

New Developments in the Formulation of Dispersions  
29 September – 1 October 2003 Manchester



**Stabilisation of Dispersions and Emulsions by  
Chemically Locking Surfactants at Interfaces**

Ian Shirley

## Scope

- Relevance
- Chemically locking surfactants at interfaces by
  - Radical chemistry
  - Nucleophilic chemistry

## Surfactants in Dispersions and Emulsions

- Diverse applications - Agrochemicals, pharmaceuticals, cosmetics, reprographics, coatings.
- Where surfactants are probably the most critical component!
  - Stabilise colloidal particles
  - Assist in obtaining or controlling particle size

syngenta

## Relevance

- Emulsion polymerisation
  - Stabilise monomer droplets and then polymer particles
- Microcapsules
  - Emulsifier - drop size of oil in water emulsion depends on degree of shear and amount of emulsifier
  - Colloid stabiliser prevents agglomeration of oil and then capsule

syngenta

## Relevance - Free surfactant

- Free / unbound surfactant can cause problems associated with either the robustness of the formulation and/or the use of the product
  - Coatings – latex film formation, barrier properties, adhesion
  - Emulsions – destabilisation, Ostwald ripening
  - Suspension concentrates – solubilisation of SC, crystallisation
  - Microcapsules, competitive surf. or thermal desorption
- **Formulations designed to be robust!** But no control over some situations → lock surfactant at interface

syngenta

**Chemically locking surfactants  
at interfaces by radical  
chemistry**

syngenta

## Latexes – chemically bound surfactants

- Latexes – to prevent migration and aggregation of free surfactant upon film formation
- Mainly in CFRP – special nomenclature
  1. Transurfs
  2. Inisurfs
  3. Surfmers

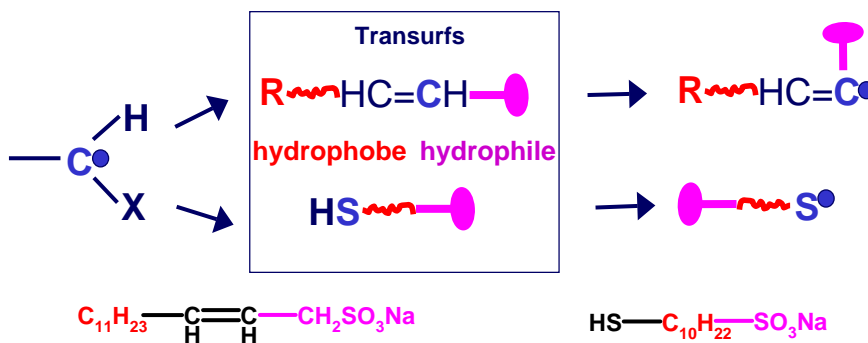
A Guyot & K Tauer, *Adv Polym Sci*, Vol 111 (1994) 43-65

A Guyot, *Surf Sci Ser* (1998), 74(Novel Surfactants), 301-332.

syngenta

## Transurfs

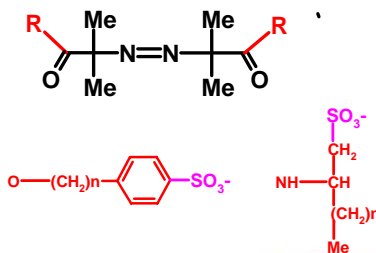
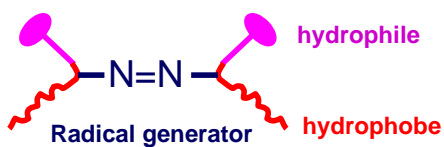
- Chain t/f agents – radical transfers to transurf which starts new polymer chain



