OPPORTUNITIES AND CHALLENGES IN ENCAPSULATION FOR HOME & PERSONAL CARE PRODUCTS

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Unilever R&D Port Sunlight

RSC Innovation in Encapsulation Symposium

Burlington House

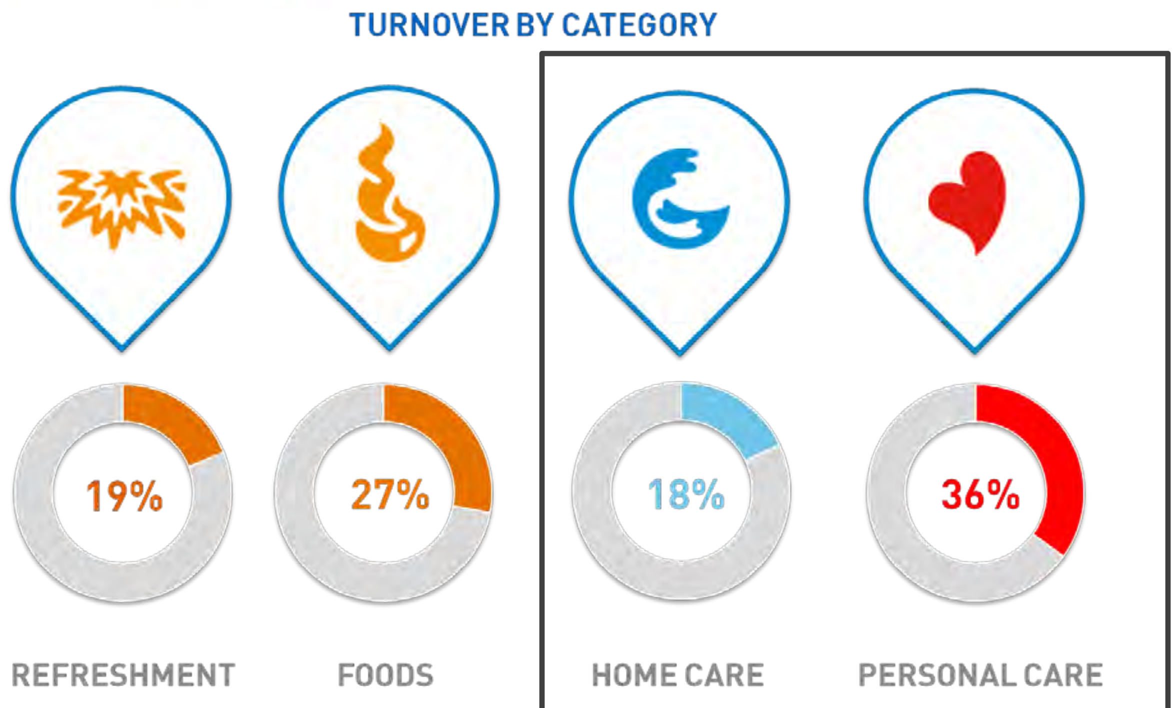
12 December 2014

INTRODUCING UNILEVER

2013 TURNOVER €49.8 BILLION

Unilever is one of the world's leading suppliers of fast-moving consumer goods.

Our products are sold in over 190 countries and used by 2 billion consumers every day.



UNILEVER'S HOME & PERSONAL CARE BRANDS

Unilever

dirt is good

Surf

Comfort

Cif

Domestos

LUX

Rexona

AXE

sunsilk

Dove

Signal

Lifebuoy

Vaseline

- Laundry Detergents & Fabric Conditioners
- Household Care
- Oral Care
- Deodorants
- Skin Cleansing & Care
- Hair Care (shampoo & conditioner)

HOME & PERSONAL CARE FORMULATIONS: TYPICAL COMPONENTS

Unilever

- Surfactants (anionic, nonionic, cationic): detergency, structuring, softening/conditioning
- Solvents (water; alcohols; glycols etc)
- Acids, alkalis
- Polymers: structuring, cleaning
- Builders, complexing agents
- Corrosion inhibitors
- Foam regulators
- Abrasives
- Humectants
- Fluorescent whiteners
- Dyes, opacifiers
- Anti-perspirant actives
- Oxidising bleaches
- Enzymes (laundry)
- Fragrance or flavour
- Antimicrobials (and preservatives)
- Antioxidants
- Sunscreens

in bars, powders, pastes, gels, liquids ….

surviving extremes of temperature and humidity to perform months or even years after manufacture

Safety, regulatory, cost and sustainability considerations all favour more efficient use of existing actives rather than development of new ingredients.

