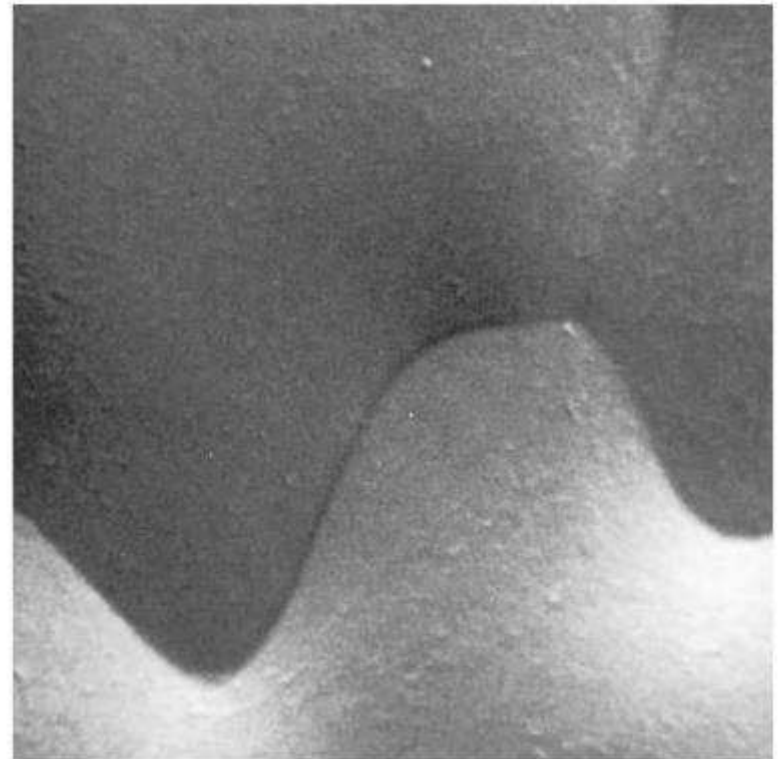
Note epicuticular wax

*<https://cals.arizona.edu/crop/presentations/2003/mccloskey092403.pdf>

Redroot Pigweed*



Scanning electron microscope – 3500X

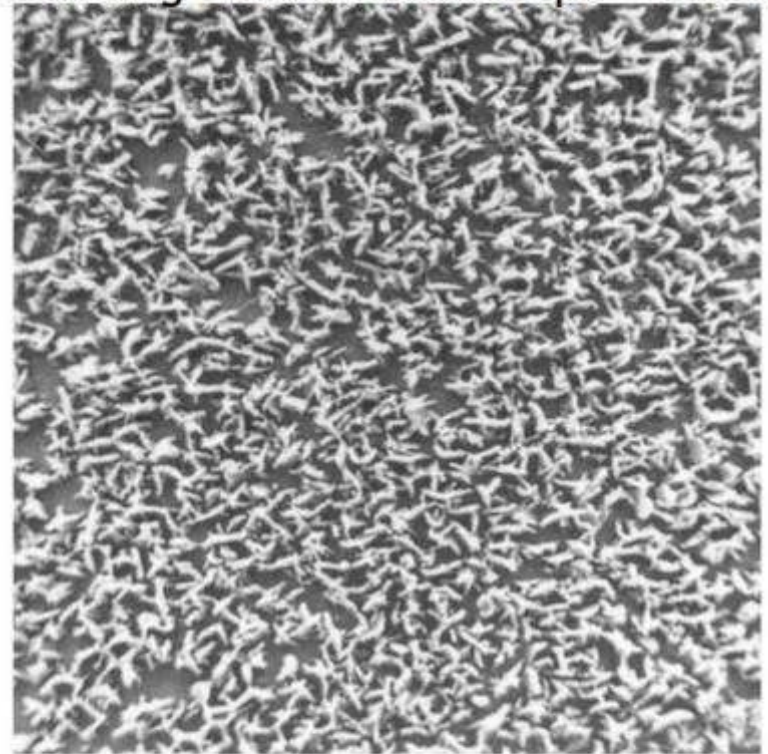


