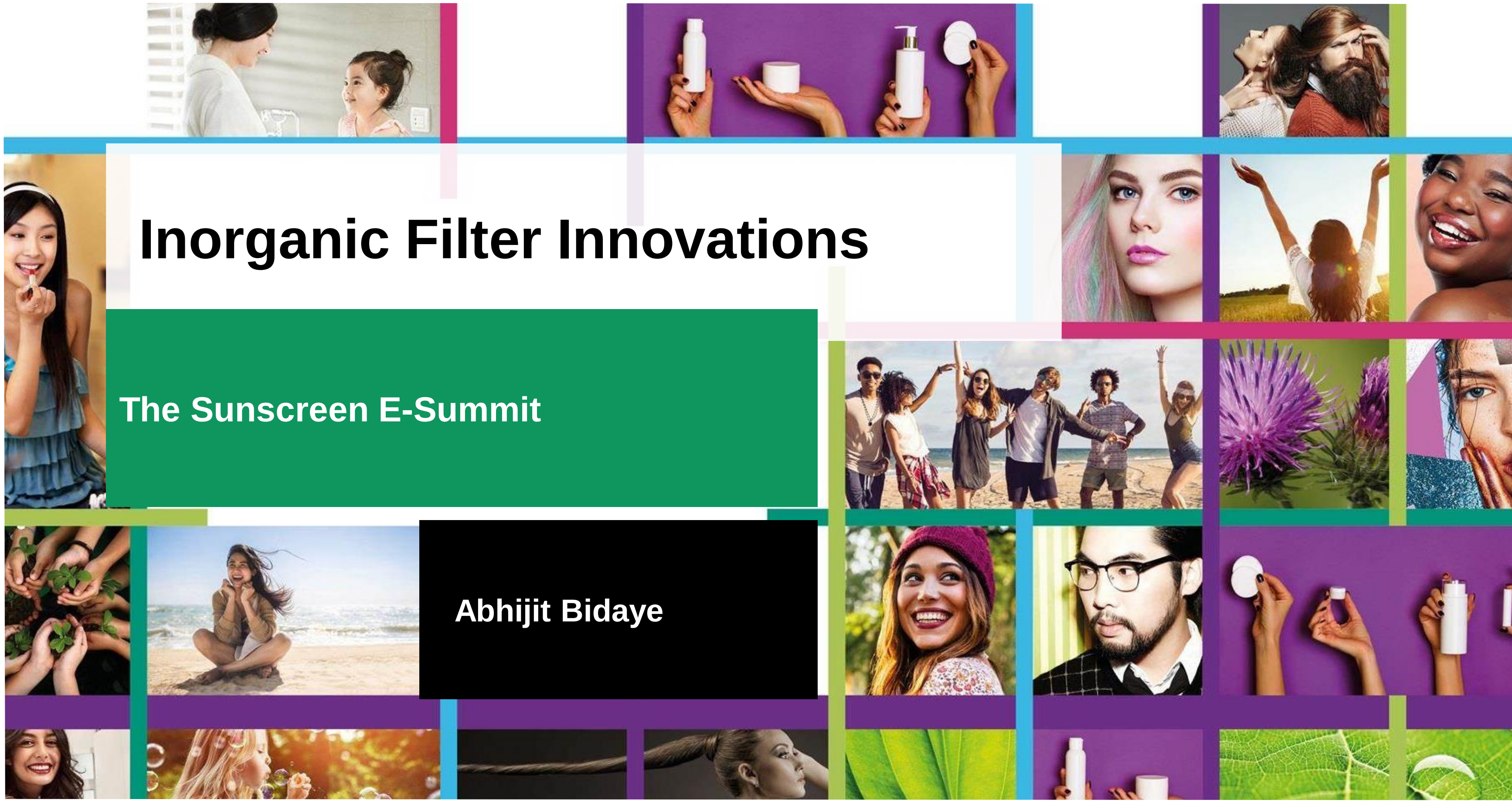


Inorganic Filter Innovations

The Sunscreen E-Summit

Abhijit Bidaye

Solar protection at Croda

Solar
Synthesis and
Dispersion
Manufacture
Croda Ditton

↑↓

Manufacture
TiO_2 Powder
Croda Mevisa

Smart science to improve lives™

CRODA

Solaveil™ physical shield

Global formulation network

Solar formulation expertise
in USA, Japan, Korea, China and Europe

Smart science to improve lives™

CRODA

Croda's commitment

Solaveil™ physical shield

To be Climate, Land and People positive by 2030

We will use our Smart Science to promote healthy lives and wellbeing through the development and application of our ingredients and technologies

By 2030, we will protect at least 60 million people annually from potentially developing skin cancer from harmful UV rays, through the use of our solar protection ingredients.

3 GOOD HEALTH AND WELL-BEING

Target 3.4 of SDG 3, Good Health and Wellbeing, references cancers as part of reducing premature mortality from noncommunicable diseases.