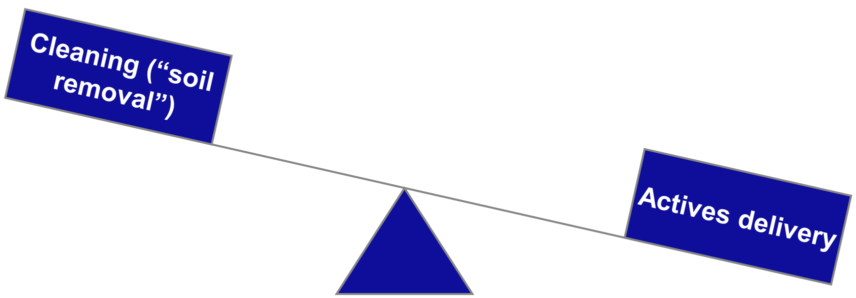
"THE DELIVERY CHALLENGE"

DELIVERY CHALLENGES WITHIN HOME & PERSONAL CARE FORMULATIONS

- **Protection** of ingredients that are
  - Intrinsically **unstable to oxidation or hydrolysis** (e.g. antioxidants, certain flavour and fragrance components)
  - **Incompatible with other formulation components,** e.g. combinations of protease and lipase enzyme cleaning aids

- **Minimising** losses by **evaporation** from surfaces, migration through packaging (volatile fragrance or flavour components)

- **Efficient deposition**
  - Delivering and retaining after rinsing efficacious levels of actives when surfaces are treated with cleansing products: surfactant based and designed to remove oils, particulates etc



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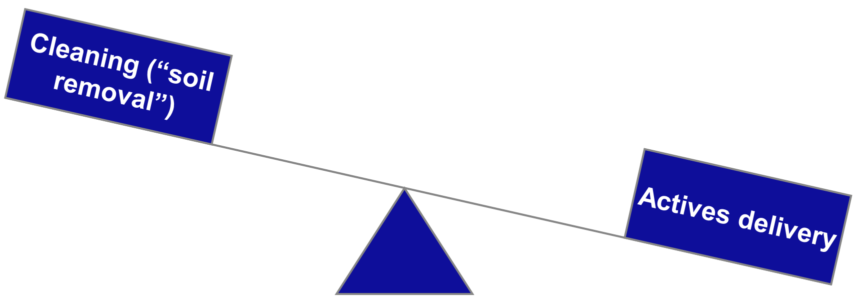


  - **Spatial Targeting**: ensuring that the active reaches **the right location**

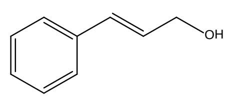
- Ensuring the active is available at the **appropriate time point**, e.g.
  - Silicone antifoam delivery at the end of the cleaning process: less rinsing → less water consumption
  - “Long lasting” fragrance

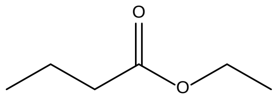
CHALLENGES IN FRAGRANCE DELIVERY (1)

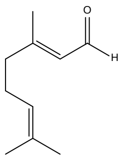
Fragrance is vital in communicating product efficacy (cleanliness, hygiene, “freshness”) and covering formulation base odour.

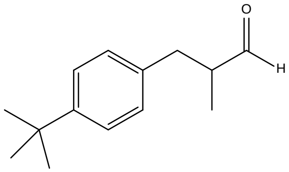
Fragrances are complex mixtures (often 50+ components) and often one of the most expensive ingredients in HPC products.

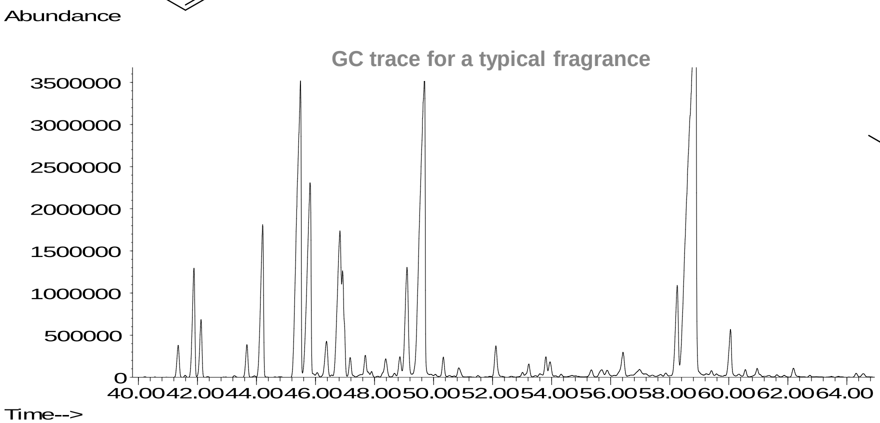
- Alcohols
- Ethers
- Ketones
- Aldehydes – liable to oxidation
- Esters & lactones – liable to hydrolysis