*<https://cals.arizona.edu/crop/presentations/2003/mccloskey092403.pdf>

Johnsongrass*



Scanning electron microscope – 3500X



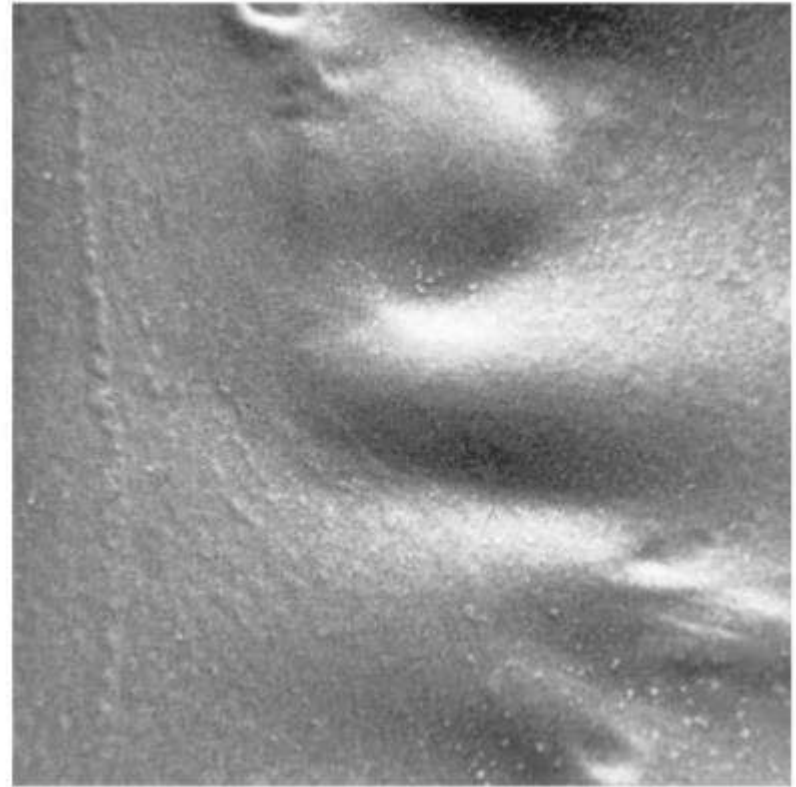
Note epicuticular wax that is characteristic of many grasses.

