FORMULATING PRODUCTS FOR OPTIMUM FOAM PERFORMANCE

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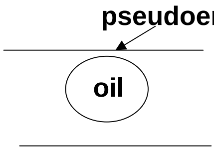
EXAMPLES OF PRODUCTS REQUIRING FOAM OPTIMISATION

PRODUCT	*REQUIREMENT*	*ANTIFOAM PRESENT?*
Detergents for machine washing of clothes and dishes	Low foam	Oil-based synthetic
Water-borne coatings	Low foam	Oil-based synthetic
Personal products, shampoos, toilet bars, shower gels	High foam	Triglyceride/fatty acid sebum
Detergents for hand washing of clothes and dishes	High foam	Triglyceride/fatty acid sebum soil
Alcohlic beverages • Beer • Champagne	 • Stable foam • High volume unstable foam	Triglyceride/fatty acid

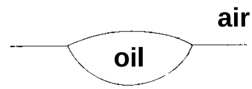
ANTIFOAM ACTION OF OIL DROPLETS



E= Entry Coefficient

$E = \sigma_{AW} + \sigma_{OW} - \sigma_{AO};$

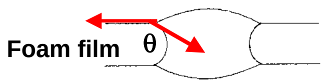
$E > 0$



B = Bridging coefficient

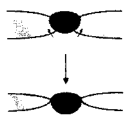
$B = \sigma_{AW}^2 + \sigma_{OW}^2 - \sigma_{OA}^2;$

$B > 0$ then $\theta > \pi/2$ and configuration unstable



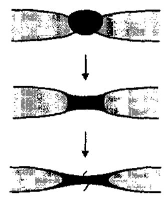
Bridging; dewetting mechanism

$\pi/2 < \theta << \pi$



Bridging – stretching mechanism

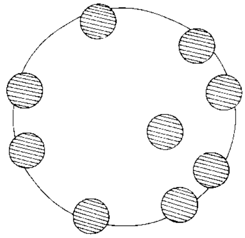
$\theta \rightarrow \pi$



MIXTURES OF HYDROPHOBIC PARTICLES AND OILS AS ANTIFOAMS

 # For defoaming of aqueous systems generally necessary to add particles to oil to yield synergistic antifoam action

 # Function as composite entities with the particles adhering to the oil-water surface



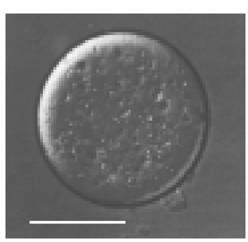


Image of hydrophobed silica/mineral oil antifoam droplet (bar 50 microns)

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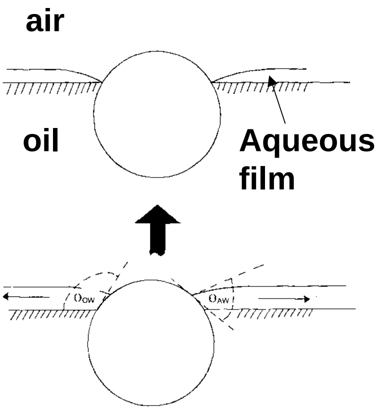
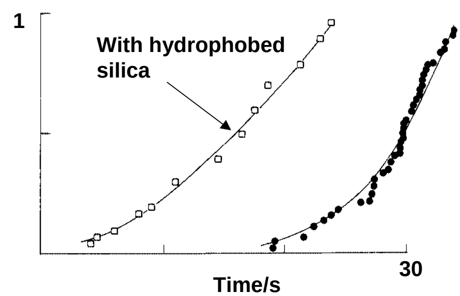
CONTACT ANGLES OF PARTICLES AND RUPTURE OF PSEUDOEMULSION FILMS



Pseudoemulsion film ruptures if $\theta_{AW} > \pi - \theta_{OW}$



Effect of hydrophobed silica on stability of pseudoemulsion film Air-ABS solution-liquid parafin

OPTIMUM FOAM

Low foam formulation using oil based antifoams relying on interaction of organic acids with calcium to form insoluble particles.