syngenta

## Inifurfs (Conventional Radical Polymerisation)

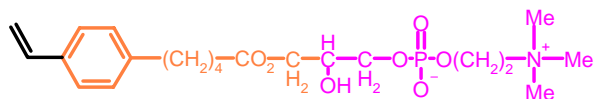
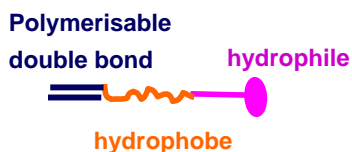
- Inifurfs incorporate a radical generator function
- Anionic and nonionic examples known



syngenta

## Surfmers

- Surfmers act as co-monomers
- Both ionic and non-ionic examples are known



syngenta

## Limitations

- Incorporating surfactant by CFRP works well where there is a 'pool' of monomer for growing chain (eg emulsion, suspension polymerisation)
- Can encapsulate materials by suspension polymerisation
  - Solids – dispersed in monomer
  - Liquids - reservoir structures - approach difficult
    - correct spreading coefficients for growing polymer/oil/water to give encapsulation rather than acorn or phase separation

syngenta

## Chemically locking surfactants at interfaces by nucleophilic chemistry

- Latexes (eg polyurethane)
- Microcapsules
- Emulsions
- Solid concentrates
- Mixtures of the above

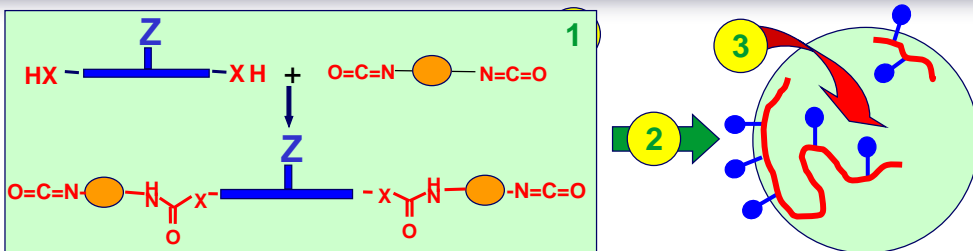
syngenta

# PU Latexes

- Early work – external emulsifiers & colloid stabilisers
- Internal surfactants for small size stable dispersions that film form to give excellent coatings
- Many procedures have been used

syngenta

# Polyurethane latexes

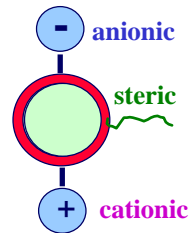


1. React ionomer or steric stabiliser with excess NCO
    - Neat or in solvent → 'low' Mw
  2. Disperse in water
  3. Chain extend → high polymer **in matrix particle**
- Approach has been extended to microcapsules

syngenta

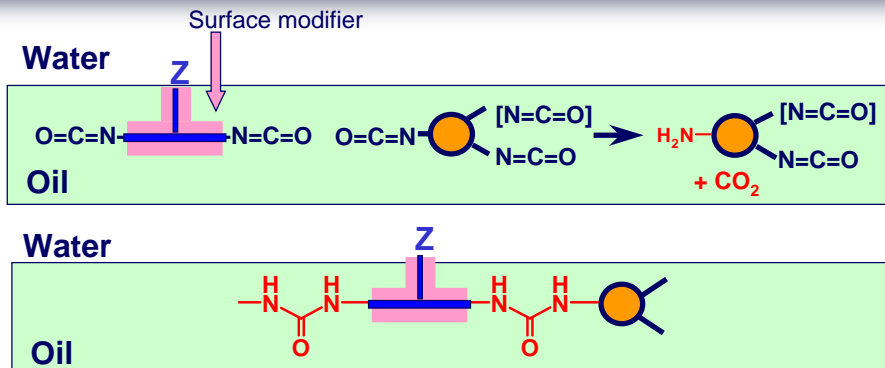
## Benefits - Microcapsule Surface Modification