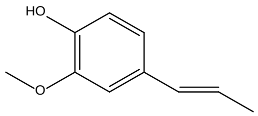


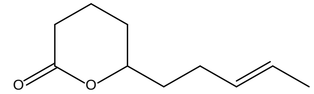










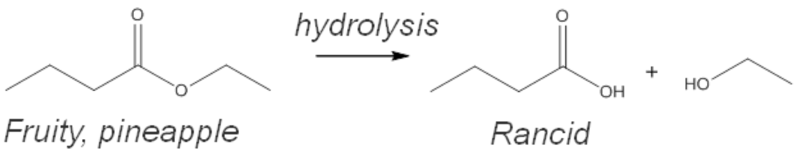


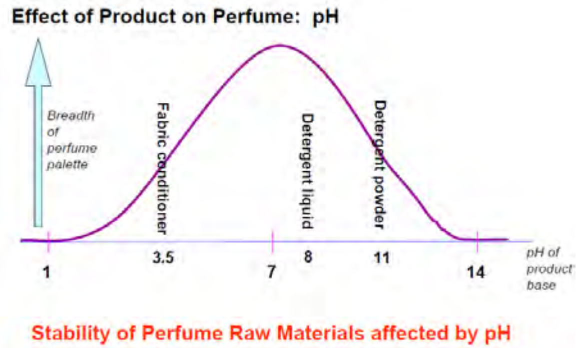
Unilever relies on collaborations with Perfume Houses to develop the most appropriate fragrance for a particular product. We also work closely together to ensure we can deliver the fragrance effectively from our products.

CHALLENGES IN FRAGRANCE DELIVERY (2)

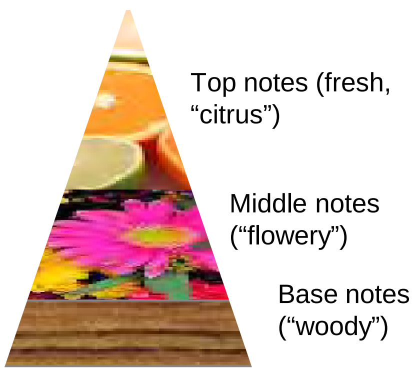
Efficient delivery of fragrance oils presents many challenges:

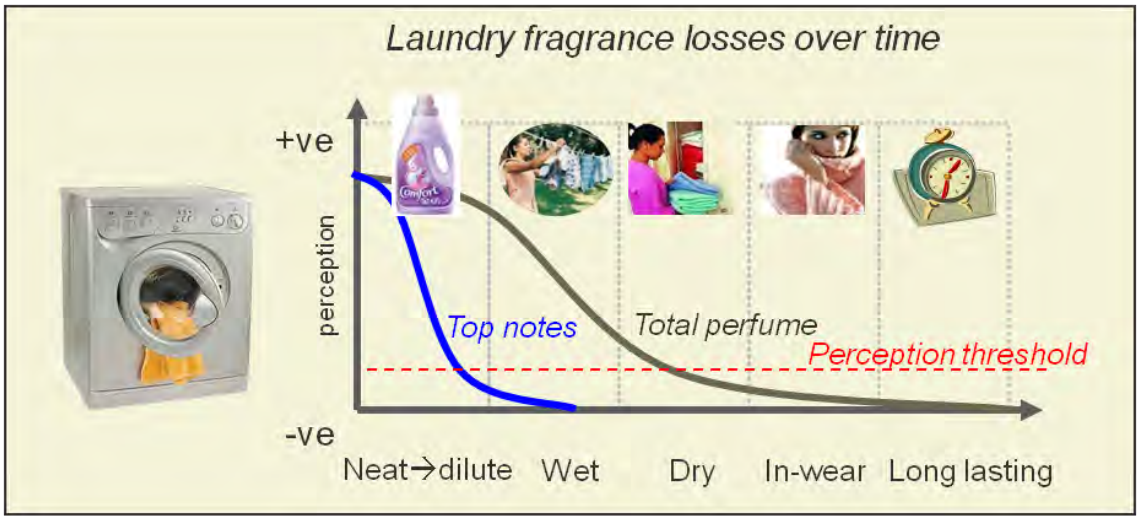
- Some fragrance components are unstable in certain product bases, risking perceivable shifts in hedonics on storage





