webinar will start at

Gaylord Chemical Company, L.L.C.

iFormulate

Welcome

The webinar will start at 3 PM CET | 9 AM EST | 8 AM CST | 6 AM PST | 2 PM UK.

Tuesday 25 February

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Change, Change, Change

A new option for Liquid Agrochemical Reformulation

Tuesday 25 February

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Programme for Today

- Introductions
- Use of solvents in agrochemicals
- Hansen Solubility Parameters for Agrochemical solvents
- DMSO in Agrochemicals
- Wrap-up and Q&A

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Today's Speakers

Dr. David Calvert
Director at iFormulate Limited

Dr. Jim Bullock
Director at iFormulate Limited

Dr. Artie McKim
Vice President of Technology at Gaylord Chemical Company

Mick Sadoudi
Director of Business Development at Gaylord Chemical Company

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Use of Liquids

Solvents in Agrochemicals

- Soluble Liquids (**SL**)
- Emulsifiable Concentrates (**EC**)
- Oil-in-water Emulsions (**EW**)
- Oil Dispersions (**OD**)
- Suspension Concentrates (**SC**)
- Spray Tank
- Application of Seed Coatings

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Solvent Properties

Solvency!
- Active, Emulsifier, Dispersant

Regulatory Approval
- Health, Safety and Environmental Properties

Miscibility/Compatibility

Post Application
- Penetration profile
- Efficacy

Availability in bulk and at a cost-efficient price

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Typical Solvents

Old and New

Water

Organic Solvents

- Xylene
- NMP

Aromatics

- Different boiling points
- Naphthalene depleted grades (ND)

Oils

- Synthetic and Natural

Blends

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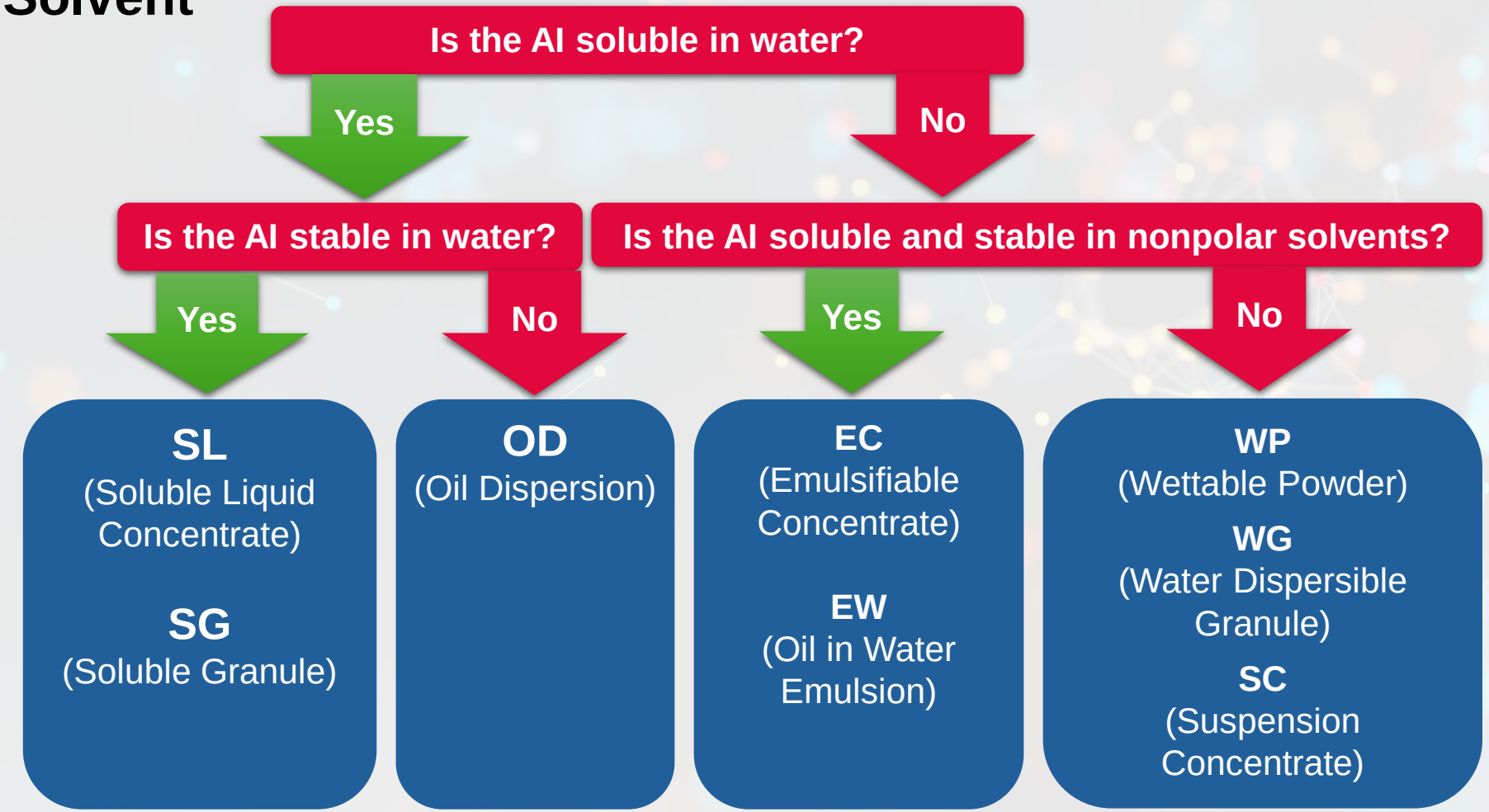
Choice of Formulation

Type/Solvent



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Hansen Solubility Parameters for Agrochemical Solvents

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Solubility:

The Challenge for Agrochemical Formulators

How can I predict solubility well enough to choose new (or replacement) solvents for my active ingredient (AI)?