Properties of TiO_2 and ZnO

TiO_2

ZnO

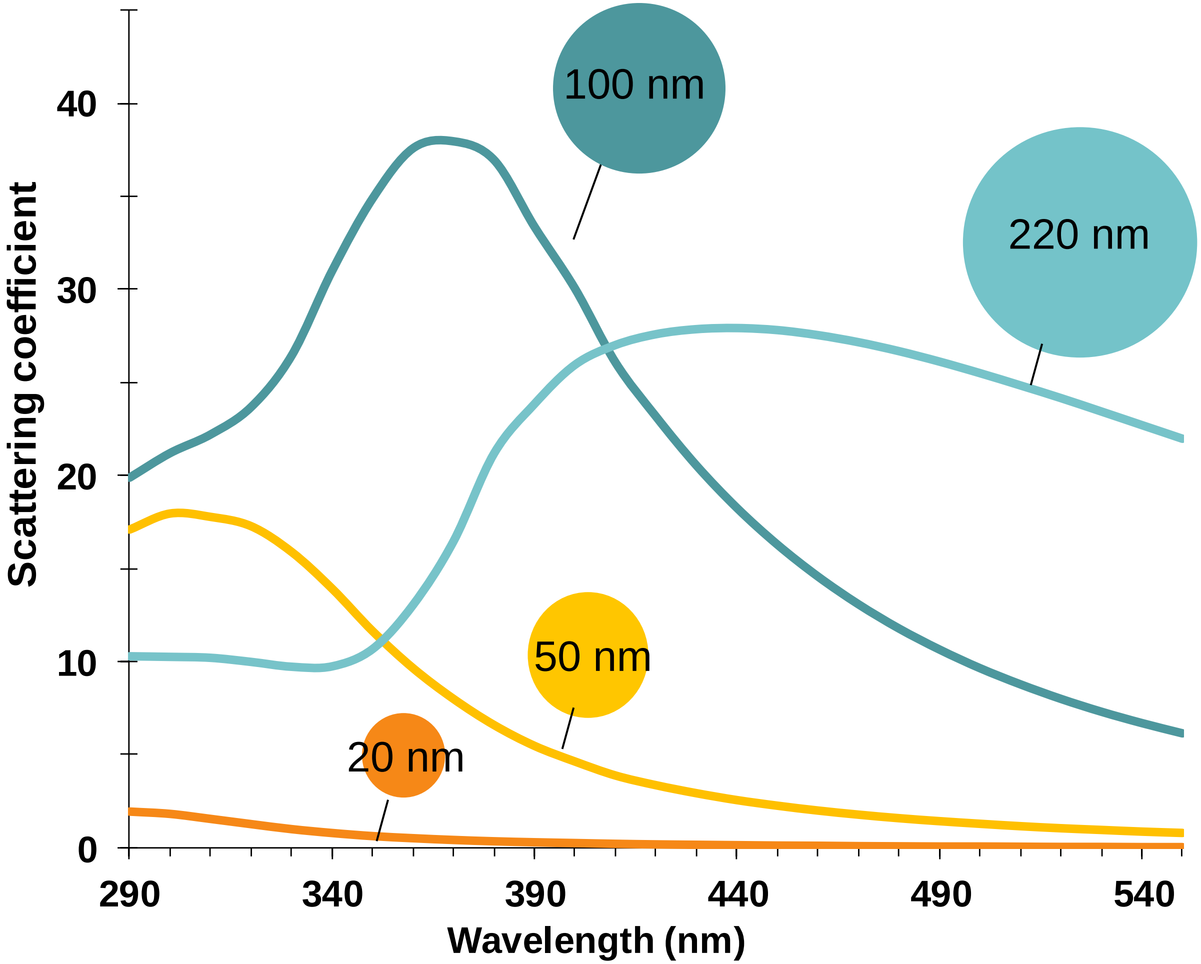
Properties are dependent on:

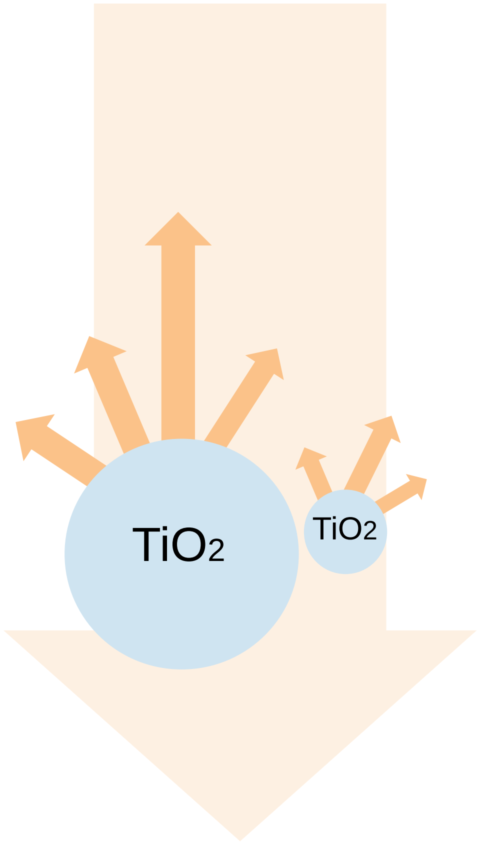
- Wavelength of radiation
- Particle size and shape
- Refractive index (chemical nature of the inorganic particles)

Influences

Scattering Absorbance

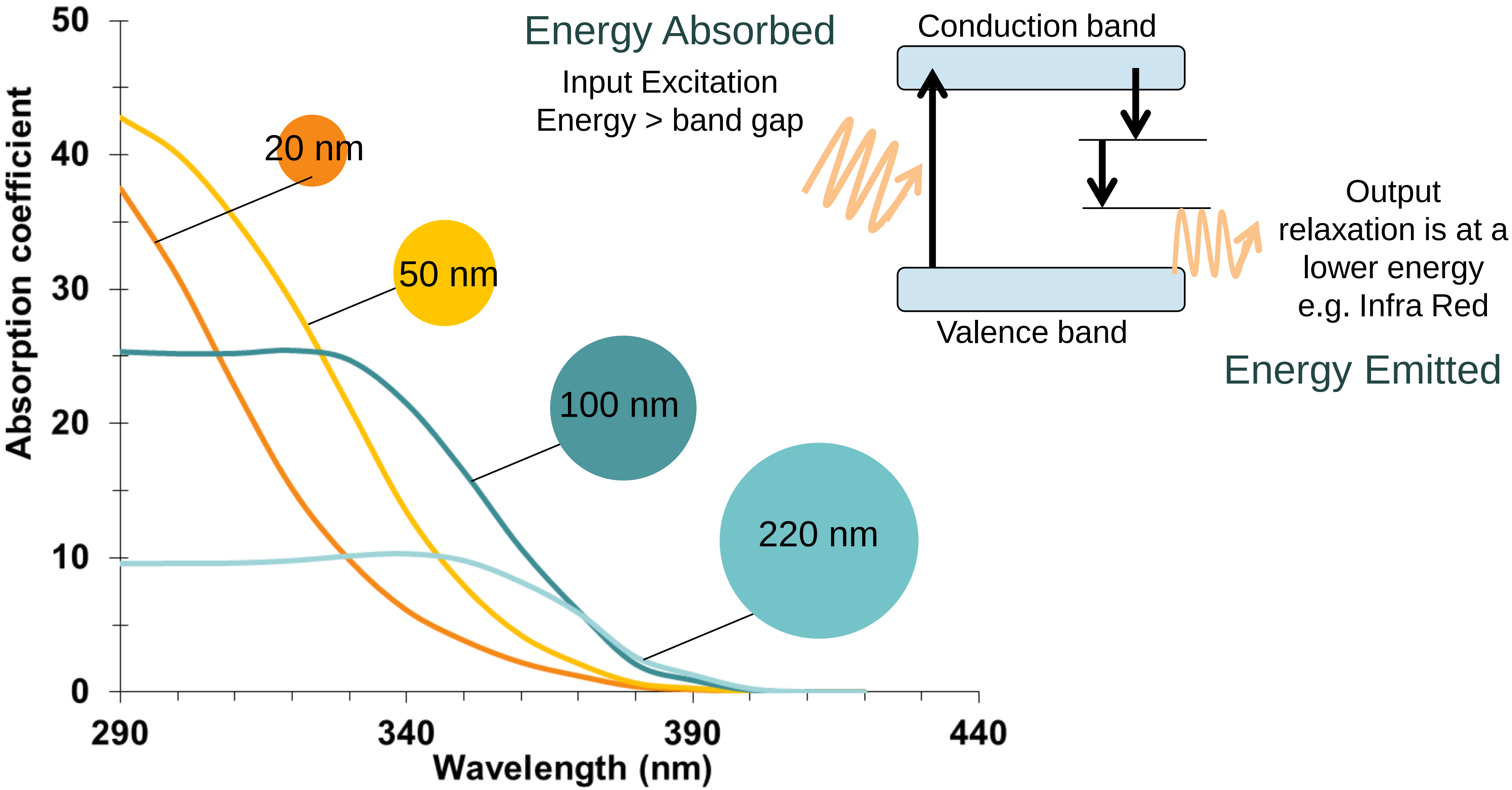
Particle scattering theory (Robb et al)