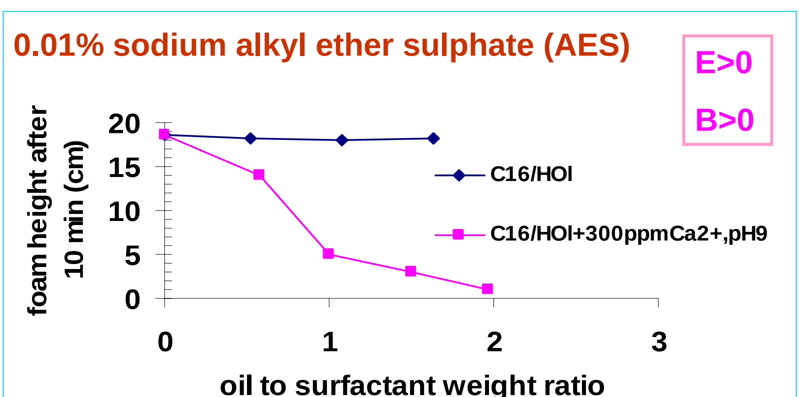
Formulation with micellar solutions of anionic surfactant homologues in the presence of antifoam

FORMATION OF OIL/PARTICLE ANTIFOAMS BY REACTION OF ALKYL CARBOXYLATES AND PHOSPHATES WITH CALCIUM AT OIL-WATER INTERFACES

ORIGIN	MAIN COMPONENTS
Oily soils removed during washing of clothes or dishes	Mainly mxtures of triglyceride oils, waxes and fatty acids
Synthetic antifoams	Mixtures of hydrocarbon or triglyceride oils and fatty acids or alkyl phosphoric acids

$RH + OH^- \Leftrightarrow R^- + H_2O$; $Ca^{2+}(aq) + 2R^- \Leftrightarrow Ca(R)_2(s)$

FOAM STABILITY OF OIL MIXTURES WITH OLEIC ACID



Oil mixtures reduce foam stability
in the presence of calcium and alkalinity

INTERACTION OF CALCIUM WITH OLEIC ACID AT THE OIL-WATER INTERFACE

- Video-microscopy contacting experiments

0.01% AES +300ppm hardness, pH9 solution

hexadecane/oleic acid mixture

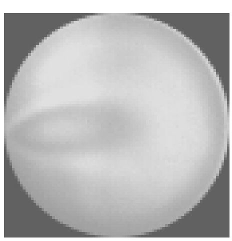
Drop size ≈160µm

calcium soap particles form at interface

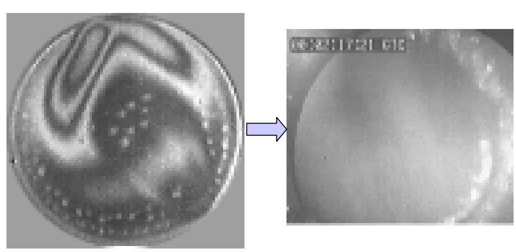
STABILITY OF AIR-WATER-HEXADECANE PSEUDOEMULSION FILMS

- Oil phase: **C16/HOl**
- Aqueous phase: **0.01wt% AES**

- Oil phase: **C16/HOl**
- Aqueous phase: **0.01wt% AES +300ppm Ca^{2+},pH9**



Metastable



Unstable, leads to drop entry

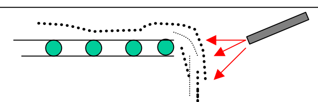
EFFECT OF ALKYL PHOSPHATE/HYDROCARBON MIXTURES ON FOAMABILITY OF SOLUTION OF A DETERGENT POWDER

Water hardness /10^{-4}M	Foam height without antifoam/cm	Foam height with antifoam/cm
0	100	100
6	100	50
12	100	15
24	100	12

Alkyl phosphate;
$ROPO_3H$ where R= C_{16-18}

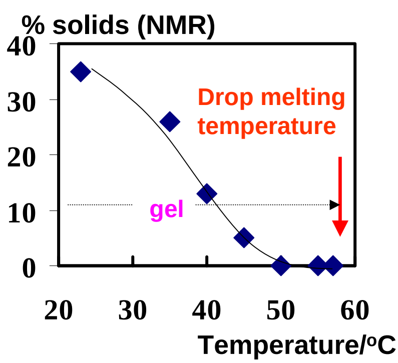
Detergent powder; 14% surfactant
Antifoam; alkyl phosphate/mineral oil (20/80 by weight)
Concn. powder = 4g dm^{-3}, concn antifoam = 0.25 g dm^{-3}
Foam height at 60^oC using dynamic Ross-Miles
Water hardness 21 parts Ca and 3 parts Mg mole ratio