- E.g. solvents for EC formulations

For a practical formulator “well enough” does not have to mean “perfectly”

Narrowing down the amount of experimental work is often justification enough for a using predictive method.

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Hansen Solubility Parameters:

The Basics 1/2

Simply speaking (i.e. without any mathematics)

- Solubility is all about interactions (or forces, in some case called bonds):
- Interactions between solute and solute molecules
- Interactions between solvent and solvent molecules
- Interactions between solvent and solute molecules

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Hansen Solubility Parameters:

The Basics 2/2

- Thermodynamics tells us:
  - Pulling molecules apart requires energy
  - Attractive interactions between molecules produce energy
  - Systems tend towards their lowest energy (stable) state
- And observation tells us:
  - “Like dissolves like” (e.g. hydrocarbons dissolve other non-polar things, salts dissolve in water)
  - …but how do we measure “like”?

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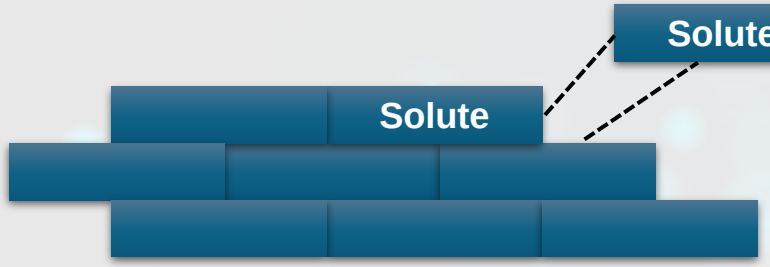
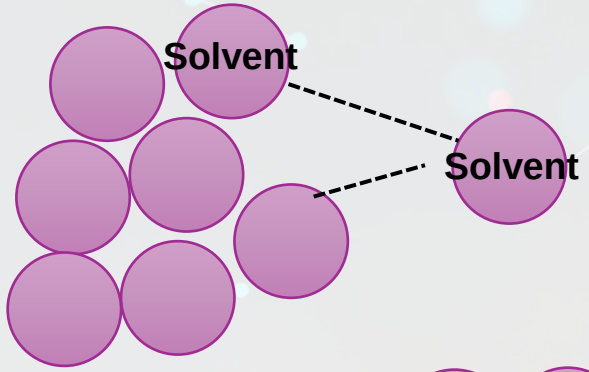
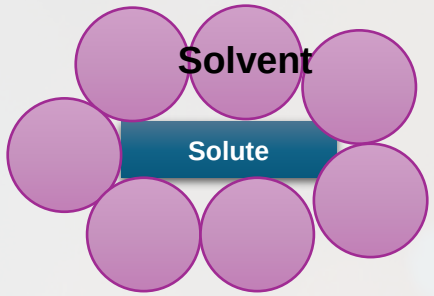
Interactions Between Molecules



Remove solute molecules from the bulk:
Doesn't depend on solvent – doesn't really matter when comparing solvents



Break solvent molecules apart:
Need to know about forces that have to be overcome



Create interaction between solvent and solute molecules: Need to know about types of interactions created

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What Are Those Interactions Anyway?

- Dispersion forces **(D)**
- Polar (dipolar) interactions **(P)**
- Hydrogen bonds **(H)**

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How Do We Quantify

"Like Dissolves Like"

Hansen Solubility Parameters (HSP) quantify the degree of "like" by describing the solvent and the solute using three numbers.

You won't be surprised to hear that these numbers relate to the three types of forces we have just heard about:

δ_D – Measure of dispersion forces (dD)

δ_P – Measure of polar (dipolar) interactions (dP)

δ_H – Measure of hydrogen bonding (dH)

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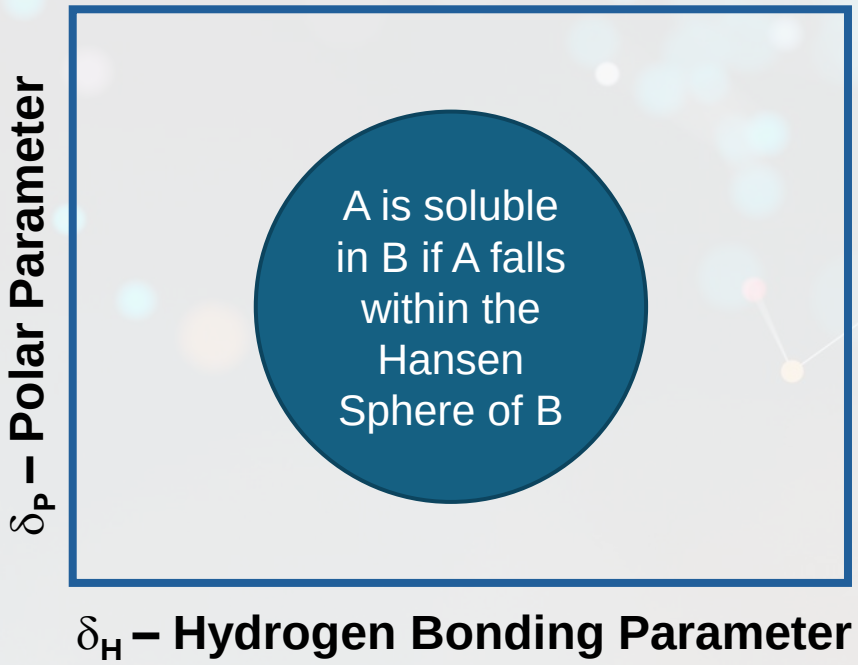
“Like Dissolves Like”

and The Hansen Sphere



In real examples the circle is a sphere, and the third dimension is δ_D the Dispersion Parameter