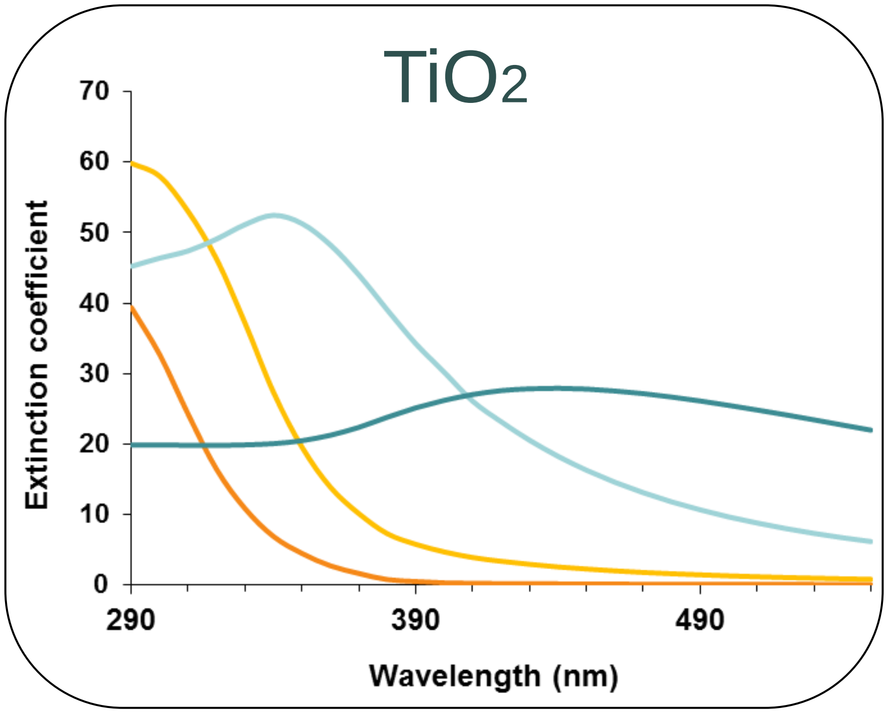
Particle size affects the wavelengths and amount of light scattered

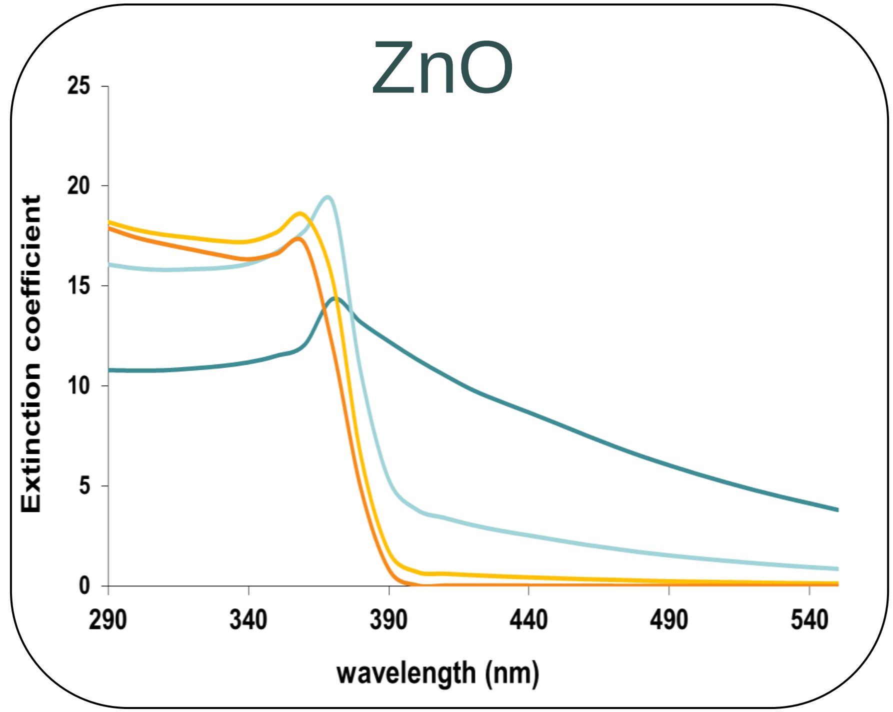
Particle absorption theory (Robb et al)