*<https://cals.arizona.edu/crop/presentations/2003/mccloskey092403.pdf>

Purple nutsedge*

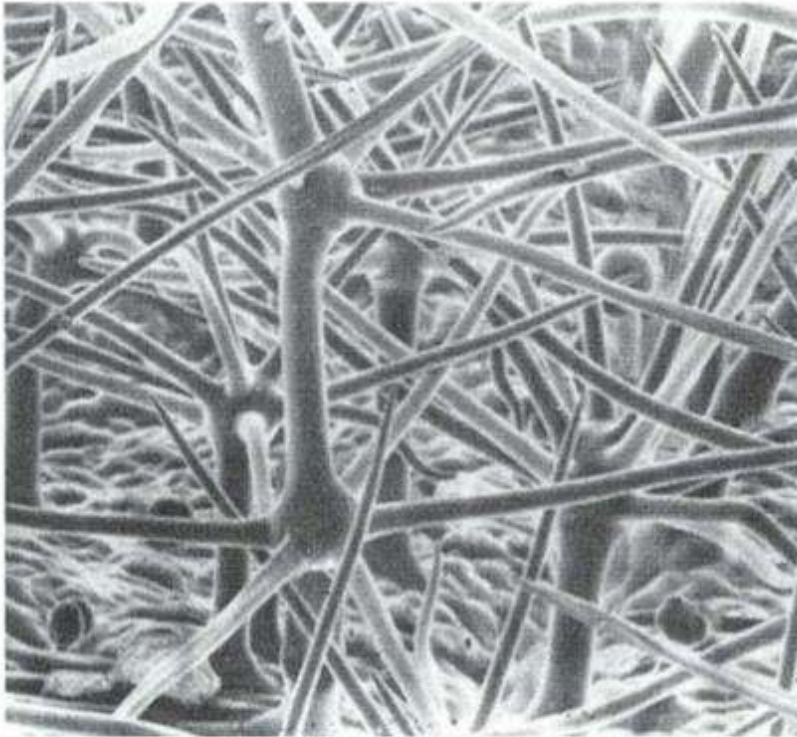


Scanning electron microscope – 3500X

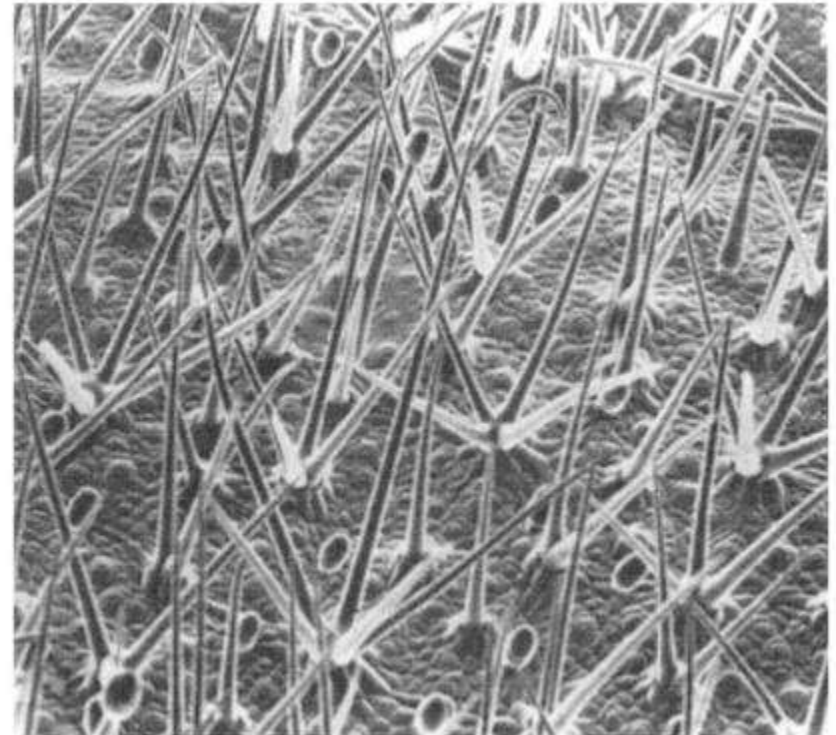


*<https://cals.arizona.edu/crop/presentations/2003/mccloskey092403.pdf>

Hairy Leaves*



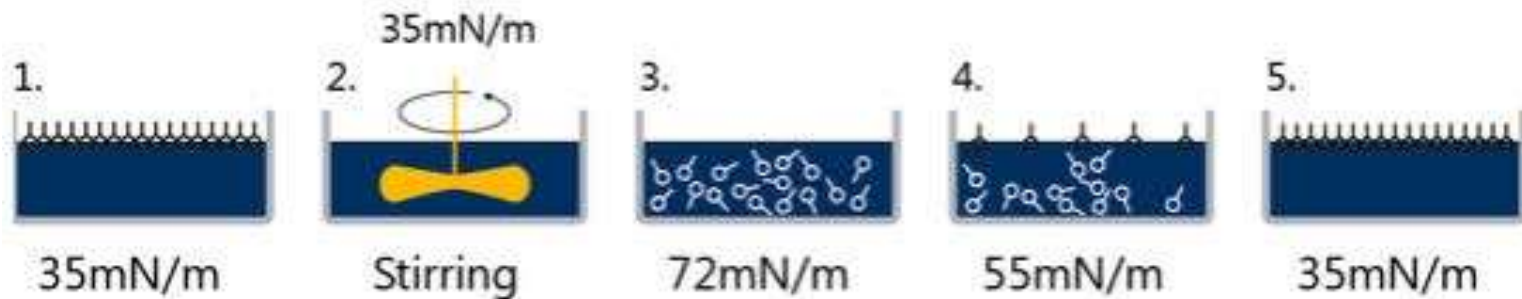
Trichomes (hairs) on common mullein



Trichomes (hairs) on velvetleaf

*<https://cals.arizona.edu/crop/presentations/2003/mccloskey092403.pdf>

Surfactant Mobility*



At equilibrium, surfactants may appear the same
When disturbed, mobility to the air liquid interface differs (dynamic surface tension)