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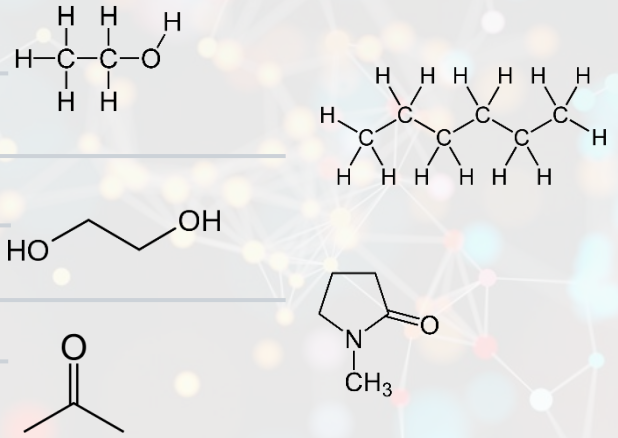
What Are Some Typical HSP Values?

Example HSP values for common solvents – related to molecular structure

Solvent	δ_D	δ_P	δ_H
Ethanol	15.8	8.8	19.4
Hexane	14.9	0	0
Ethylene Glycol	17	11	26
N-Methyl-2-Pyrrolidone	18	12.3	7.2
Acetone	15.5	10.4	7



Limitations – or care needed:

- Water (very small and H-bonding - choose HSP values depending on conc.)
- Ionic or metallic materials (parameters don't describe bonding adequately)
- Complexes or molecular aggregates or ordering (e.g. surfactants)

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How Do I Know What HSP Values To Use?

Literature

- HSP values are published for many common (and uncommon) solvents and other materials

Commercial software

- Extensive databases within the HSPiP software

Estimation from molecular structure

- QSAR methods (also within HSPiP software)
- May need to do this e.g. for your AI

Measurement

- Choose solvents from across Hansen space - construct a Hansen sphere by measuring solubility of an unknown material in a test set of solvents of known HSP
- May need to do this e.g. for your AI

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How Do I Calculate HSP Distance?

- The “Eyeball Method”
- Own spreadsheet or algorithms/macro
- Commercial software

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How Could I Use HSP?

Numerous applications are known from many industries

For agrochemicals (especially EC formulations) these could include:

- Matching solvent(s) to a new AI
- Choosing replacement solvent(s) for an AI
- Choosing a non-solvent (e.g. OD)

Making use of “unexpected” solvent blends

- Mix two “bad” solvents to get a “good” solvent

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A New Option for Liquid Pesticide re(Formulation)

Dr. Artie McKim
Mick Sadoudi

Gaylord Chemical Company

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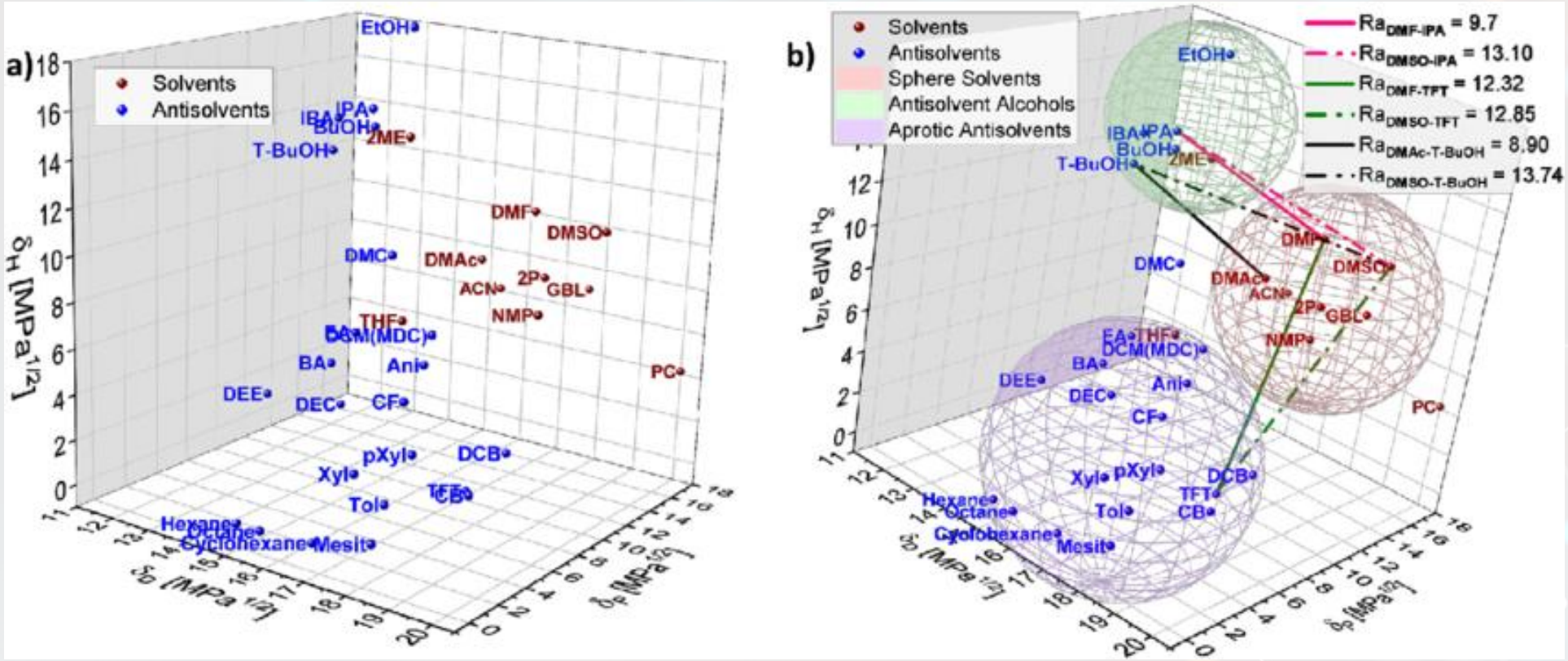
Solvent Selection

for Liquid Delivery Systems



Hansen-solubility-space-including-a-solvents-and-antisolvent-b-spheres-enclosing-the.png (850×358) (researchgate.net)