Particle size affects the absorption of UV wavelengths

Attenuation = Absorption + Scattering





20 nm | 50 nm | 100 nm | 220 nm

Particle size affects the attenuation of UV wavelengths for both ZnO & TiO_2

Croda UV filter range

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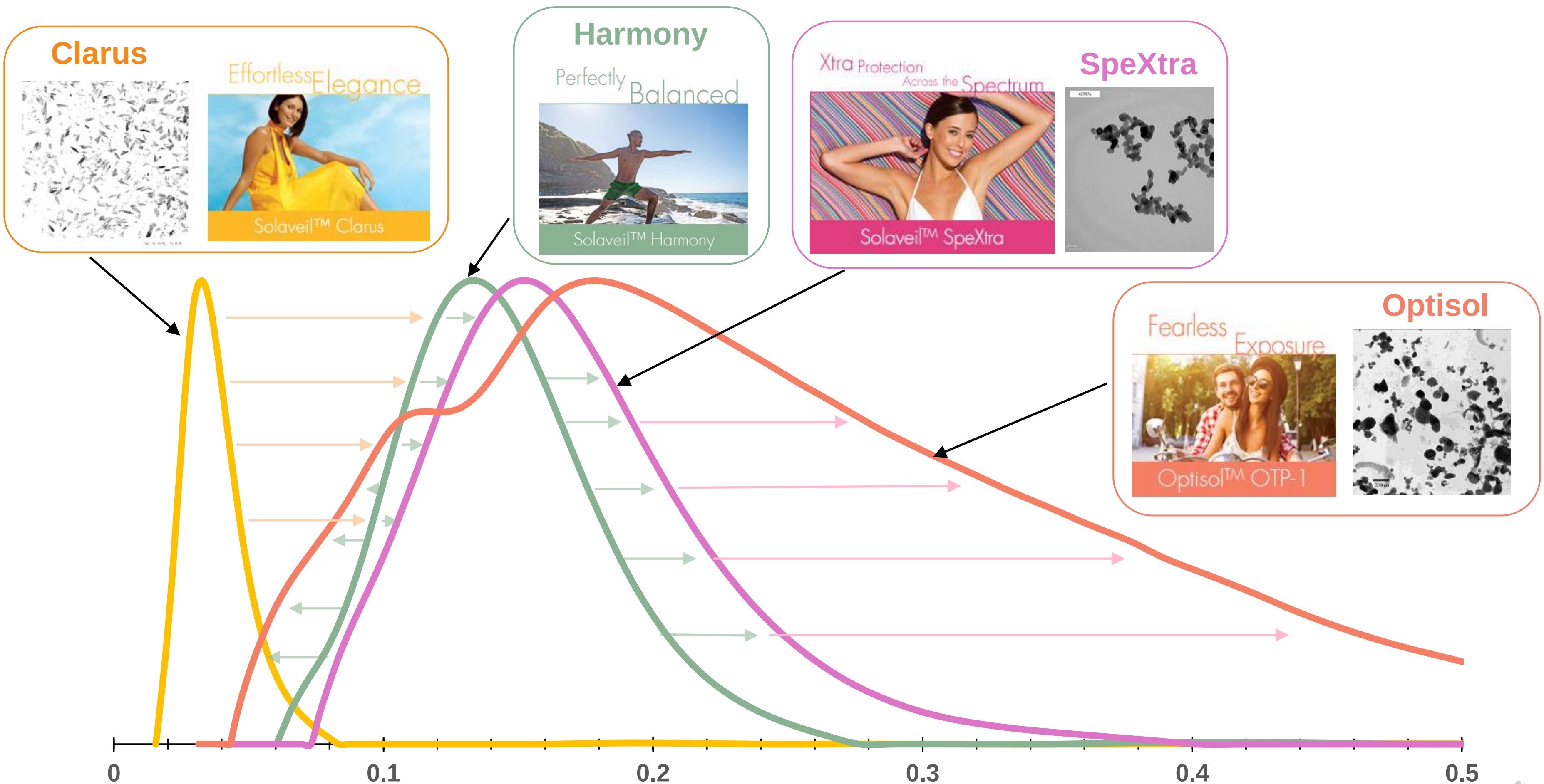
Solaveil™
physical shield

TiO_2 range particle size & distribution



Diameter / Microns

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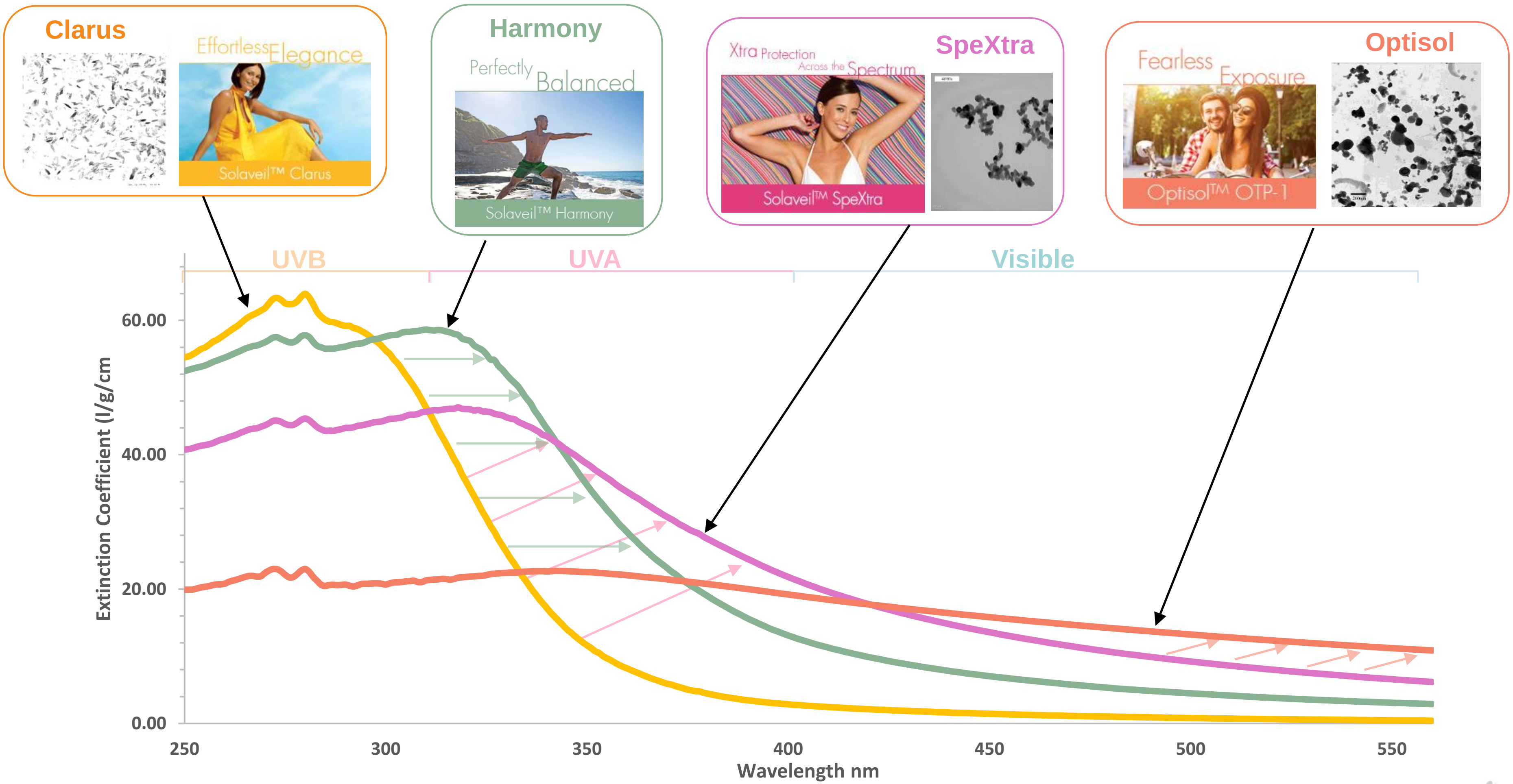
* Please note: Optisol OTP-1 is not registered as a UV filter in the US

Particle size & distribution influence protective properties



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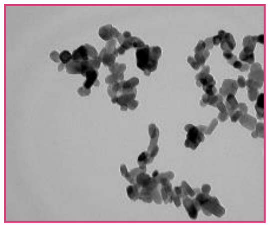
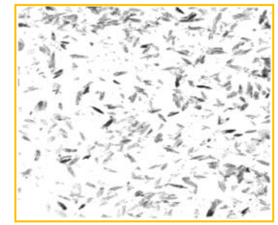
* Please note: Optisol OTP-1 is not registered as a UV filter in the US