- Improved product robustness
  - bound stabilisers not desorbed; improved formulation compatibility
  - improved re-suspension of settled cs (and spray drying)
- Process advantages
  - allows us to make ‘smaller particles’ which have new bio-performance
- Improved bio-performance
  - alter release rate - residuality - improve bioefficacy
  - avoids free surfactants that may cause phytotox



syngenta

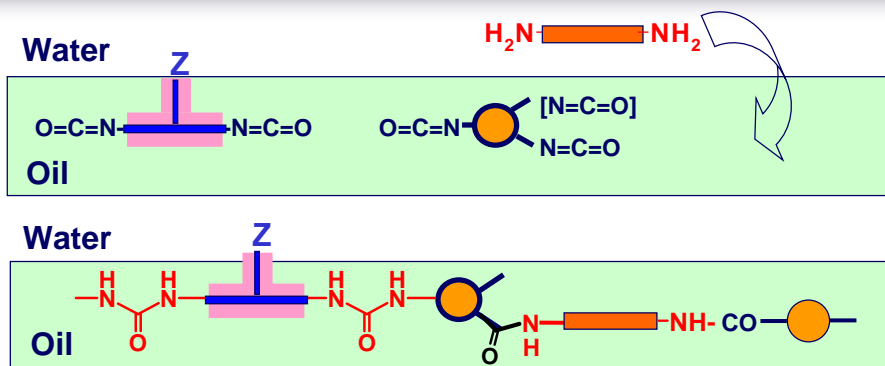
## ‘In Situ’ Modified Poly(urea) Microcapsules



- Modifiers: sulphonates phosphonates, carboxylates and poly(ethylene glycols)
- WO 01/94001

syngenta

## 'Two phase' Modified PU Microcapsules

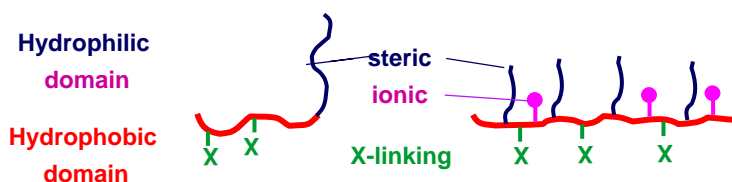


- WO 01/94001

syngenta

## New Reactive Surfactants

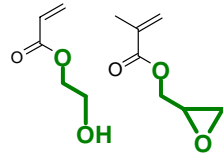
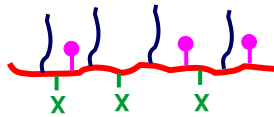
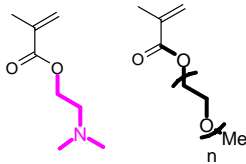
- New approaches – 'structured polymers' & 'reactive polymeric surfactants'
- Di-block and random comb copolymers with **reactive groups (X)** located in **hydrophobic domains**
- Stabilising groups - **ionic** &/or steric



syngenta

## Structured Polymers

hydrophile	type	hydrophobe	X-linking
MMA-MAA macromonomer	-ve	EHA	HEA
DMAEMA	+ve	EHA	HEA
PEGMA	Steric	BA	GMA

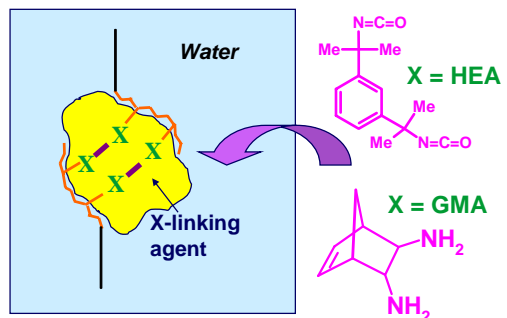


US 6,262,152

syngenta

## Quinacridone Pigment Dispersions

- Quinacridone pigment dispersion made with structured polymer
- Cross-linker added through the aqueous phase



syngenta

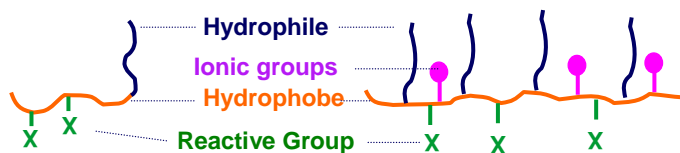
## Benefits of Structured Polymer Pigment Dispersions