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Regulatory trends

Amide solvents

EU REACH

Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling			Spec. Conc. Limits, M-factors
				Hazard Class and Category Code(s)	Hazard state-ment code(s)	Pictogram, Signal Word Code(s	Hazard statement code(s)	Suppl. Hazard statement code(s)	
606-021-00-7	N-methyl-2-pyrrolidone; 1-methyl-2-pyrrolidone	212-828-1	872-50-4	Repr. 1B Eye Irrit. 2 STOT SE 3 Skin Irrit. 2	H360D*** H319 H335 H315	GHS08 GHS07 Dgr	H360D*** H319 H335 H315		Repr. 1B; H360D: C ≥ 5 % STOT SE 3; H335: C ≥ 10 %

US EPA

Condition of Use	Action	
Subcategory	Proposed Regulatory Action	Primary Alternative Action
Industrial and commercial use in fertilizer and other agricultural chemical manufacturing, processing aids and solvents	Prohibition	NMP WCPP

1. Proposed Rule ‘N-Methylpyrrolidinone (NMP); Regulation under the Toxic Substances Control Act (TSCA); 4 July 2024 p. 105

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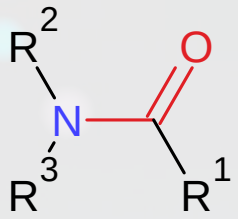
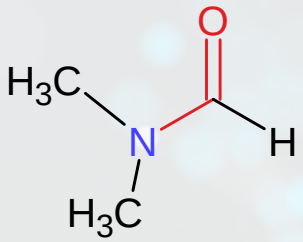
Regulatory trends

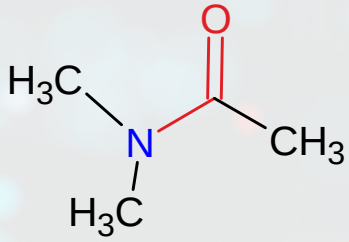
Amide solvents



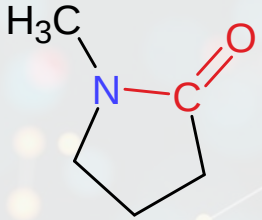
R^1= C_8-$C_{10,}$ -CH_2OH…
R^2= alkyl, morpholino..



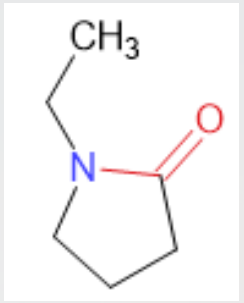
DMF
Dimethylformamide



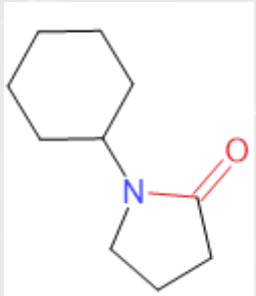
DMAc
Dimethylacetamide



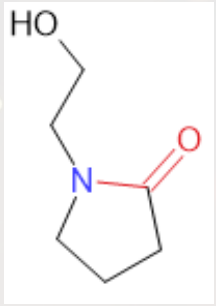
NMP
N-methyl-2-pyrrolidone



NEP
N-ethyl-2-pyrrolidone



CHP
N-Cyclohexyl-2-Pyrrolidone



HEP
Hydroxyethyl-2-Pyrrolidone

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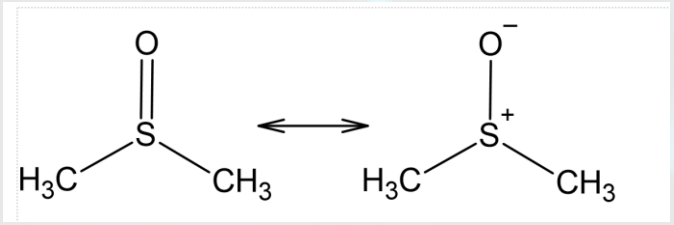
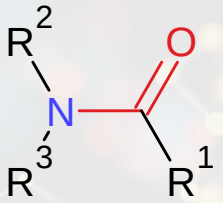
A fresh look at Dimethyl Sulfoxide



AgXalt™

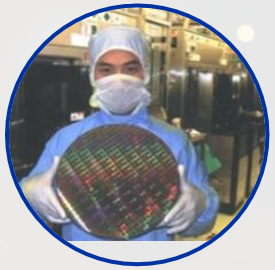


Generic alkylamide

Agriculture

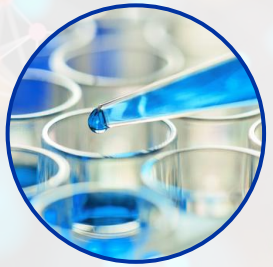
Pharmaceuticals

Coatings



Semiconductors

Carbon Fiber & Polymer Manufacturing



Performance Chemicals

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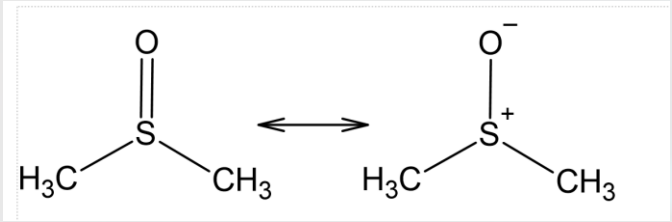
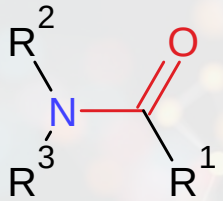
A fresh look at Dimethyl Sulfoxide



AgXalt™



Generic alkylamide

In 2022, US EPA removed all limitations on the use of DMSO as an Inert Ingredient used pre-harvest (40 CFR 180.920).