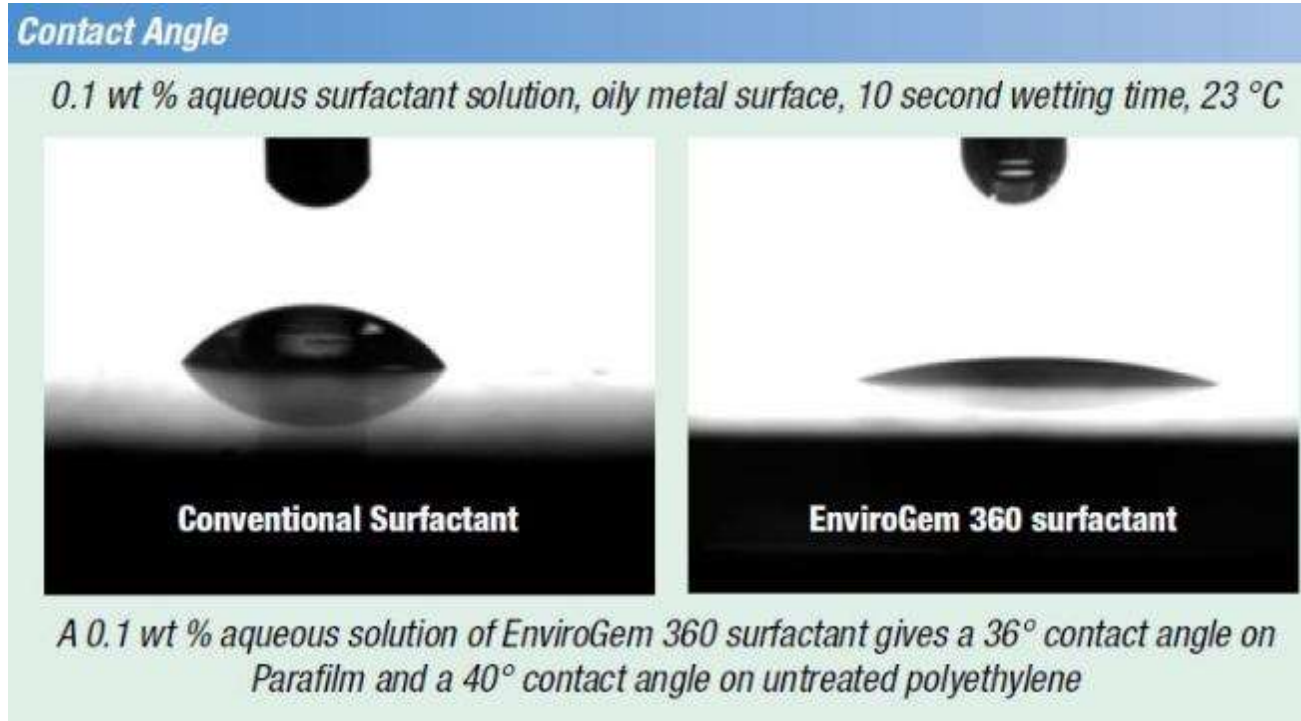
In spraying two stages

After leaving spray head

When landing on the leaf

* <https://www.kruss.de/services/education-theory/glossary/dynamic-surface-tension/>

Drop Spreading



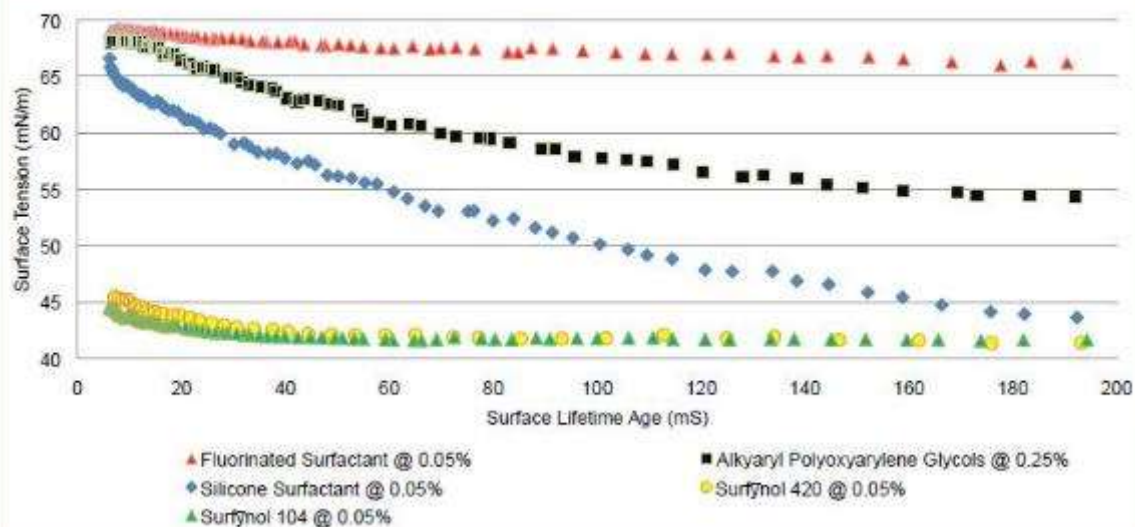
<http://www.airproducts.co.uk/~media/Files/PDF/industries/chemicals-agrochemical-adjuvants-guide.pdf>