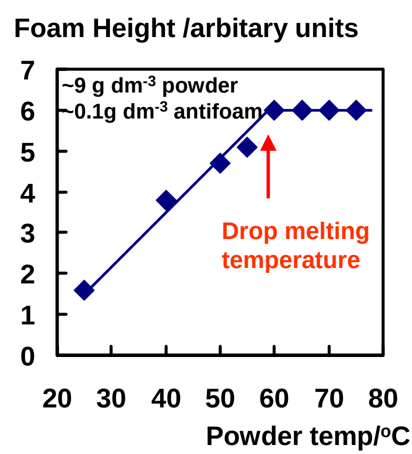
EFFECT OF TEMPERATURE ON INCORPORATION OF ALKYL PHOSPHATE/HYDROCARBON ANTIFOAM IN DETERGENT POWDER



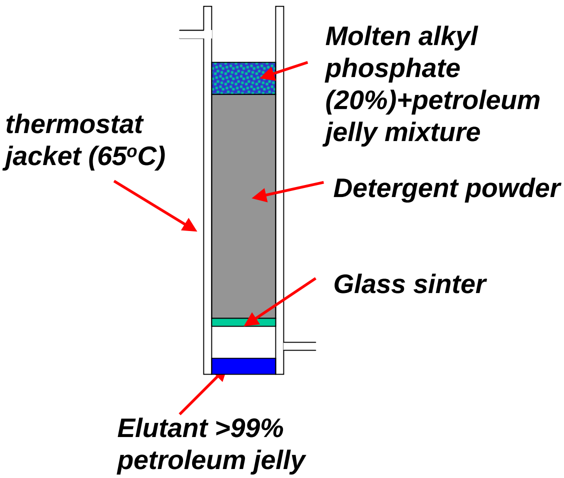
Process of spray onto detergent powder

Hydrocarbon = petroleum jelly
Detegent powder; 10% surfactant





INTERACTION OF MOLTEN ALKYL PHOSPHATE/PETROLEUM JELLY MIXTURES WITH DETERGENT POWDER



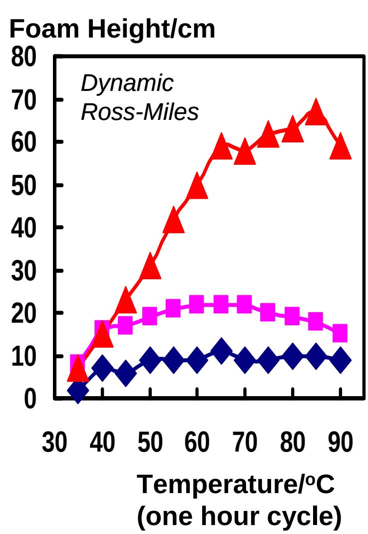
- **Complete separation of alkyl phosphate from the hydrocarbon occurs**

EFFECT OF SEPARATE ADDITION OF ANTIFOAM COMPONENTS

— (red) Alkyl phosphate & hydrocarbon dispersed ultrasonically at 70°C in separate 50 cm^3 aliquots of solution; aliquots subseqently shaken together for 300s at 30°C before adding to bulk of solution of 2400 cm^3.

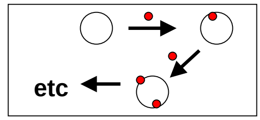
— (magenta) As above but aliquots shaken together for 3600 s at 70°C.

— (dark blue) Molten mixture of alkyl phosphate & hydrocarbon dispersed ultrasonically at 70°C in 100 cm^3 aliquot of solution; aliquot subsequently added to bulk of solution of 2400 cm^3.



Surfactant concentration 0.43 g dm^{-3} (commercial C_{12}ABS + C_{12-14}E7); antifoam concentration 0.2 g dm^{-3} (80% hydrocarbon)

HETEROCOAGULATION OF ANTIFOAM COMPONENTS



ASSUME OIL DROPLET CONCENTRATION REMAINS CONSTANT

$$dn_p / dt = -K_{po} n_p n_o / W_{po}$$

$$dn_o/dt = 0$$

n_o = no. concn. oil droplets, n_p = no. concn. particles, W_{po} is a stability ratio

HETEROCOAGULATION

Shear controlled $K_{po} \approx 0.667 \dot{\gamma} r_o^3$; *Diffusion controlled* $K_{po} \approx \left(\frac{kT}{\eta}\right)\frac{r_o}{r_p}$

after e.g. van de Ven, where $\dot{\gamma}$ is shear rate, η is viscosity, r_o and r_p are oil droplet and particle radii where $r_o >> r_p$

HALF-LIFE OF PARTICLES (AS ANTIFOAM FORMED)

Shear $\Delta t_{1/2} \approx q_s W_{po} / \dot{\gamma} c_o$; *Diffusion* $\Delta t_{1/2} \approx q_d r_p r_o^2 W_{po} / c_o$

where q_s and q_d are numerical factors and c_o is weight concn. oil droplets.