- Not on the EU's Banned Co-formulant List (referenced in Article 27 of Regulation EC 1107/2009); Authorized PPP co-formulant.
- Becoming the dominant vehicle for urease/nitrification inhibitor formulations
- AgXalt X-100™ is supported with exclusive safety data needed for post emergent registrations

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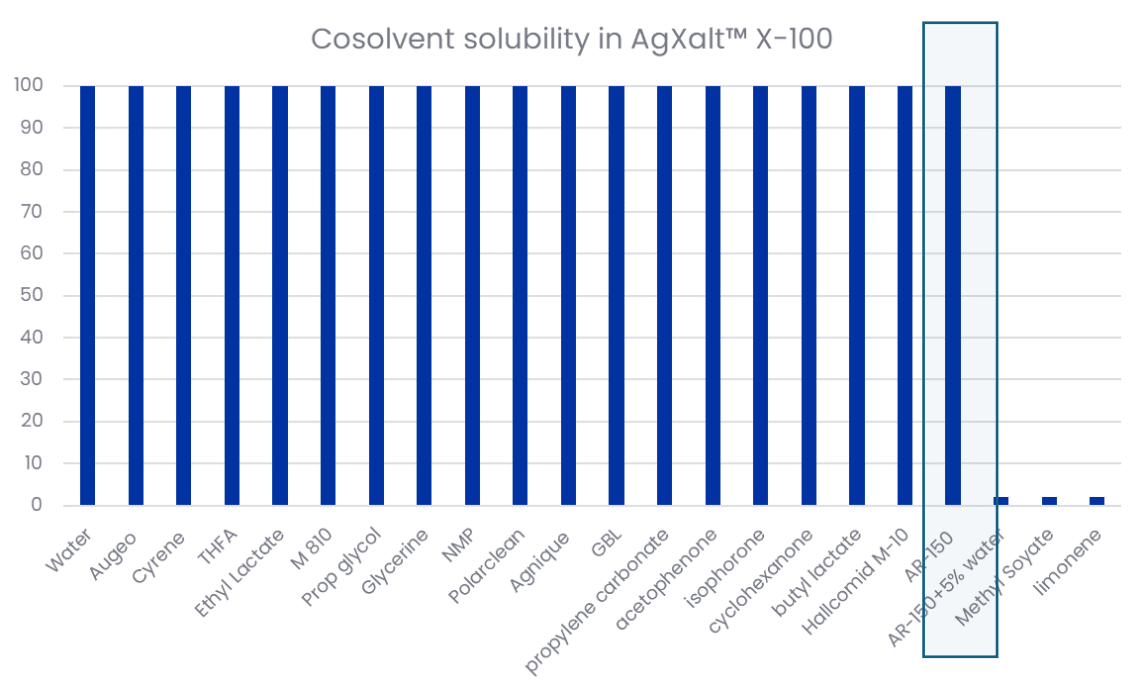
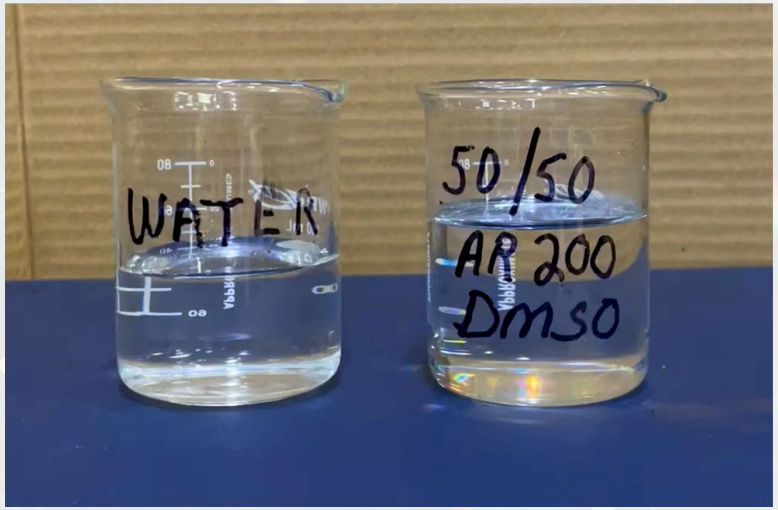
Formulation development





Interestingly, DMSO is miscible in aromatic hydrocarbons …until water is added.