Drop Spreading

Surface Age of droplets at leaf impact can be less than 60ms

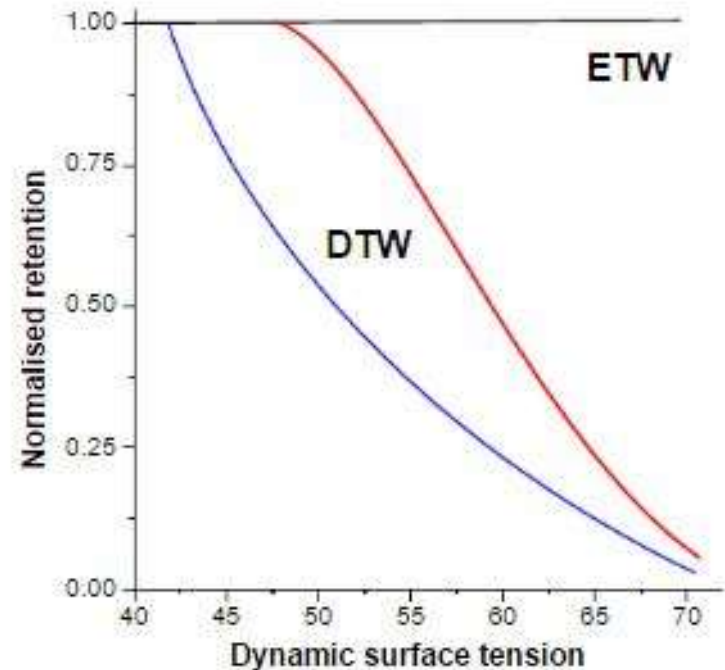
<http://www.airproducts.co.uk/~media/Files/PDF/industries/chemicals-agrochemical-adjuvants-guide.pdf>

Comparison of Dynamic Surface Tension Profiles of Surfynol 104, Surfynol 420 and Commercial Benchmark Surfactants



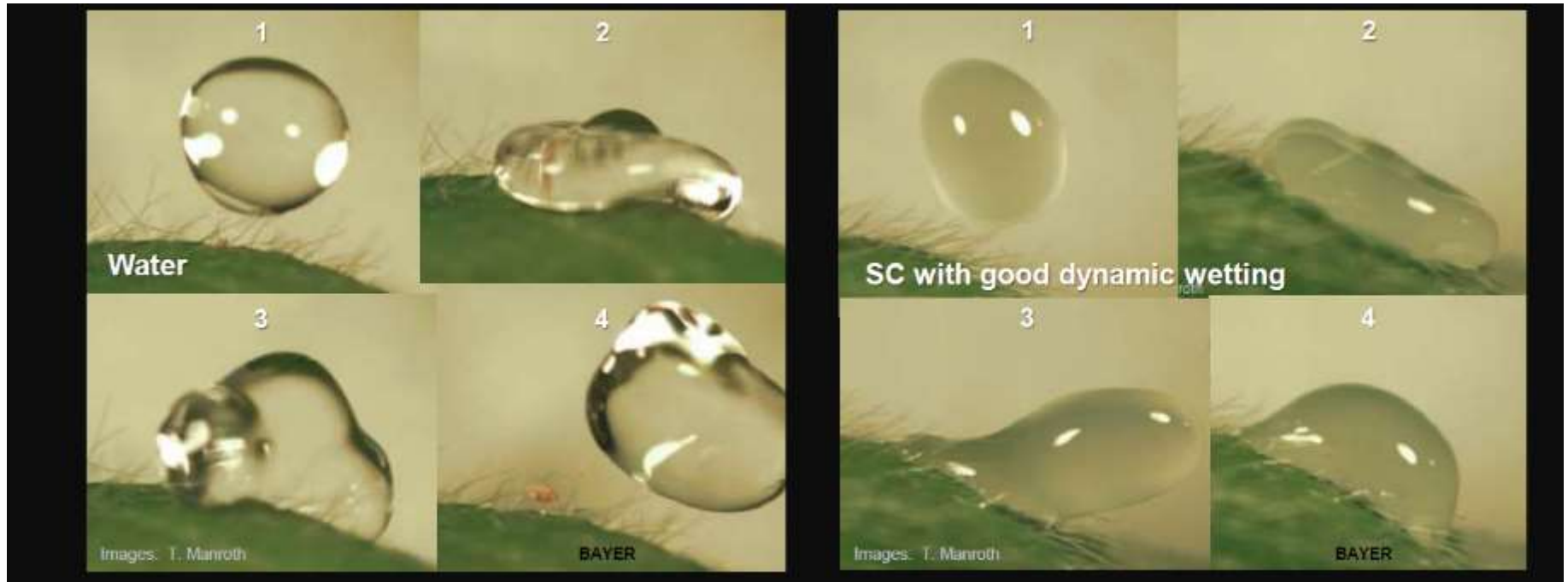
Dynamic Surface Tension

- Influence of Dynamic Surface Tension dependent on substrate
- Easy to wet (eg vine) no effect
- Difficult to wet (barnyard grass) a distinct effect of dynamic surface tension



