



Agriculture Division of DowDuPont™

Challenges with Slurries and Dispersions In the Agricultural Products World

John Green PhD

Senior Consultant

Wilmington, Delaware.

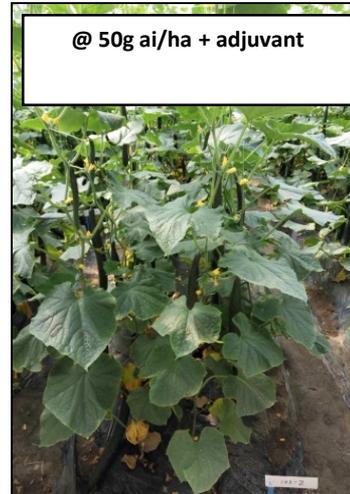
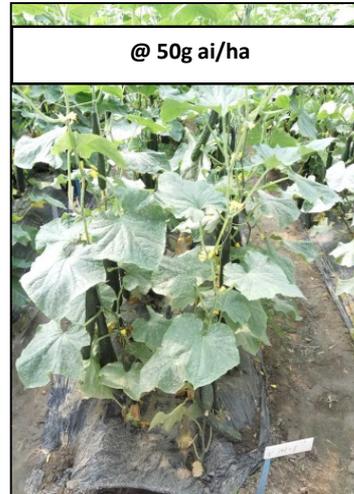
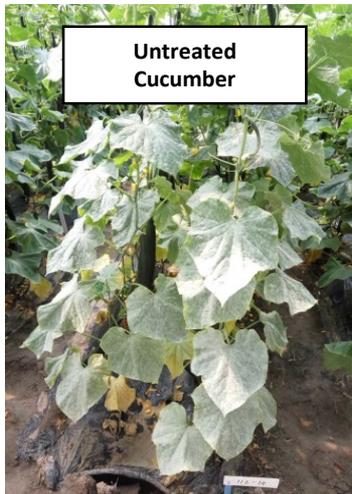
22ND JUNE 2018

Introduction

Manufacture and Use of Agricultural Formulated Pesticides

Scope of this discussion

- Active Manufacture.
- Manufacture of the formulated active.
- Use by the customer.
- Very demanding and variable use practices.
- Regulatory constraints.

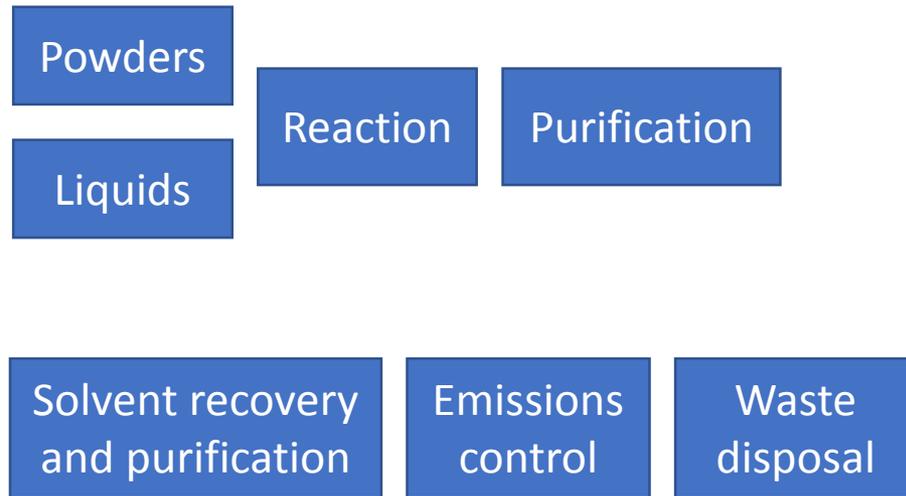


Treated vs untreated rice paddy



Manufacture of Active Ingredient

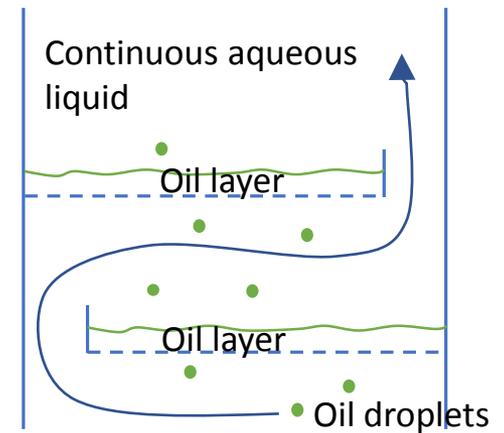
Elements of Manufacturing Process for an Active Ingredient