Appearance on skin and particle size

Solaveil SpeXtra | Solaveil Harmony | Solaveil Clarus



180nm*



30nm*

Skin Type I

Skin Type III

Skin Type V

Formulations containing TiO_2 7.5% solids

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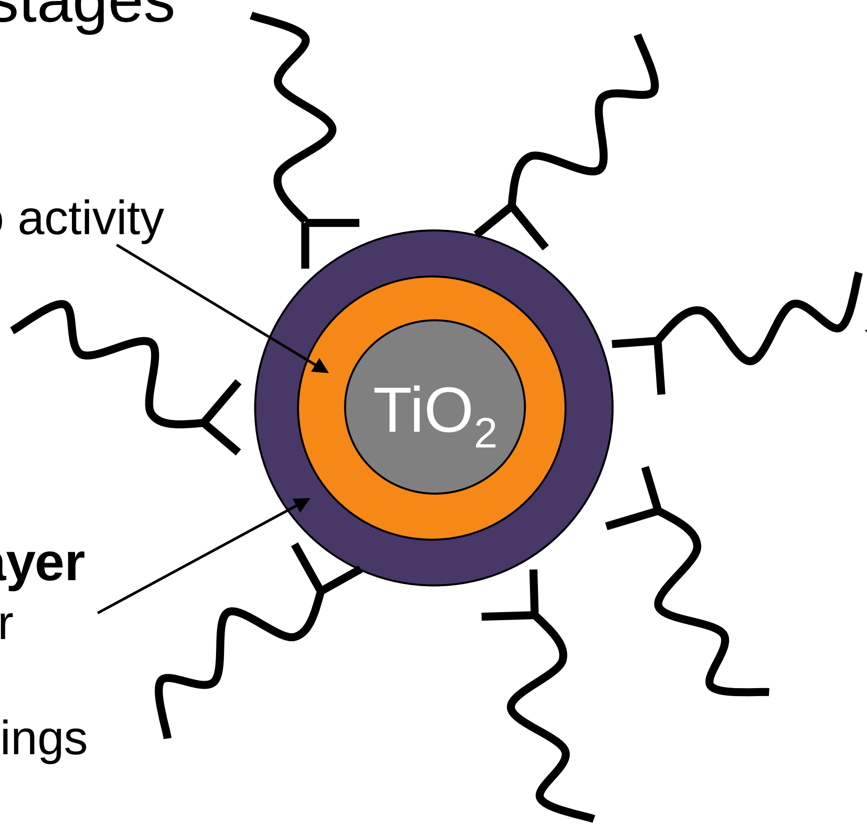
*Mean size by X-Ray Disc Centrifuge

Surface modification

- Multilayer coatings
- Applied in stages

1. Base Layer
- Reduces photo activity



3. Outer layer
Aids in dispersion and formulation

2. Secondary layer
- Anchor point for organics or secondary coatings

Particle dispersion

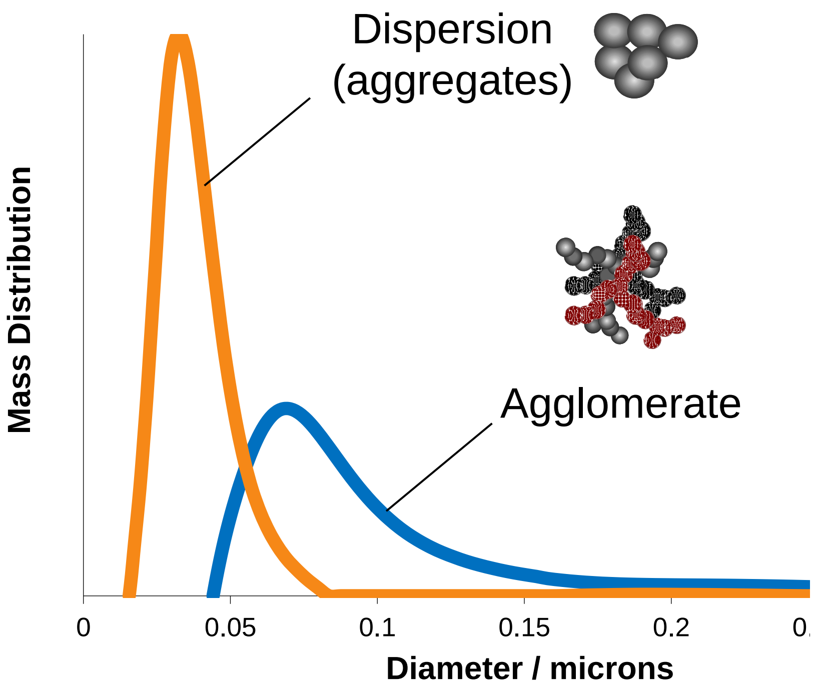
- Particles are dispersed in a carrier fluid using a dispersing agent and high energy bead milling

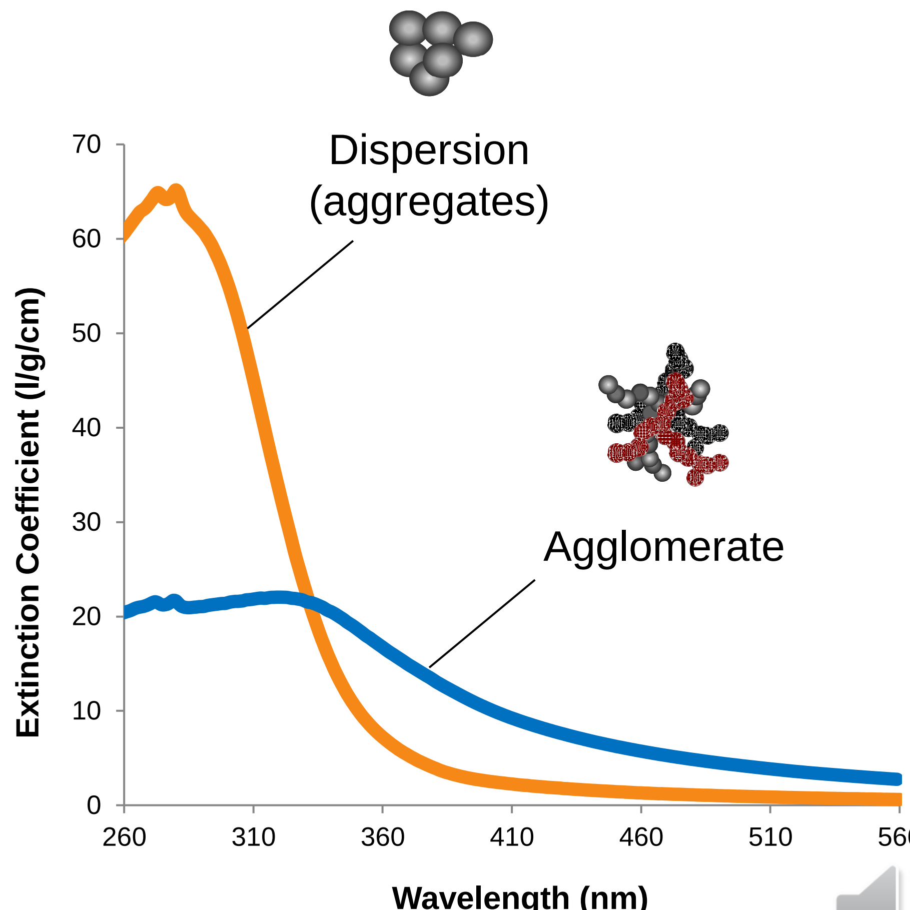
- The dispersing agent bridges between the carrier fluid and the particle coating