*P. Taylor Current Opinion in Colloid and Interface Science 16 (2011) 326 - 334

Spray Retention and Dynamic Wetting



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Wetting on Leaves with MSO Adjuvant

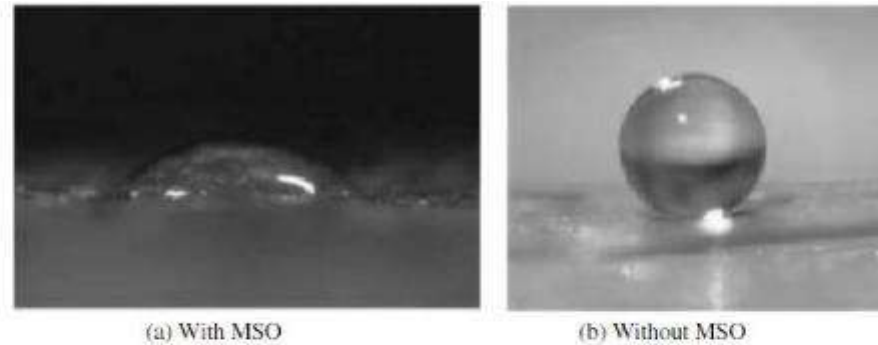


Figure 3. A 500 µm water droplet (a) with and (b) without the adjuvant MSO on the surface of a waxy leaf.

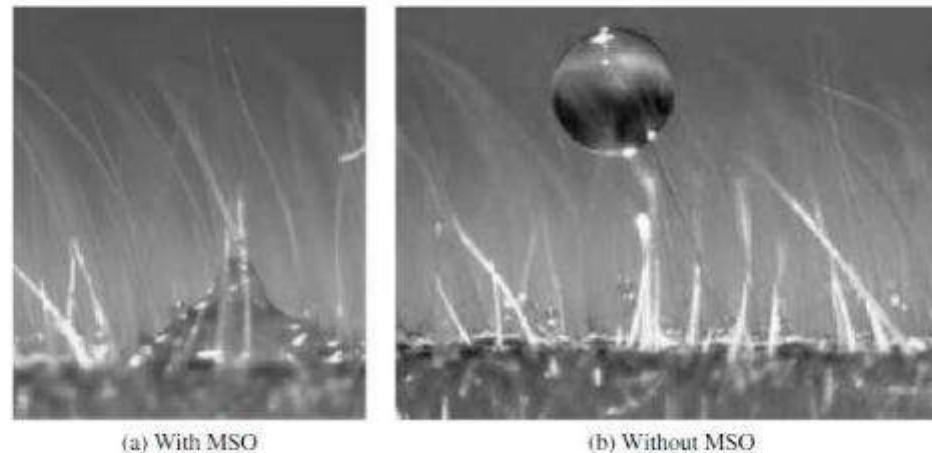


Figure 4. A 500 µm water droplet (a) with and (b) without the adjuvant MSO on the surface of a hairy leaf.

Xu, Linyun et al, Pest Management Science Volume 67 (7) 2011

Formulation Spray – Key Steps in the ‘Biodelivery’ Process

(for the case of plant mobile active ingredients)