Purification	Extraction
	Distillation (including concentration, solvent exchange)
	Precipitation/crystallisation
	Drying
Solvent recovery/purification	Distillation
	Extraction
Waste disposal	Wastewater treatment (including neutralisation)
	Incineration, scrubbing

- Can be ten or more steps in the process.
- Can be many intermediates.
- Often multiple different unit operations in same vessel.
- Actives can be soluble, insoluble, hydrophilic and hydrophobic.
- Higher solids improves economics but risks upsets.

Some Problems



The slurry/ emulsion unexpectedly becomes viscous/ solid during reaction where the quick solution is to dilute, due to phase inversion resulting from a process upset, on scale-up resulting from unrealistic small scale process.

Liquid-liquid extraction and separations can be hampered by rag layers and poor coalescence resulting from surface active impurities, particulate impurities etc. during phase cuts,
In countercurrent liquid-liquid extraction with perforated trays.

Filter and centrifuge cakes are not always readily and repeatably washable, easy to dewater and re-disperse.
Not well understood.
Care needed for scale-up.

Slurry pumping problems are common in particulate laden intermediate transfers. These are not occasions for elegant solutions and engineering approaches are common e.g. dilution, increasing transfer line velocity, attention to piping layout etc.

Wastewater treatment requires the use of flocculants. Whilst the polymer science behind flocculation is reasonably well understood, reduction to practice is limited, largely because information on industrial flocculants is not available to practitioners. Consequently, screening approaches cannot be avoided.

Manufacture of Formulated Product

Product Types

Different physical forms

Dry

- Water Dispersible Granules.
- Wettable Powders.

Liquid

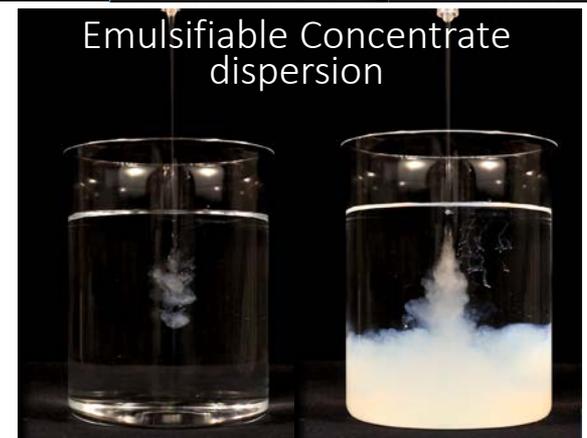
- Suspension Concentrates.
- Emulsifiable Concentrates.
- Oil Dispersions.
- Suspoemulsions.
- Others.



Pouring granules with minimal dust and good flow



Granule dispersion in water



Emulsifiable Concentrate dispersion

Typical Manufacturing Process

Suspension Concentrate Example



Usually re-using equipment from another product so often sub-optimised.

Products often campaigned, so equipment used for different products in any given year.

Different formulations process quite differently, particularly milling time, which is often the rate limiting step.

Critical to Quality

Assay.

No settling or separation in the product container.

If an applicator used a partial container without resuspending then under dosing would result, followed by over dosing.

Resuspending requires more time from the applicator, particularly when hundreds of jugs have to be transferred.

Particle size targets.

Finer results in less settling but greater demand on the dispersants for colloid stability.

Finer can increase product efficacy.

Cannot tolerate oversize that would block spray nozzle screens.

No re-agglomeration in the product container e.g.

coagulation,

flocculation,

coalescence.