- Fragrances are inherently volatile and evaporate from treated surfaces:
Fresh "top notes" - lost after the ca. 15 minutes; "middle" notes - evaporate over a few hours, "base" notes – last many hours





- Fragrance physico-chemical properties are similar to oily soils: typically < 2% of free fragrance dosed from laundry detergent products is retained on the substrate after rinsing (> 98% lost down the drain)

ROUTES TO ENHANCED FRAGRANCE DELIVERY

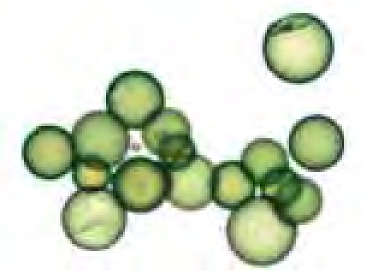
Improved fragrance impact can be achieved by:

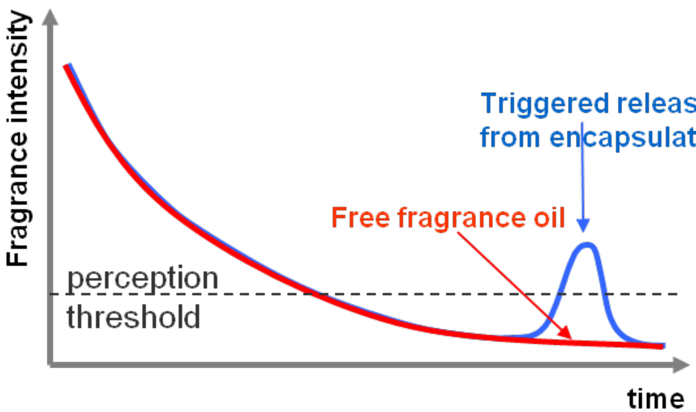
1. **Overdosing unstable/highly volatile components**: expensive; changes hedonics

2. **Use pro-fragrances** (generate fragrance in situ, e.g. by hydrolysis): single components only; expensive

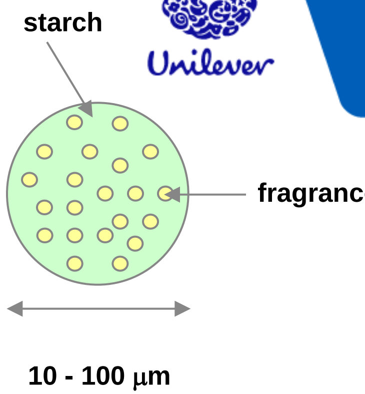
3. **Encapsulation:** offers control of deposition and release profile but presents new questions

   - **How efficient is encapsulation:** Is the loading sufficient to deliver the sensory benefit in a cost effective manner ?
   - **How stable is the coating ?** Will it survive manufacture and storage, preventing leakage of the contents ?
   - **How and when will the contents be released ?** Friction/pressure (mechanical rupture), change of temperature, diffusion through the polymer wall, dissolution of the coating...
   - **For "rinse off" (e.g. cleansing products), how substantive will the encapsulates be to the target substrate ?**
   - **Will encapsulation impact on the physical stability of the formulation (e.g. phase separation, viscosity changes) ?**





FRAGRANCE ENCAPSULATION TECHNOLOGIES: STARCH



Spray dried emulsion of fragrance with hydrophobically (typically e.g. C_6 ester) modified starch: “matrix” particles (perfume dispersed through starch honeycomb structure).

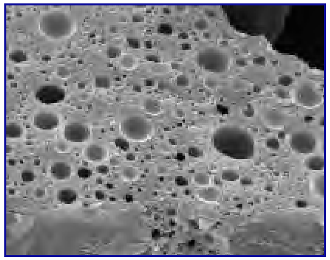
Can contain up to 40 or 50% fragrance by weight.