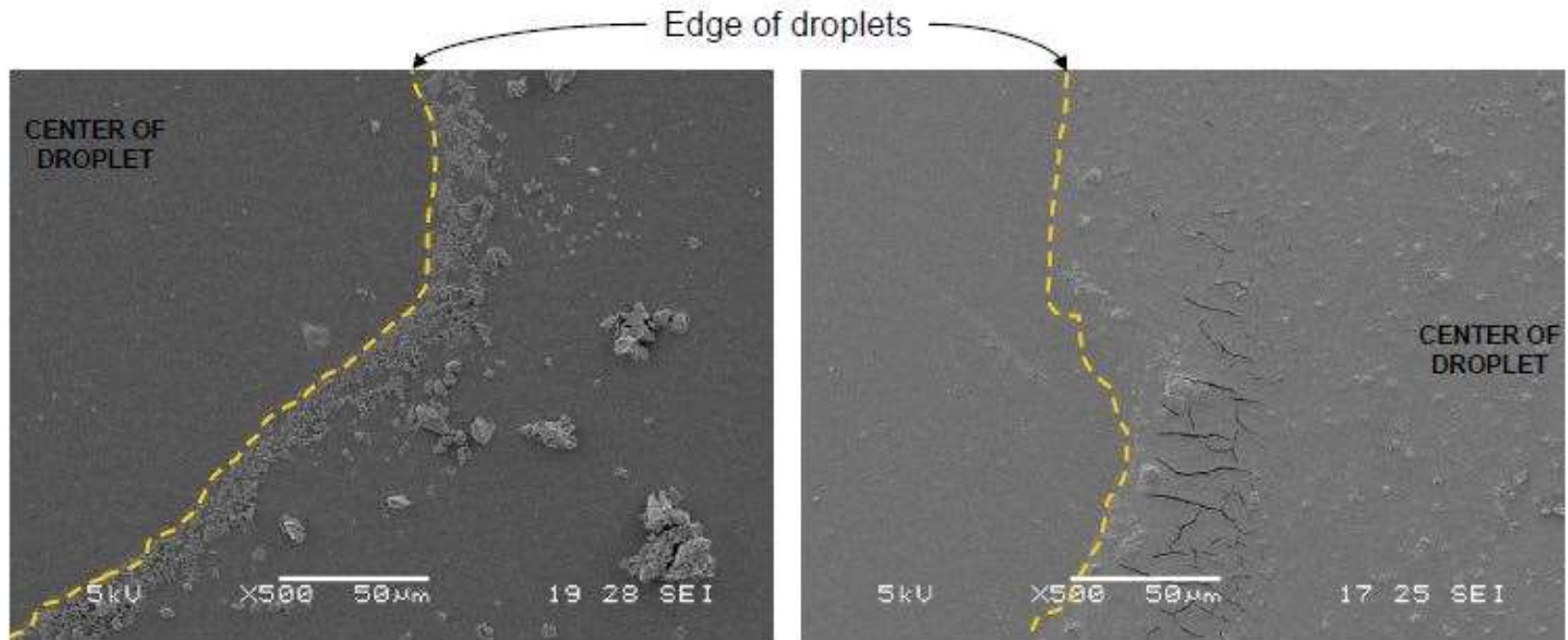


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Deposit Dry Down

- Traditional assumptions
- Higher coverage = higher performance
- Better uptake as deposit area increases
- Is consistent (homogeneous) coverage desirable?