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Emulsifiable Concentrate

Example: Fluoxypyr-Meptyl

NMP Replacement Formulation

	Component	Weight % (wt/wt)
	Fluroxypyr-meptyl, 98.56%	39.87
1.	**AgXalt X-100™**	17.63
2.	Aromatic 200	17.50
	Propylene Glycol	5.00
	Calcium Alkylbenzene Sulfonate	6.00
3.	Fatty Acid Ethoxylate	6.00
	Castor Oil Ethoxylate	8.00

1. ‘Solvency Booster’
2. Serves as ‘oil’ phase in the tank mix
3. Surfactants to form oil/water emulsion, to disperse active for delivery

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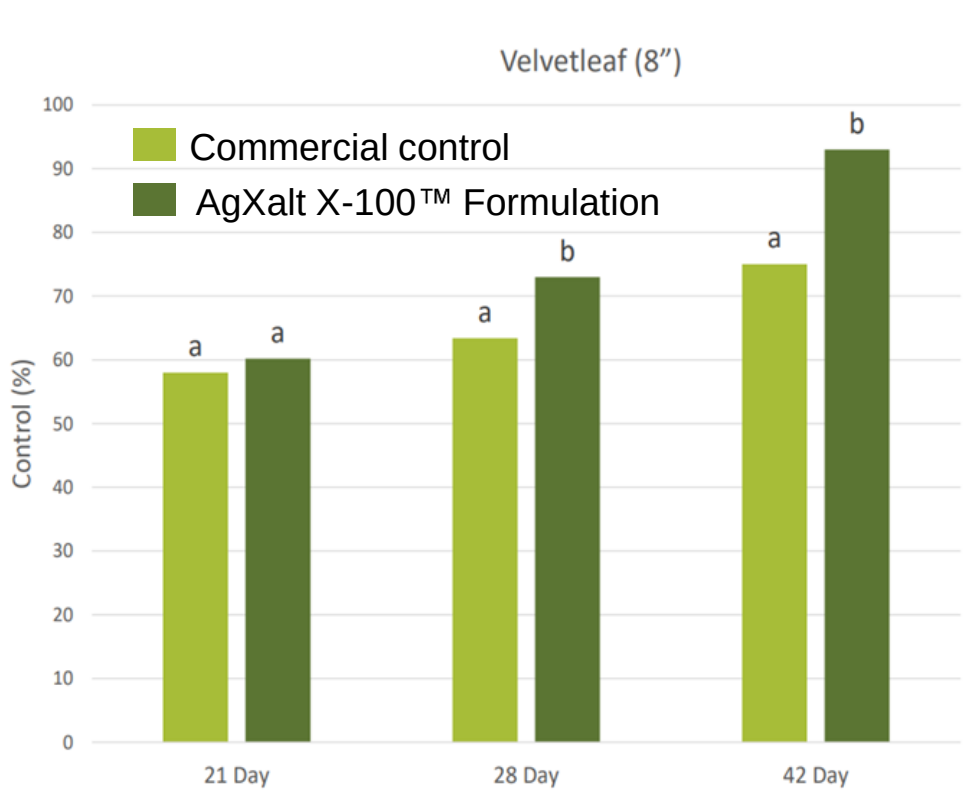
Emulsifiable Concentrate

Example: Fluoxypyr-Meptyl



42 days after treatment: 8" Velvet leaf

Commercial Control

AgXalt™ X-100 Formulation

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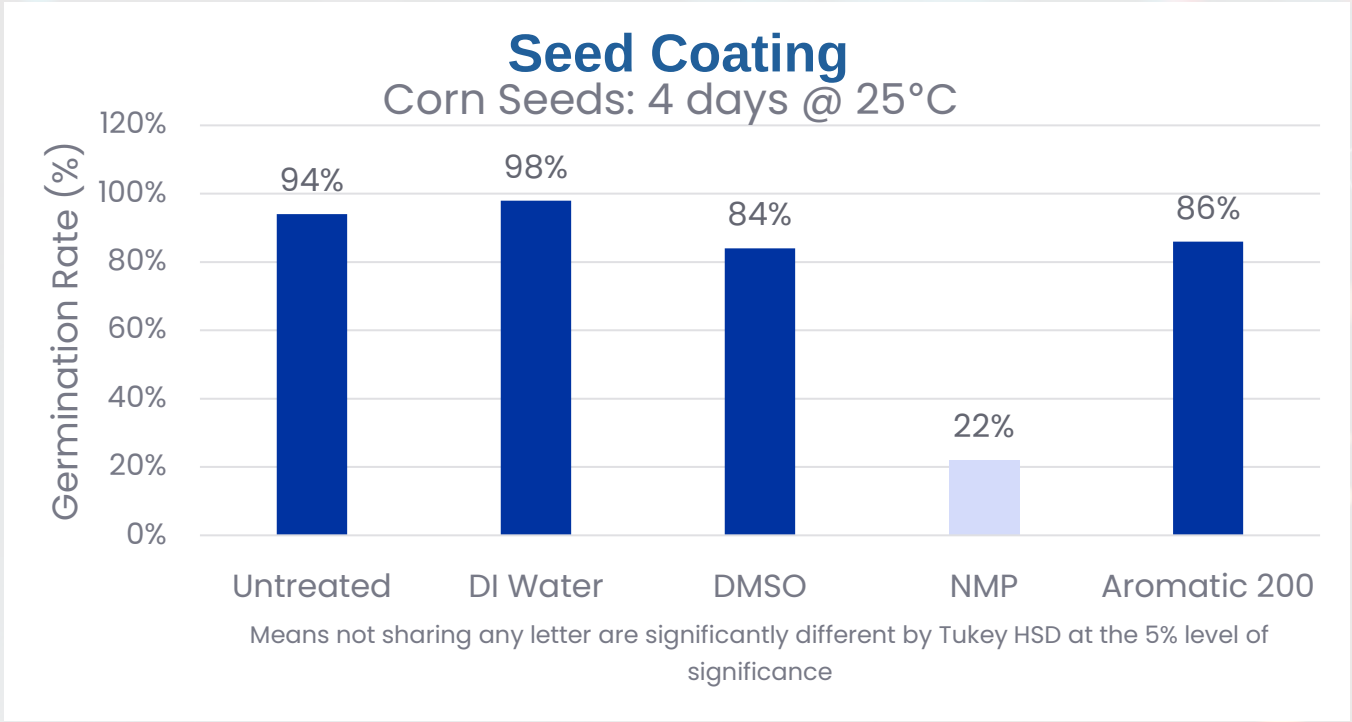
Potential for additional formulation uses