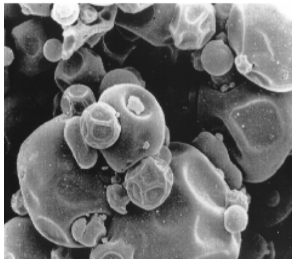
The starch is water soluble – only suitable for non-aqueous products.

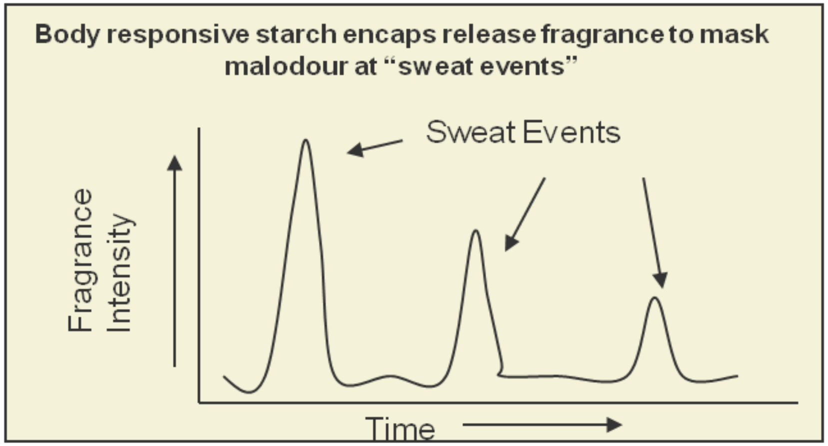
Used in:

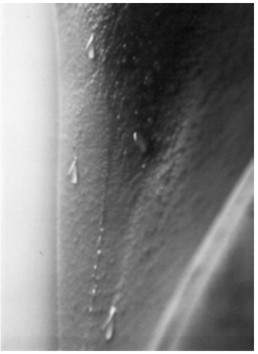
- laundry detergent powders: provide “bloom” in hand-wash

- antiperspirants: the particles dissolve in body moisture and deliver a “fragrance burst” when the consumer sweats, helping to counteract malodour









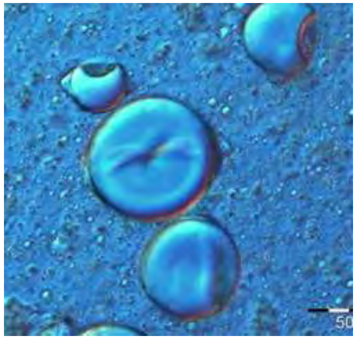
FRAGRANCE ENCAPSULATION TECHNOLOGIES: CORE-SHELL CAPSULES

"Core-shell" particles: a protective coating formed around a droplet of oil, e.g. fragrance

Gelatine "complex coacervates" (Carbonless copy paper, "scratch & sniff" technology): precipitate gelatine (cationic below pH 4) with anionic polysaccharide around droplet; protein is cross-linked (e.g. with glutaraldehyde) to increase wall rigidity for processing.

Fragrance content: 40-80% by weight

Used in toothpastes, skin creams etc

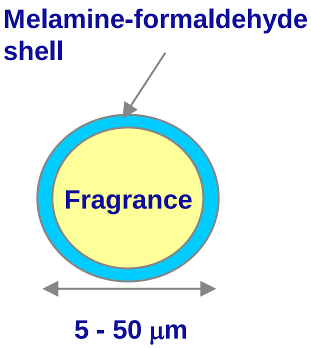


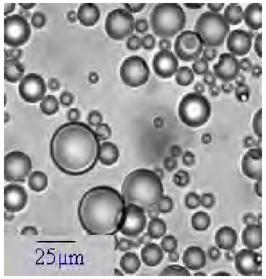
Both types of encapsulates can be used in aqueous formulations and release their payloads when ruptured by mechanical shear.

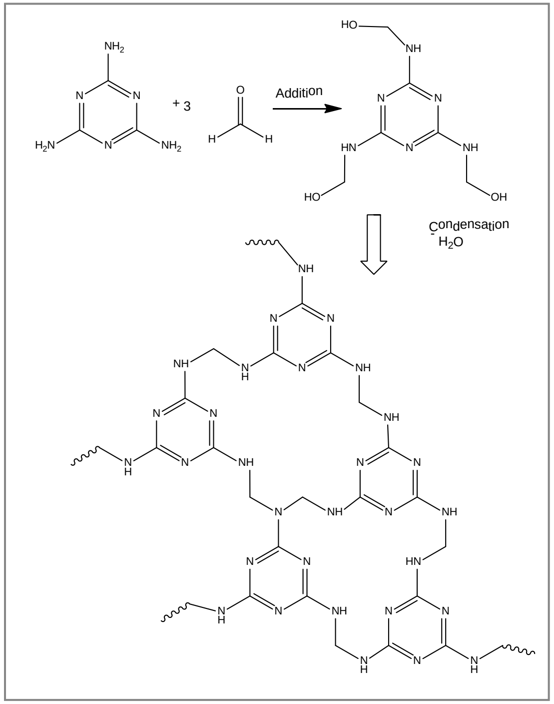
Melamine-formaldehyde ("aminoplasts", MF)
Condensation polymerisation around droplet.