Powder

Liquid

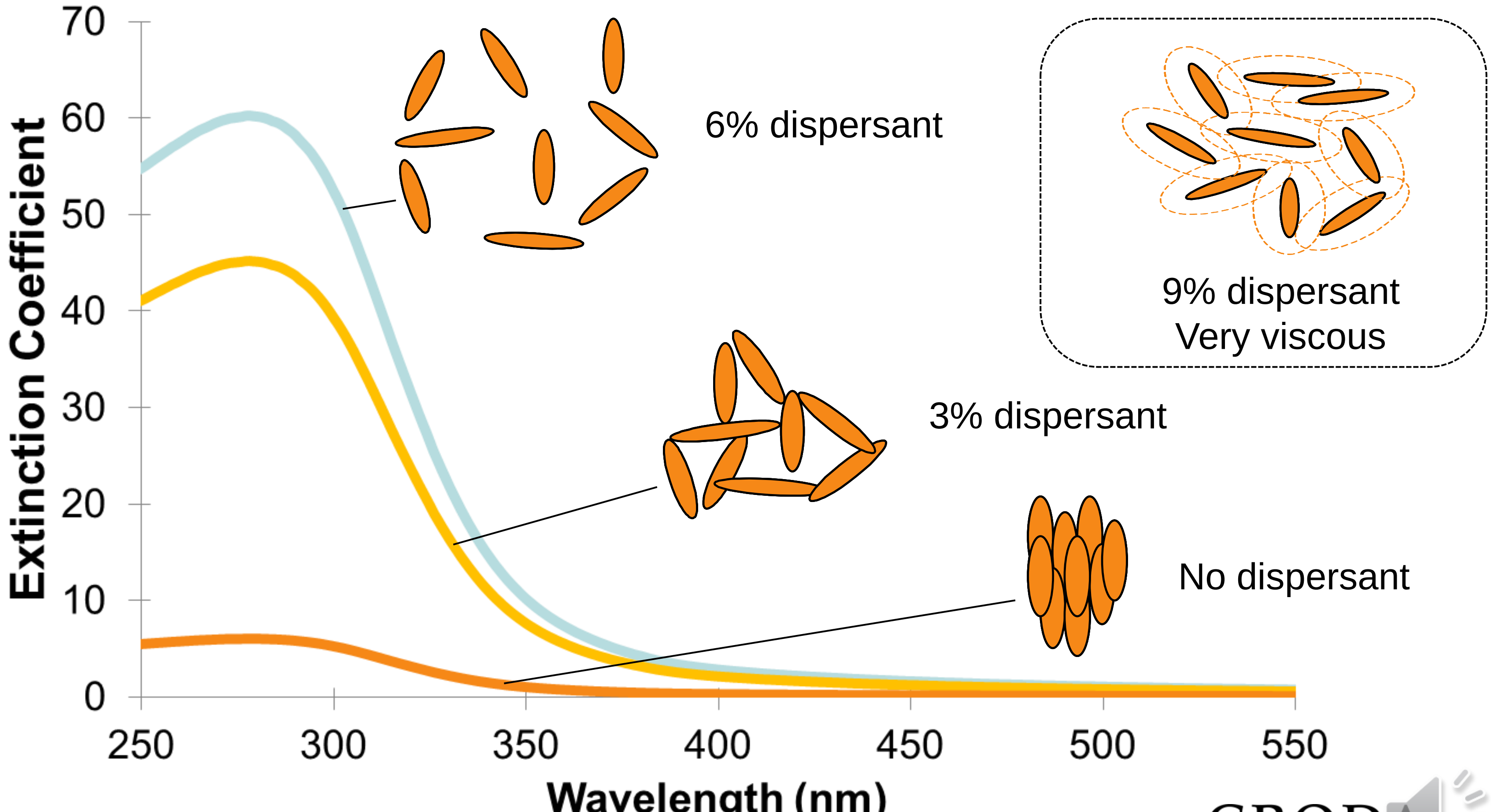
Particle size vs. UV attenuation





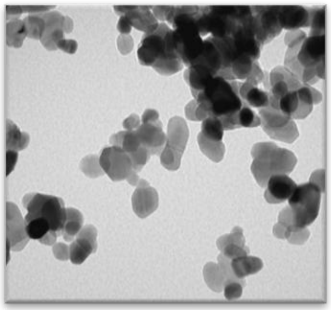
Optimising dispersions

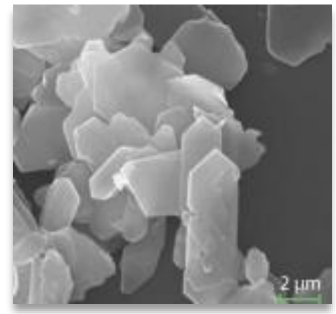
Decreasing flocculation gives higher efficacies and rheology control