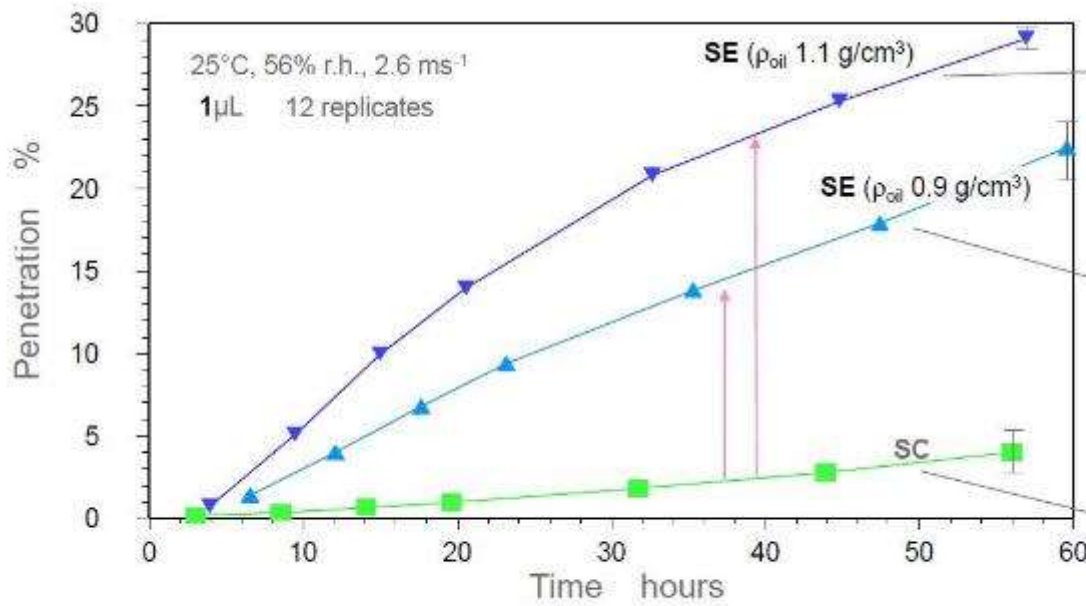
Deposit Formation



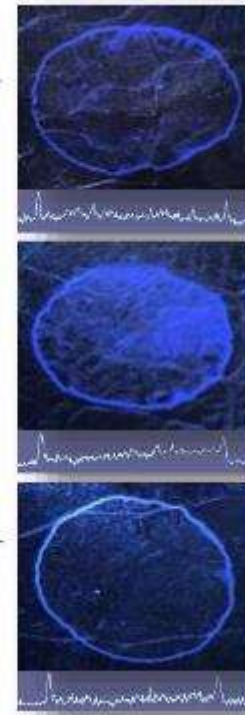
With this SC formulation, Al crystals segregate to periphery of droplet, and dry in a classic “coffee ring.”

With this SC formulation, Al crystals are more evenly dispersed and trapped within a complex formed by formulation additives.

Cuticle Penetration



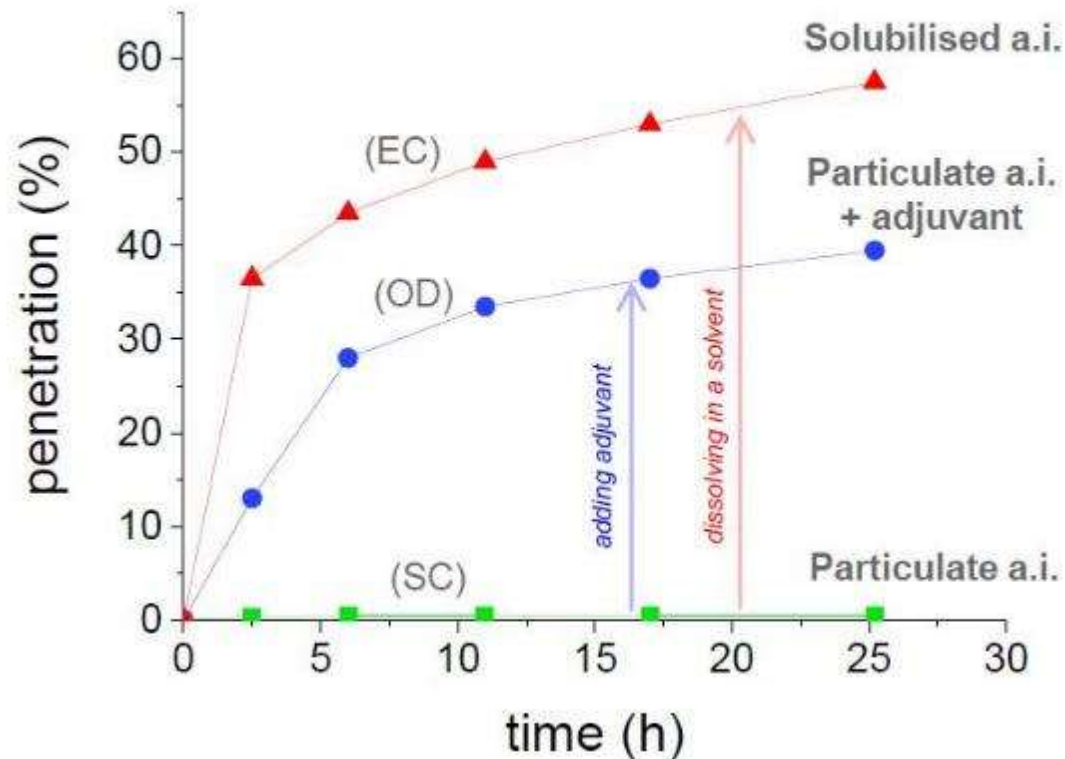
- Addition of oil results in a large increase in penetration
- The location of the oil is significant, in annulus > in centre



M Faers, K Tsangaris, R Pontzen & A Bismarck, ISAA2010

Penetration/Uptake

Cuticle penetration studies from an a.i. in different formulation systems



(a.i. = active ingredient)

Ref: R Pontzen, BCS

Summary

- Adjuvants a key area for Agrochemical Formulation
 - Spray Drift
 - Deposit Formation
 - Penetration
 - Uptake
 - Processing
- Will increase in importance with less new active ingredients
- Science developing and challenging established “knowledge”