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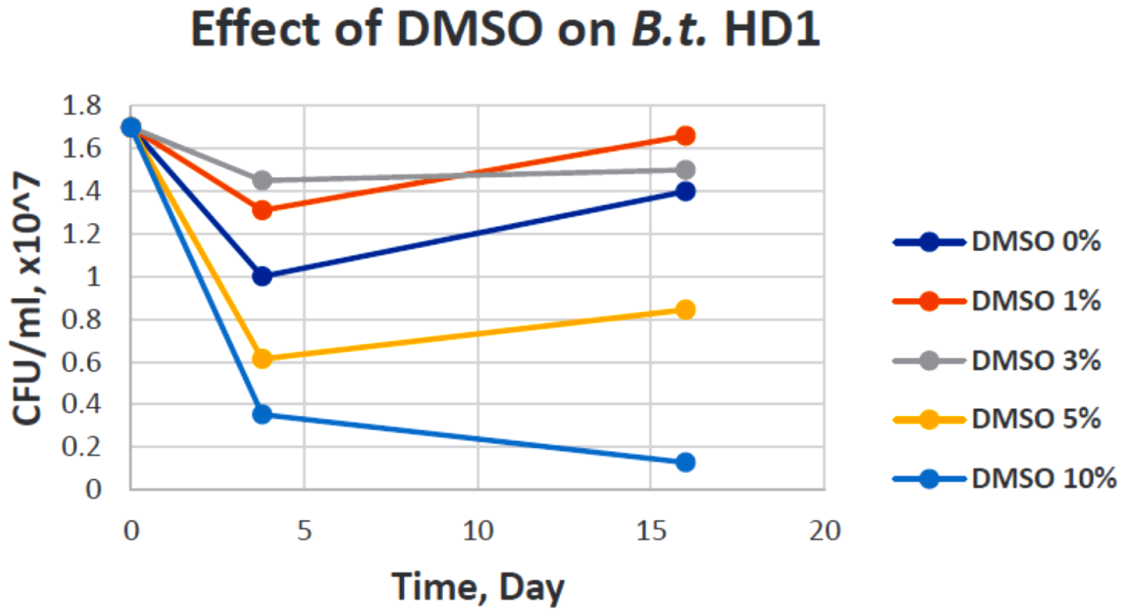
Potential for additional formulation uses

Biological formulations



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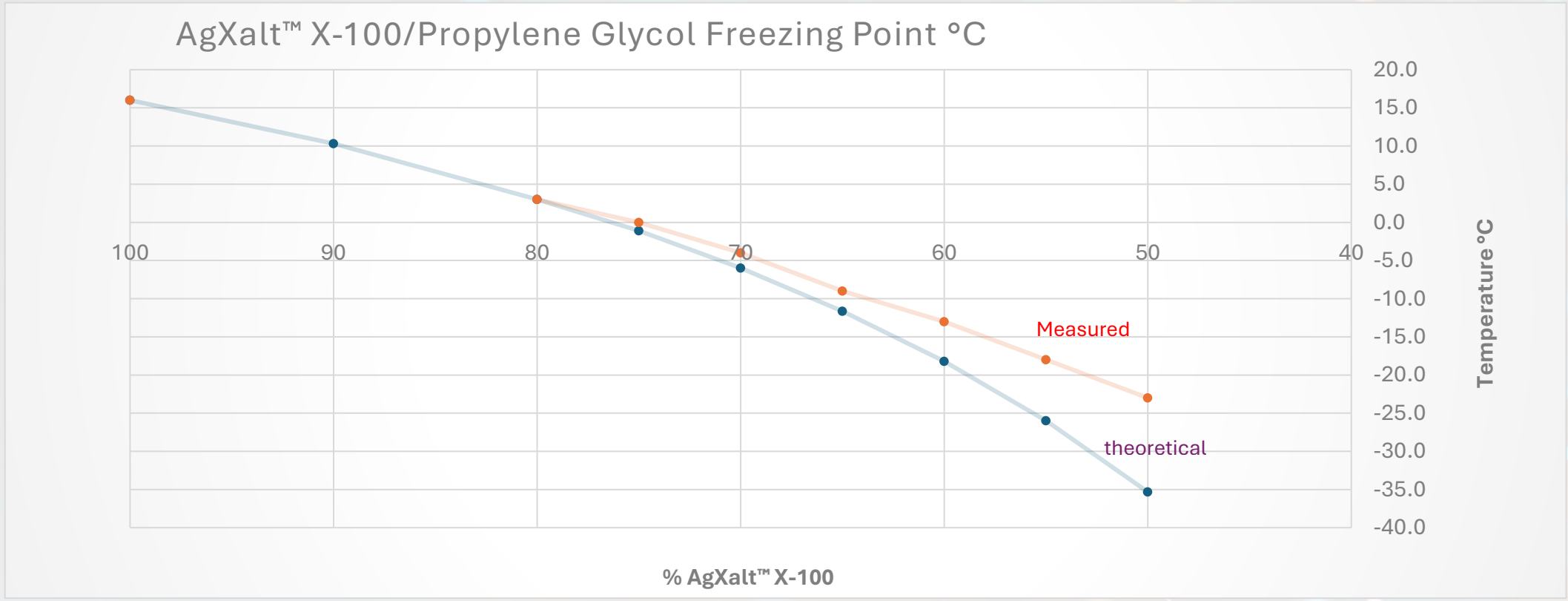
Formulation Considerations