- Flocculation stability
  - cross-linked dispersions more stable than non-cross-linked to butyl cellosolve
- Ink formulations
  - cross-linked more stable than non-cross-linked dispersions and 'conventional' ink formulations to freeze-thawing

syngenta

## Reactive Polymeric Surfactants

- Reactive polymeric surfactants (RPS) afford emulsions and microcapsules with enhanced formulation robustness and bioperformance.

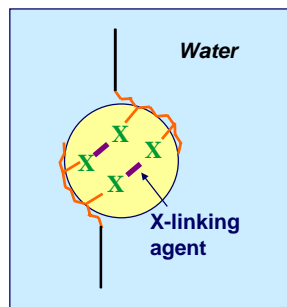


WO 02/100525

syngenta

## Reactive Polymeric Surfactants

- Designed to physically adsorb at the interface between water and an oil droplet to provide a stable colloid dispersion.
- Subsequent cross-linking with x-linking agent (wall forming monomers) gives surfactant which cannot be desorbed.
  - PVOH – US 5,925,464
  - RPS's - WO 02/100525



syngenta

## Synthesis of Reactive Polymeric Surfactants

- Conventional free-radical polymerisation offers poor control over polymer architecture.
  - Poor control over molecular weight and MW distribution.
  - Cannot easily make block copolymers.
  - Poor distribution of comonomers.
- Use “living”/controlled radical polymerisation technique.
  - Area of intense academic and some commercial interest – several techniques available, all applicable to RPS..

syngenta

# Amphiphilic polymer architecture

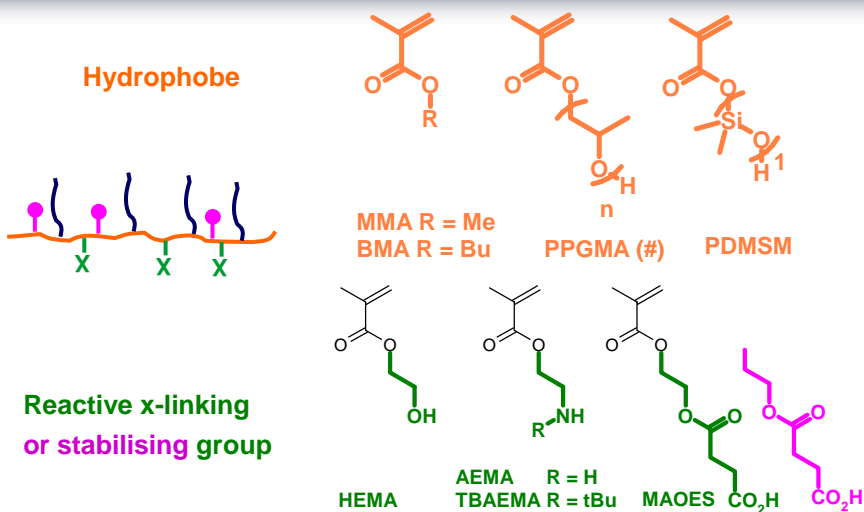
- Diblock and random graft copolymers with reactive functional groups located in hydrophobic domains.



Hydrophile	Addnl. Ionic	Hydrophobe	Reactive gp.
PEO	Carboxylate	Methyl MA	Hydroxyl
Sulphonic acid (block)	Sulphonic acid	Butyl MA	Amine
Quat. amine (block)	Quat. amine	PDMS	Carboxylic acid
	Sulpho-betaine	(multiple graft)	
	Carboxy-betaine		