ESTIMATION OF RATE OF ANTIFOAM FORMATION AFTER SEPARATE ADDITION OF COMPONENTS; "RAPID" COAGULATION CONDITIONS WITH W_{PO} =1

Conditions	Shear* $\Delta t_{1/2}$/s	Diffusion $\Delta t_{1/2}$/s	comment
C_o = 0.004g cm^{-3}; r_p = 0.1 micron R_o = 1.0 micron	~100	~50	Experiment shows significant heterocoagulation after 3500s. Suggests lnW_{po} ~ 4- 5
C_o = 0.004g cm^{-3}; r_p = 0.1 micron R_o = 10 micron	~100	~5000	Convection more important as increase oil droplet size
C_o =0.0002g cm^{-3}; r_p = 0.1 micron R_o = 10 micron	~2000	~10^5	"

* $\dot{\gamma}$ ~ 10 s^{-1} (shaker bath @ 1.5 s^{-1})

OPTIMUM FOAM CONTROL OF DETERGENT POWDERS WITH HYDROCARBON ANTIFOAMS

Ensure that oil and particle antifoam components do not separate during incorporation.

Utilise encapsulation, capillary entrapment, gel formation etc.

ISOTROPIC HARD SURFACE CLEANING LIQUID WITH CONTROLLED FOAM

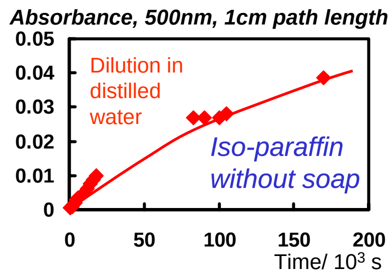
Presence of antifoam entities of different density and refractive index from cleaning liquid unacceptable.

Dissolve soap and solubilised hydrocarbon (forming an oil/water microemulsion) in alkaline cleaning liquid so that calcium soap and hydrocarbon co-precipitate upon dilution with water containing calcium. An oil-particle antifoam should then be formed in-situ.

ISOTROPIC HARD SURFACE CLEANING LIQUID WITH CONTROLLED FOAM

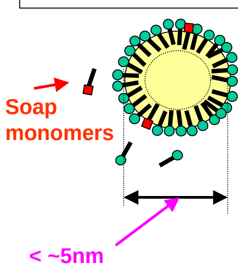
Antifoam additive/g dm^{-3}	Time for foam collapse/s	
	Dilution with destil. water	Dilution with 2.5 x 10^{-3}M Ca^{2+}
Coconut soap/0.12	>1200	~180
Coconut soap/0.12 + Iso-paraffin/0.3	180-240	~26

- ***Liquid composition ~ 8% surfactant (C_{10-12} NaABS, C_{9-11}E5); 0.4% soap, 1% iso-paraffin; rest water, butyl digol, water & minors***
- ***Diluted by factor of 33 with water or calcium chloride solution***
- ***Foam measurement by cylinder shaking***



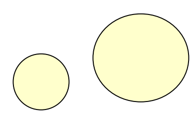
ISOTROPIC HARD SURFACE CLEANING LIQUID WITH CONTROLLED FOAM

O/W microemulsion



Dilution in absence of calcium gives slow process of precipitation of bulk oil phase

Hydrocarbon/W emulsion

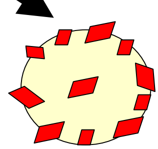


Fraction oil released

= {1-[(c-cac)/(c_p-cac)]Y}

where Y is dilution factor (for c > cmc, assuming microemulsion initially saturated)

Dilution in presence of calcium gives relatively fast process of nucleation of hydrocarbon onto calcium soap precipitate (K_{sp} > ~10^{-16})



Calcium soap + hydrocarbon antifoam

SURFACTANTS AND ANTIFOAM EFFECTIVENESS (assuming particles always effective in rupturing pseudoemulsion films)