Pourable.

Higher viscosity results in extended transfer times from product jugs into the sprayer equipment.

Non-freezing.

Chemically and physically stable over 2 or 3 years on the shelf.

Some Problems

Dispersing particulate actives in high electrolyte dispersions are problematic e.g.

when one of the actives is a salt, the other is insoluble, stability is a challenge.

Gels form upon ageing.

One example resulted from the antifoam ingredient.

Prevention of separation of oil dispersible formulations

Structuring agents do not work well in liquids such as methylated seed oils and aromatics.

Small amounts of water can be problematic, e.g. result in gels.

Prediction of settling/ agglomeration in the product container

Accelerated ageing e.g. 2 weeks at 54C is reasonable for chemical reactions but questionable for physical phenomena like settling, structuring, rheology etc.

Although colloid stability theory is reasonably well refined its implementation is limited and largely only directional in the agricultural formulation world. Improvements could include

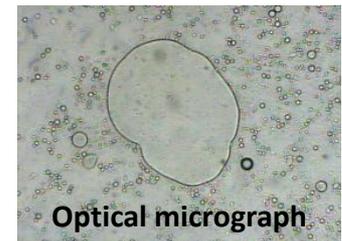
prediction of stabilising ingredients,
understanding how to account for surfactants and dispersants not being pure, having molecular weight and structure distributions,
prediction of stability, or accelerated measurement of stability.



Separation in an oil dispersible formulation



Gel on screen



Optical micrograph

Use of Formulated Product

Typical Use Practices

Most fungicides, insecticides and herbicides are diluted in a tank and sprayed onto the crop/ field.

Equipment can include

- backpack sprayer (2-5 gal),
- truck or tractor driven boom sprayer (2-300 gal),
- self propelled sprayer (800-1200 gal),
- aircraft sprayer (300-500 gal),
- drones.

Time to transfer from jugs and mix can be as short as 10 minutes with

- vigorous agitation at the point of mixing in some equipment, little or none with backpack sprayers,
- poor, or no agitation during spraying.

Concentration of active can vary from ppm to around 2 % depending upon biological activity, crop and spray equipment.

Applicators often mix many products to reduce cost of application including

- fertilisers (high salt),
- adjuvants (surfactants, oils and anything else to increase activity/ performance),
- other crop protection products.



Critical to Quality

Biological performance.

No settling or separation up to 24 hours without agitation. Can result from weather, e.g. storm, prevents spraying before dark, mechanical failure.

Good physical stability, no flocculation, coagulation, coalescence.

No chemical degradation.

Challenges

How to resist surfactant desorption after dilution as time proceeds.

Tank mix compatibility with

- many different combinations of formulation types and additives (other AG products, fertilisers, specialised additives etc.),
- different dilution levels,
- different site water (hard, soft, temperature, pH etc.),
- different mixing equipment,
- multiple failure modes possible resulting in unsavory agglomerations that block in-line filters, spray nozzle screens and result in shut down of spray equipment for clean out.

Hard packed tank sediments cannot be re-dispersed.

Industry shift towards lesser dilution for application is resulting in less colloid stability.

- Previously the higher concentrations were for aircraft application,
- larger farms make transporting water more difficult so less dilution preferred, e.g. Brazil, Canada,
- now drones are being introduced but higher concentrations, still, are demanded because of more significant weight constraints.



“cotton balls” in a 1200 gal tank SC mixed with EC

Some Limitations

Specific to the agricultural chemical industry

The additives, surfactants and ingredients that can be included in a formulation are regulated and limited.

Introduction of new surfactants and additives is severely limited by the cost of testing and registration so few new additives have been introduced in recent decades.

After registration of a product there is little incentive to change ingredients or the process until renewal which requires re-registration and is costly and time consuming.

Summary

Robust dispersion performance is required

From product concentration to high dilution,
with an uncontrolled assortment of conditions and other tank mix partners,
in a very wide range of equipment.

Some dispersion/ slurry problems are solved by engineering.

Opportunities exist for new developments and improvements in methods and measurement systems.