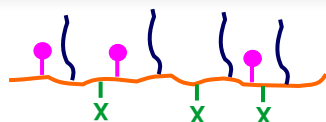
syngenta

# Examples of RPS Monomers

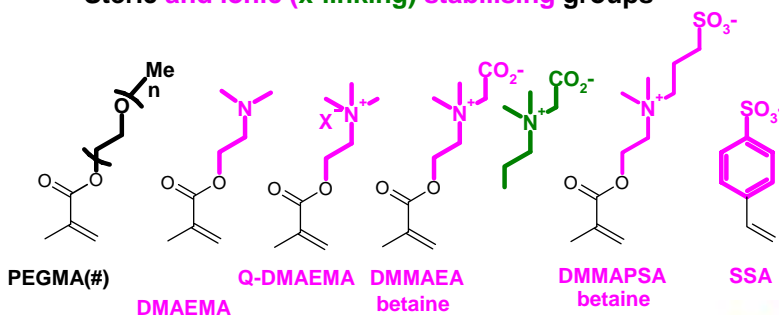


syngenta

## Examples of RPS Monomers



Steric and ionic (x-linking) stabilising groups



syngenta

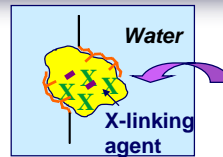
## Characterisation by NMR solvent relaxation

- RPSs can be cross-linked on solids (cf above)
- Cross-linking can be probed by NMR spin-spin relaxation time ( $T_2$ ) of solvent molecules - faster at surface than in bulk
- Plots of specific relaxation time ( $R_2^{SP}$ ) vs ratio of mass of particles to solvent are linear for fast exchange & linear increase of surface area with increasing concentration
- Slope depends on nature of particle surface – aggregation or surfactant ad-/de-sorption will change  $R_2^{SP}$

syngenta

## RPS's on silica

1. RPS's physically adsorbed on silica
2. Sample cross-linked cf above
3. Silica dispersed with NP5

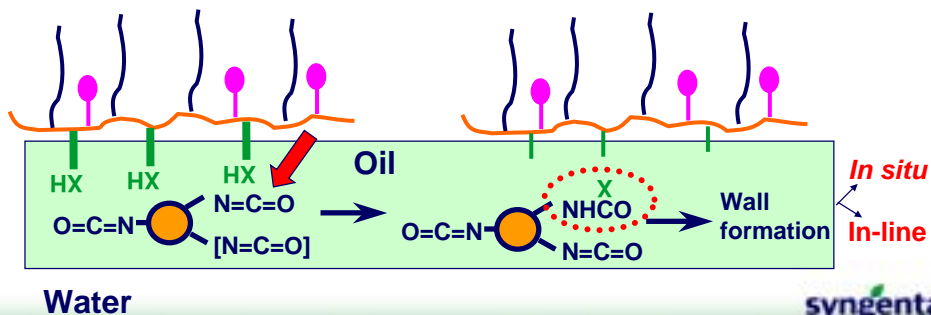


- NMR - different slope plots were obtained for physically adsorbed (1), x-linked (2), and NP5 (3) samples.
- NP5 added separately to (1) and (2)
  - Slope of (1) changes to same slope as (3) – non-cross-linked can be competitively desorbed
  - Slope of (2) remains unchanged – **RPS not desorbed**

syngenta

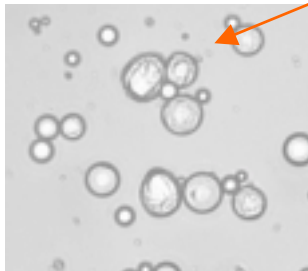
## RPS – isocyanate crosslinking

- Multi-functional RPS amino or hydroxyl groups cross-link multi-functional isocyanates
- Stabiliser irreversibly bound to capsule surface
- Isocyanate amount – determines barrier properties

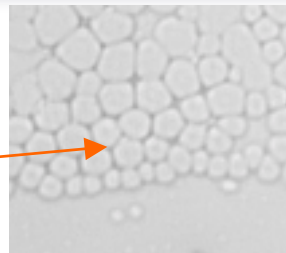


# Pesticide isocyanate cross-linked emulsions and capsules

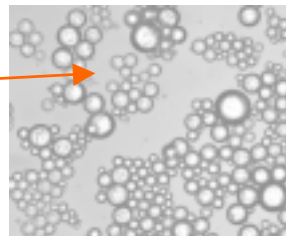
Pesticide oil 50% phase volume EW with 4% cross-linked RPS.