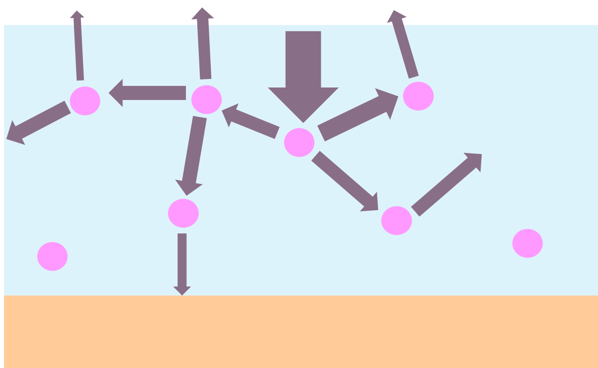


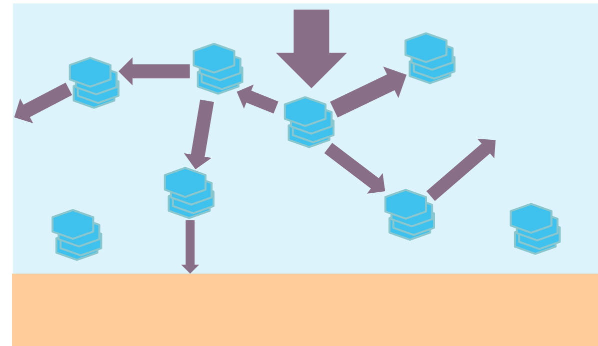
CRODA

Novel particle shape: ZnO







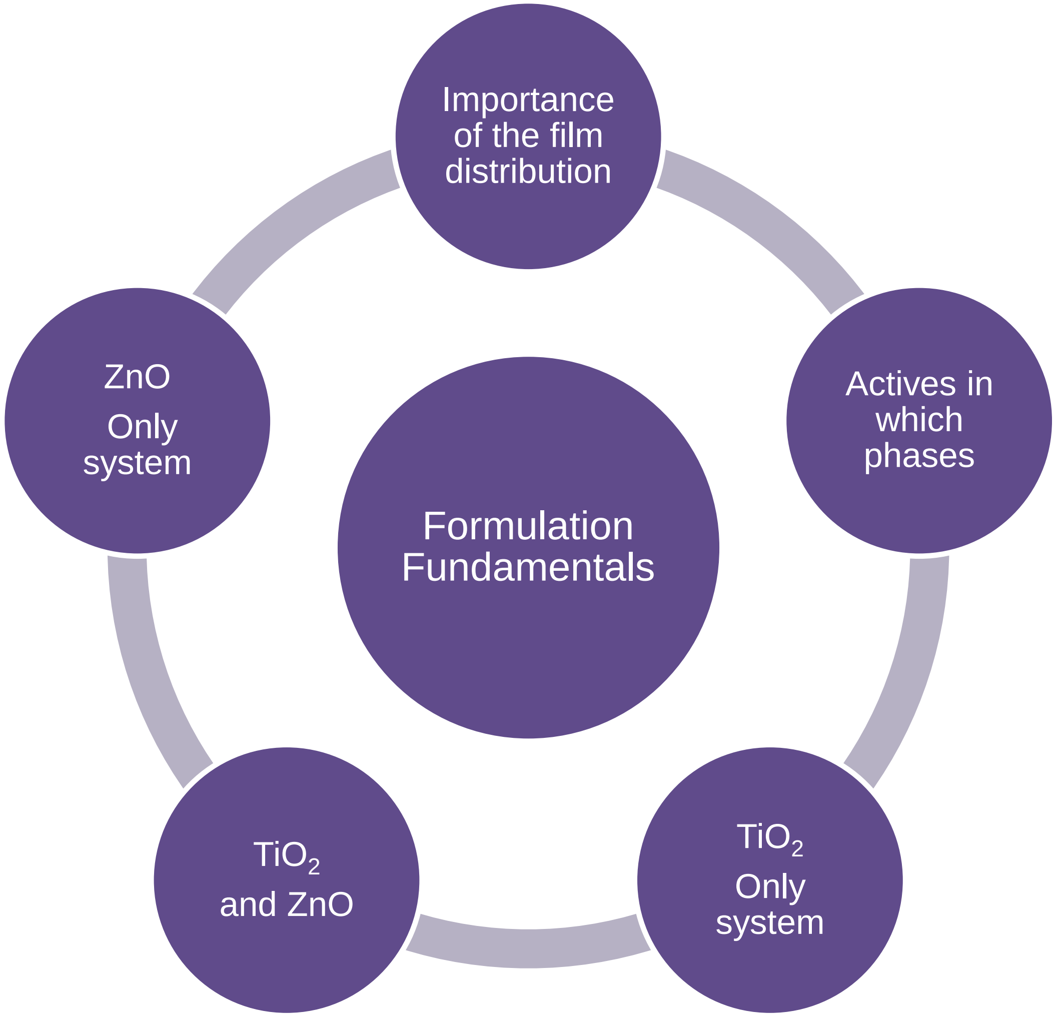


Conventional ZnO sunscreen:
Scattering/reflection of visible light back to the surface leads to a white appearance on skin

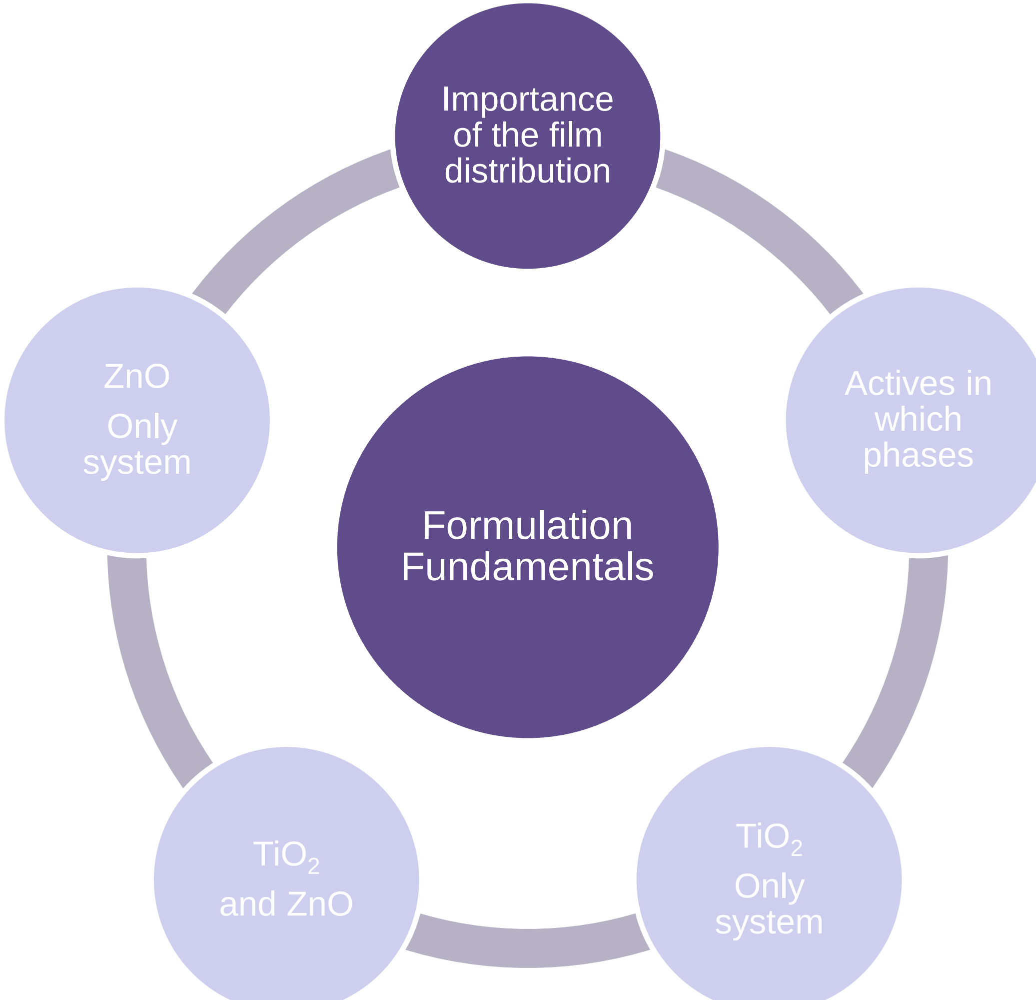
Solaveil MicNo ZnO sunscreen:
Platelets ordered structure results in less scattering/reflection to the surface and therefore unrivalled **transparency**