Freezing point of pure ~material



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Formulation Considerations

Impurity Odor

- Product Purity is key!
- Decomposition by-products addressed with odor masked DMSO

  - **DMS:** Odor threshold ranges from 0.001 ppm
  - **Methyl Mercaptan:** Odor threshold 0.002 ppm
  - **Ethyl Mercaptan:** Odor threshold .0004 ppm
  - **Carbon disulfide:** Odor threshold .1 - .2 ppm

2. Committee on Acute Exposure Guideline Levels; Committee on Toxicology; Board on Environmental Studies and Toxicology; Division on Earth and Life Studies; National Research Council. Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 15. Washington (DC): National Academies Press (US); 2013 Sep 26. 1. Ethyl Mercaptan Acute Exposure Guideline Levels. Available from: https://www.ncbi.nlm.nih.gov/books/NBK201325/
3. Leonardos, G., Kendall, D., & Barnard, N. (1969). Odor Threshold Determinations of 53 Odorant Chemicals. *Journal of the Air Pollution Control Association*, *19*(2), 91–95. https://doi.org/10.1080/00022470.1969.10466465

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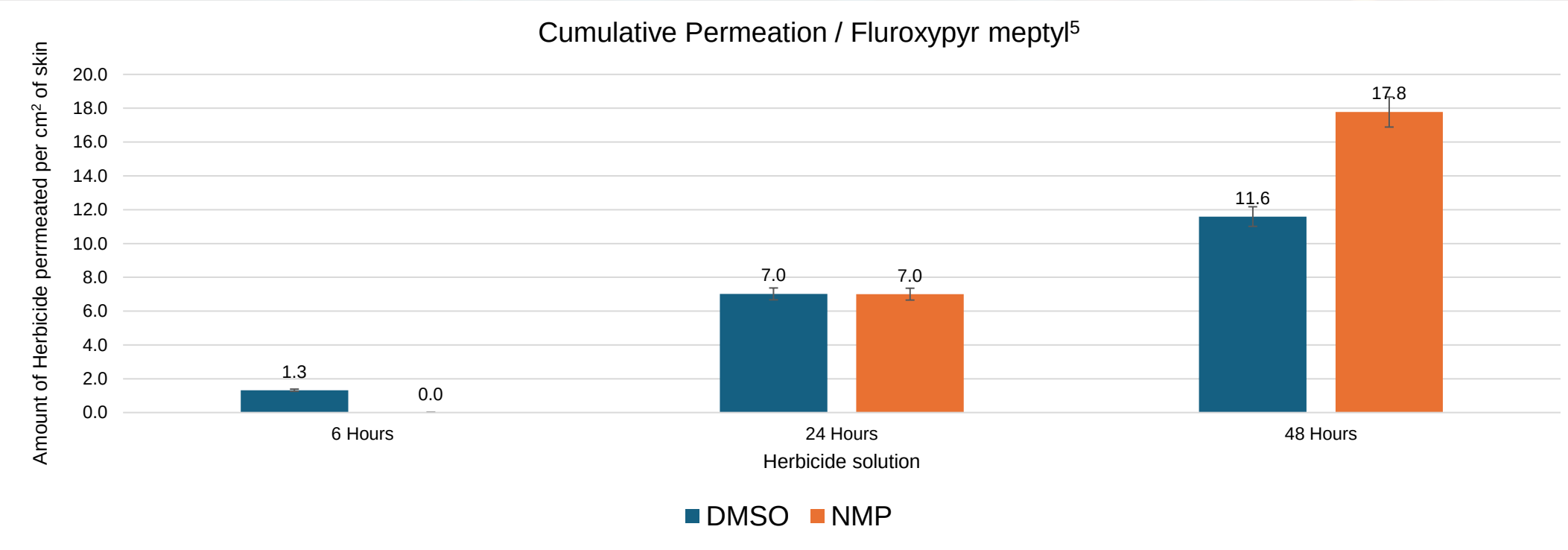
Formulation Considerations

Skin Exposure



4. Ursin, C.; Hansen, C.M.; Van Dyk, J.W.; Jensen, P.O.; Christensen, I.J.; Ebbehoej, J. *Am. Ind. Hyg. Assoc. J.*
5. Michniak, B.; Matharoo, N. Rutgers University Study (unpublished) 2024

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Overall Conclusions

Amide solvents like NMP are being phased out – DMSO is gaining new regulatory clearances

DMSO is well established in agrichemical formulation and is quickly growing in use

DMSO is the new solvent of choice for replacing NMP. It is:

- **Approved**
- **Readily available**
- **Cost effective**
- **Brings formulation improvements and flexibility**

Special thanks to Stepan Chemical, for developmental and training support

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Join us the following events in 2025…

Trade Show	Date	Location
BPIA	March 31 – April 3	Sacramento, CA
ISAA	April 6 – April 11	Rio De Janeiro, BR
CPDA	May 5 – May 8	Cape Coral, FL
Southwest Fertilizer Conference	July 14 – 18	Nashville, TN
Specialty and Agro Conference	July 28 – July 31	Savannah, GA
ASTM	Oct 6 – Oct 9	Atlanta, GA

Mick Sadoudi
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Dr. Artie McKim
VP, Technology
AMcKim@gaylordchem.com

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Q&A

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“Change, Change, Change – A New Option for Liquid Agrochemical Reformulation”

Thank you for attending