Entry Coefficient

$E = \sigma_{AW} + \sigma_{OW} - \sigma_{AO}$

E > 0 if oil emerges into air-water surface

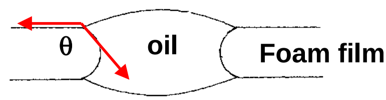
Bridging Coefficient

$B = \sigma_{AW}^2 + \sigma_{OW}^2 - \sigma_{OA}^2$

B > 0 then $\theta > \pi/2$ and configuration unstable

$\sigma_{OW} << \sigma_{AW}\ ;\ \sigma_{OW} << \sigma_{AO}$

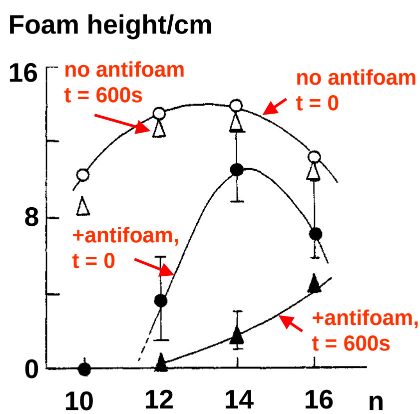
so B > 0 reduces to $\sigma_{AW} > \sigma_{AO}$

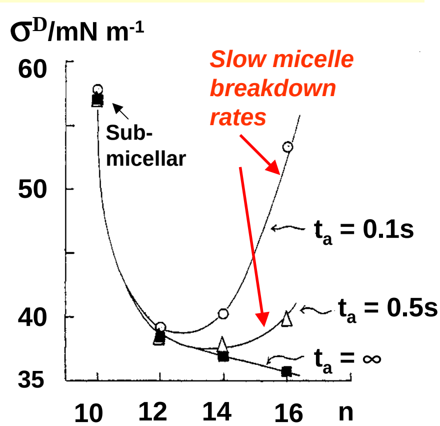


Therefore antifoam effectiveness can be largely determined by σ_{AW}

ANTIFOAM EFFECTS IN HOMOLOGOUS SERIES OF ANIONIC SURFACTANTS

Solutions of fatty acid methyl ester sulphonates C_nH_{2n+1} $CHSO_3Na.COOCH_3$



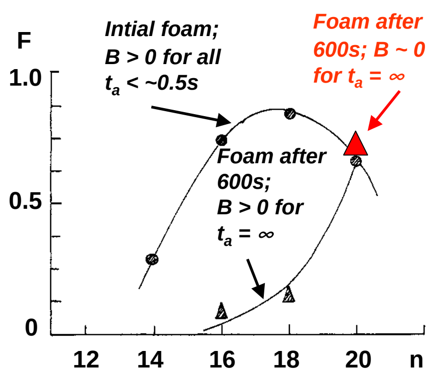


4×10^{-3}M surfactant in 7×10^{-3}M Na^+; 50°C; antifoam 1 g dm^{-3} triolein/calcium stearate; Ross Miles

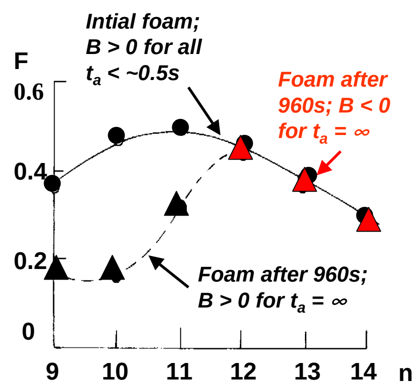
At all surface ages $\sigma^D > \sigma_{AO}$ (~ 30.5 mN m^{-1}) so B > 0

ANTIFOAM EFFECTS IN AN HOMOLOGOUS SERIES OF ANIONIC SURFACTANTS

F = Volume foam + antifoam/Volume foam - antifoam



$C_{n-1}H_{2n-1}COOK$, 10^{-2}M in 10^{-2}M KOH, 75°C; antifoam 1 g dm^{-3} calcium alkyl phosphate/ mineral oil; Ross Miles



$C_nH_{2n+1}.C_6H_4.SO_3Na$ isomer blends, 5 x 10^{-3}M in 4 x 10^{-3}M NaCl; 25°C; antifoam 1g dm^{-3} hydrophobed silica/mineral oil; Ross Miles

OPTIMISATION OF FOAM OF MICELLAR SOLUTIONS OF ANIONIC SURFACTANT HOMOLOGUES

An optimum chain length for high foamability exists; too high or too low chain length means high surface tensions (at relevant surface ages) and rapid drainage of films to thicknesses where capillary pressure exceeds disjoining pressure for upper regions of foam.

An optimum chain length in presence of an antifoam also exists. If antifoam particles always rupture pseudoemulsion films then antifoam effect is determined by the condition B > 0 (at relevant surface age). The greater the magnitude of B the greater the effect. B may change sign as the foam ages leading to cessation of antifoam effect.

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