Fragrance content: 50-80% by weight.

M-F walls are deformable when wet (in formulation) but become rigid and brittle when dry.





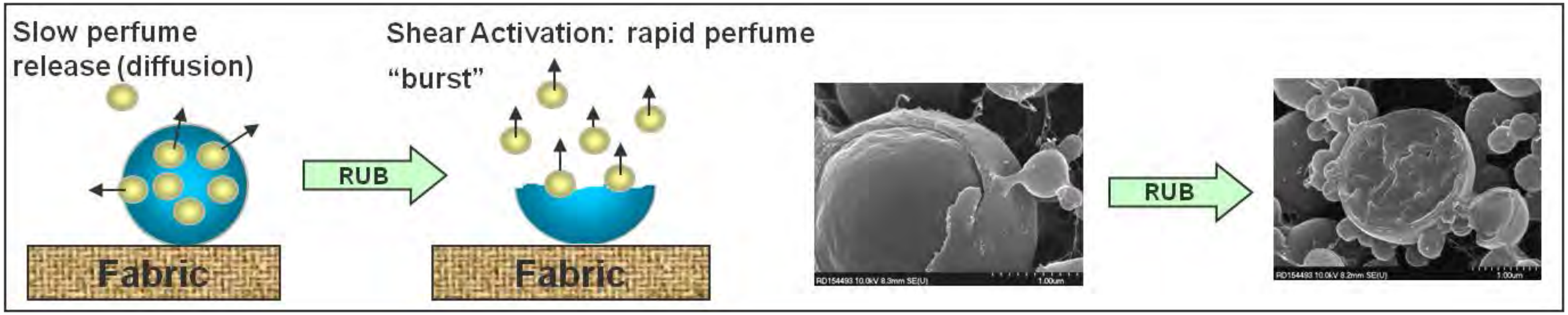


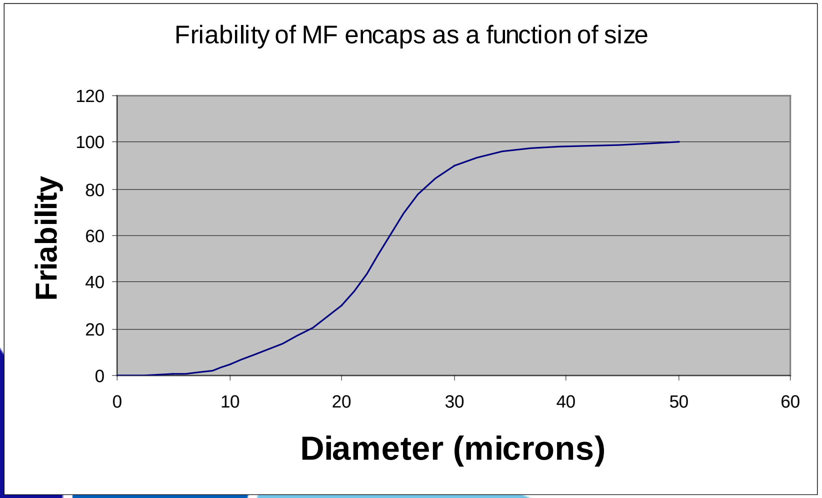
MF CAPSULES IN UNILEVER LAUNDRY PRODUCTS

Gelatine coacervates give unacceptable leakage in laundry products and would be unstable to protease enzyme (cleaning aid).

MF capsules are used in some Unilever powder detergents and fabric conditioner liquids:

- enhanced fragrance delivery (typically 5-10 fold improvement)
- long-lasting fragrance benefits (perfume still perceivable days or weeks after washing).