As EW dries walls collapse leaving annuli of polymer.



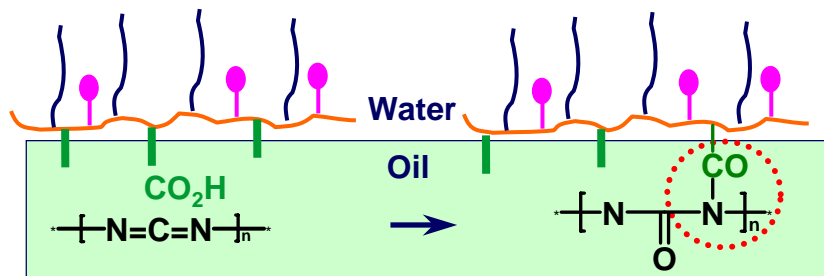
Addition of DETA to react with excess PMPPI gives capsules with strong walls that retain structure on drying & resuspension



syngenta

## RPS – carbodiimide crosslinking

- RPS CO<sub>2</sub>H groups cross-link multi-functional carbodiimides



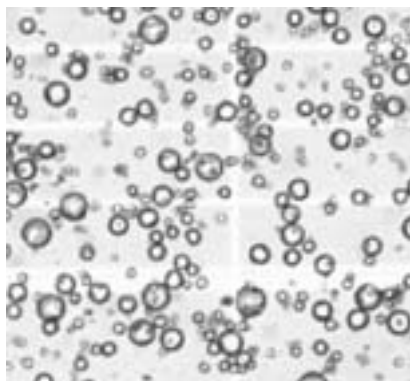
syngenta

## Pesticide carbodiimide cross-linked emulsion

Pesticide 50% w/w emulsion  
with 4% w/w  
polycarbodiimide cross-linker  
and 4% w/w carboxylic acid  
functional RPS.

Robustness to electrolyte  
assessed relative to:

- (i) non-x-linked RPS
- (ii) Conventional surfactant  
(Atlas G5000)



syngenta

## Salt stability of stable emulsions

- Comparison of pesticide emulsions in salt solution.
  - Diluted emulsions into sodium sulphate solution to give 5% w/w pesticide in 0.7 moles/L salt. (0.5 % w/w surfactant)
  - Continuous phase removed and replaced with DI water (simulate dilution in clean water), then shaken.

Surfactant	RPS (XL)	RPS (not XL)	Atlas G5000
In salt	Flocculated and settled	Flocculated with significant coalescence	Flocculated and settled
On dilution	Redispersed, no change in size	Did not redisperse	Redispersed but significant growth

syngenta

## Cross-linking aids resistance to coalescence

- Solvesso 200 10% phase volume EW in 0.5 molL<sup>-1</sup> sodium sulphate.



Atlas G5000

RPS uncross-linked

RPS cross-linked

syngenta

## Suspensions

- Locking surfactant at interfaces
  1. Overcomes unwanted interactions between oil and solid phases
  2. Removes free surfactant that may affect bioperformance
  3. Simplifies the complexity of SE's in using a single surfactant

syngenta

## Summary

- Locking surfactant at interfaces can overcome problems associated with either the robustness of the formulation and/or the use of the product.
- The approach is not advocated here as a panacea but as a powerful supplement or alternative to other established practice.

## Acknowledgements

- To the many colleagues who have made possible the advances in technology described here, particularly
  - H Scher, J Chen, I Mazeaud, D Kane, J Padget, P Wade, A Heming, P Mulqueen
  - All involved in characterisation studies