The size of the encapsulates has a significant impact on:

- the force required to fracture the shell and release the contents;

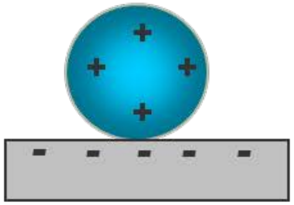
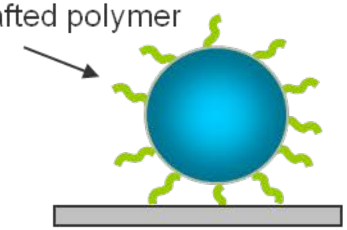
- how efficiently the particles deposit on textiles (although the geometry of the fibres also plays a role);

- how readily particles can be suspended in liquid formulations (risk of creaming or sedimentation) – density matching can only take you so far!

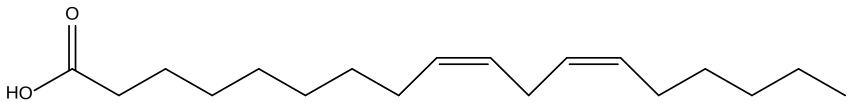
IMPROVING CAPSULE DEPOSITION FROM DETERGENTS

Detergent products are designed to remove particulates ("dirt") which presents a potential conflict when trying to deposit encapsulates.

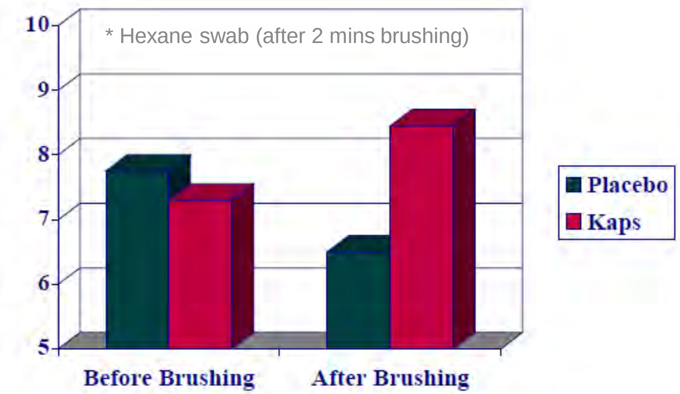
Several approaches to improving delivery of encapsulates are described in the patent literature:

	Approach	Selected examples
Covalent bond formation	Substrate reactive materials, e.g. thiols for disulfide bond formation with proteins, triazine bond formation with cotton (c.f. reactive dyes) (Semi-)permanent attachment Typically requires extreme reaction conditions Unsuitable for HPC product usage	WO 0556 110 (Exsymol) WO 2007063001 (Ciba)
Charge: cationically modified particles	Electrostatically favoured interactions with negatively charged surface, e.g. textiles, skin. Disadvantage: incompatibilities with anionic surfactant bases 	WO 2011 123730 (Proctor & Gamble) US 20040138093 (IFF Ltd) US 6589562 (Salvona LLC)
"Surface recognition"	Inspired by use of "hairy particles" for improved colloidal stability Textile substantive polymers e.g. polysaccharides for cotton, polyaromatics for polyester Grafted polymer 	WO 2011 020652 WO 2009 037060 (Unilever) US 8021436 (Procter & Gamble)

DELIVERING OILY BENEFIT AGENTS FROM A TOOTHPASTE



Sunflower oil recovery (ug)* from gum tissue before and after brushing



Sunflower oil (linoleic acid) delivers gum health benefits but is only deposited at low levels from (anionic surfactant based) toothpastes.

Encapsulation in shear sensitive capsules improves delivery.

- Agar based coacervates: leaked in the formulation
- Gelatine-gum arabic core-shell particles: stable

Controlling wall thickness and particle size is vital:

- Must release when crushed during brushing (0.1-0.2 N force) but survive processing
- Optimum diameter was found to be approx. 1 mm: smaller (5-50 um) particles may get trapped between interdental spaces and do not experience sufficient shear from toothbrush bristles to rupture

- Large particles can also be seen in the toothpaste, giving a clear visual cue to consumers.

F Schafer et al, Int. Dental Journal, 2007, **57 (S2)**, 119; A K Green et al, Int. Dental Journal, 2007, **57 (S2)**, 124

IMPROVING STABILITY OF INCOMPATIBLE ACTIVES

Effective sunscreen compositions require protection from both UV-A and UV-B light.

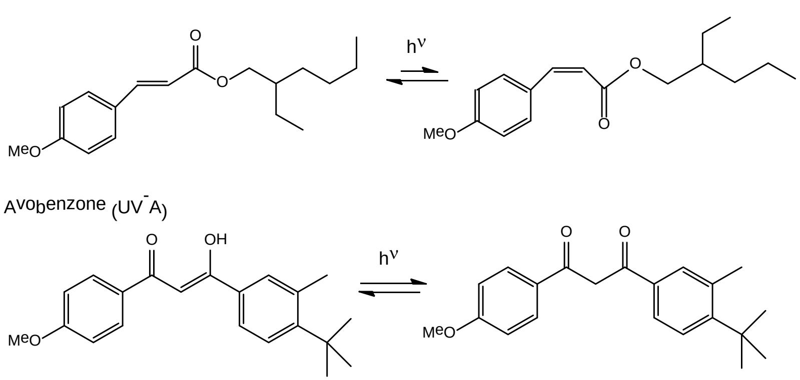
Mixtures of two of the most efficacious (high extinction coefficient) sunscreens, avobenzone [UV A] and octyl methoxycinnamate [UV-B] undergo radical mediated mutual decomposition when irradiated.*

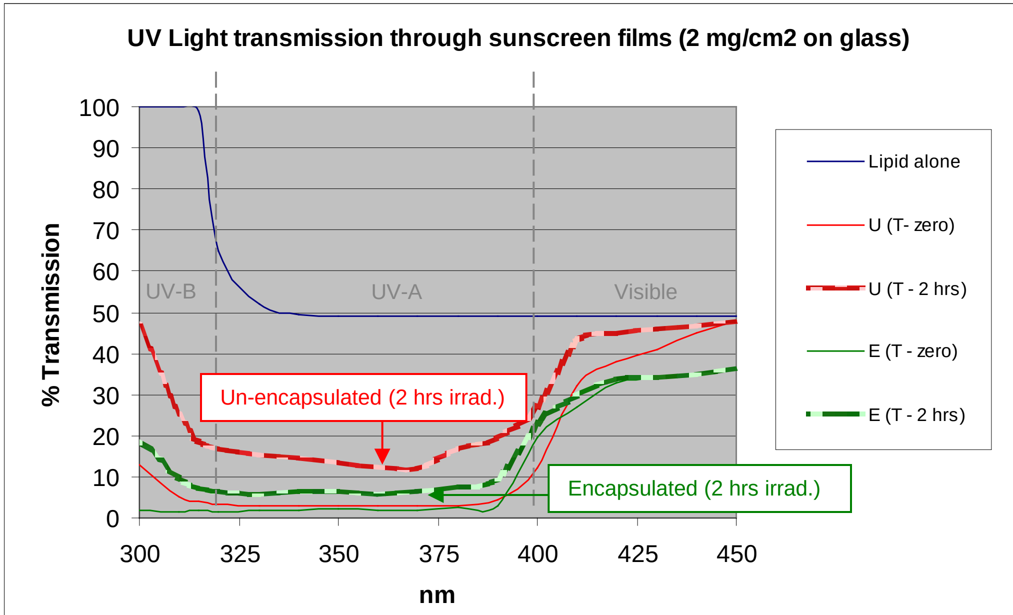
Encapsulating the more unstable avobenzone component in a lipid based microparticle reduces instability and extends the period over which treated skin is protected.

* R M Sayre et al, *Photochem. Photobiol.*, 2005, **81**, 452.

OMC (UV-B)

Avobenzone (UV-A)





Stability is further enhanced by mixing lipid with antioxidants (e.g. tocopheryl acetate).

% UV Transmission (350 nm)	no irradiation	2 hours irradiation
Unencapsulated	3.1	13.5
Encapsulated	2.1	6.7

U = 1% AVB + 1% OMC unencapsulated mixture
E = 1% OMC + 1% AVB encapsulated in 20% cetyl palmitate

Patent number: WO 2007/042259

SUMMARY

Encapsulation can help overcome many formulation problems but may create new challenges.

To be commercially viable, the benefits must clearly outweigh any complications that incorporating encapsulates in the product may bring.

- Segregation of incompatible materials
- Improved delivery:
    - More active delivered to the surface
    - Released at the most appropriate time

- An effective way to communicate with consumers

Vitamin A (retinol) in Dove Daycream

Fragrance in Comfort Fabric Conditioner

Sunflower oil, keratin and pigment in Mentadent Toothpaste

THANK YOU FOR YOUR ATTENTION

R&D PORT SUNLIGHT