Skin images from skin phototype III (for details click here)

Formulation fundamentals



Formulation fundamentals



Product distribution on skin

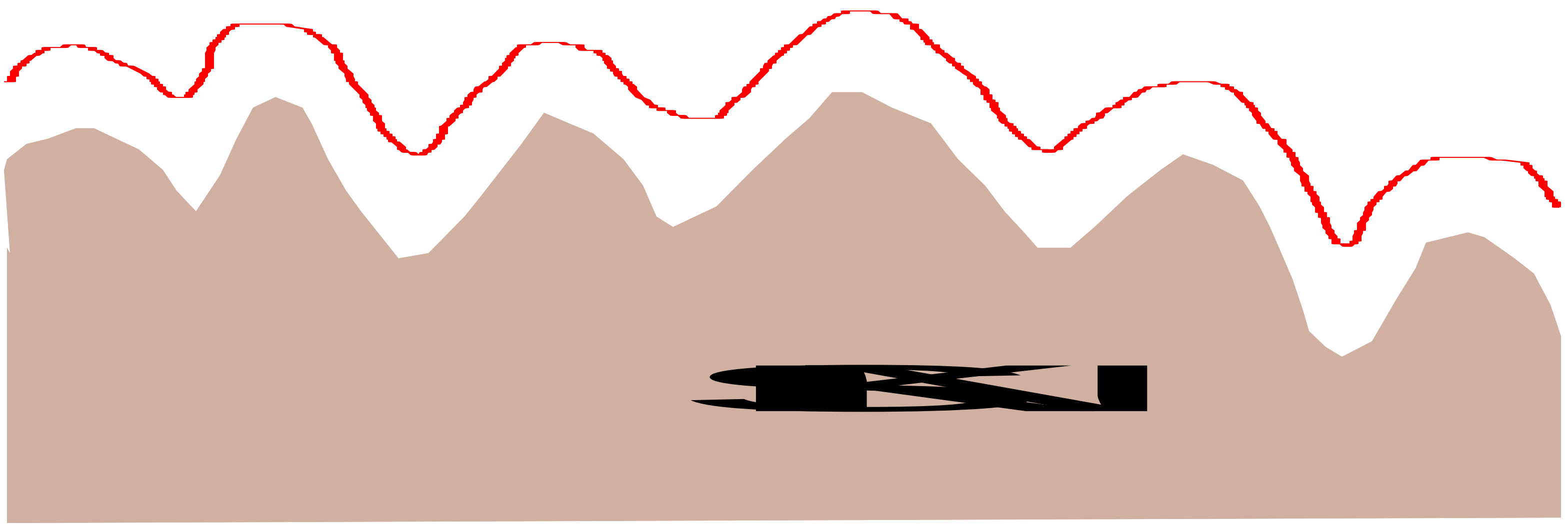
- In order to achieve high efficacy of sunscreen actives, it is essential that the sunscreen is evenly distributed on the uneven skin surface

- This principle applies to all sunscreen actives, whether organic or inorganic, but is particularly important for mineral sunscreens, since efficacy is critically influenced by size and distribution of particles

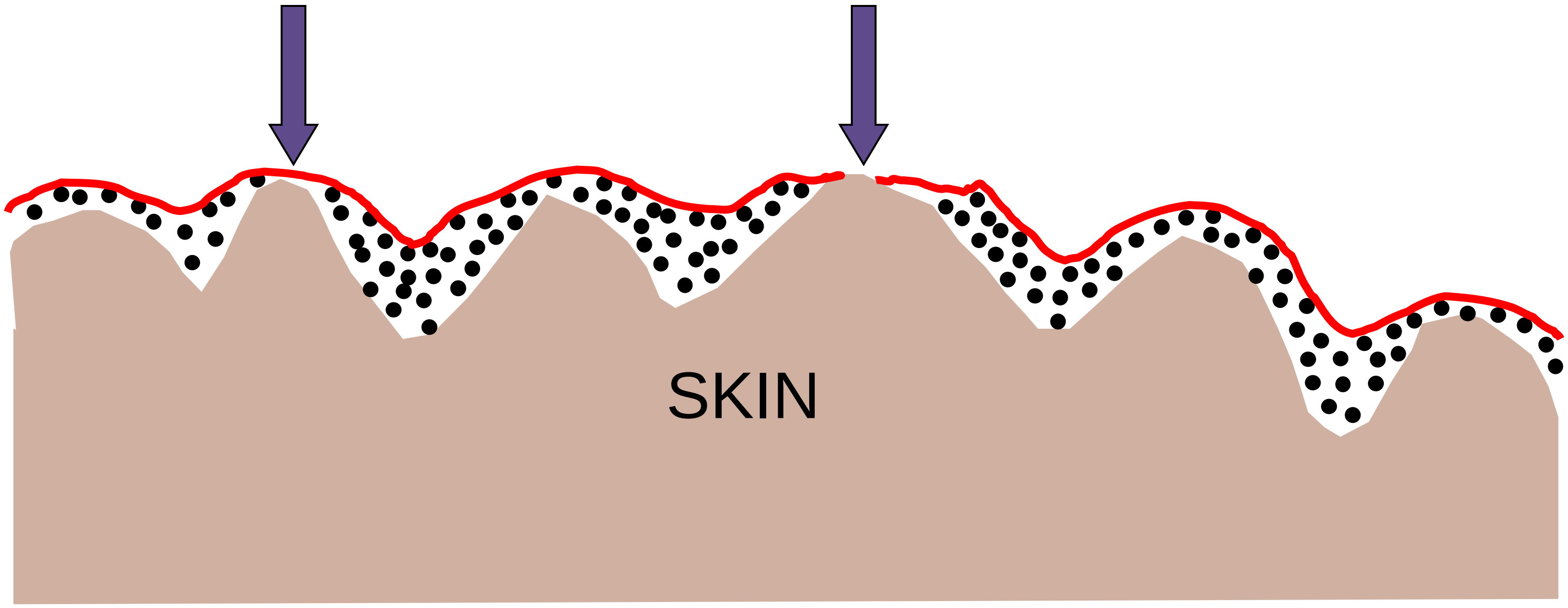
- For high efficacy, therefore, there are four main requirements:
  1. Coherent protective film on skin after application and dry-down
  2. Maximum amount of sunscreen active within this film
  3. Even distribution of sunscreen particles
  4. Optimum particle size

Optimal efficacy

- Even product film on skin
- Even distribution of actives within this film

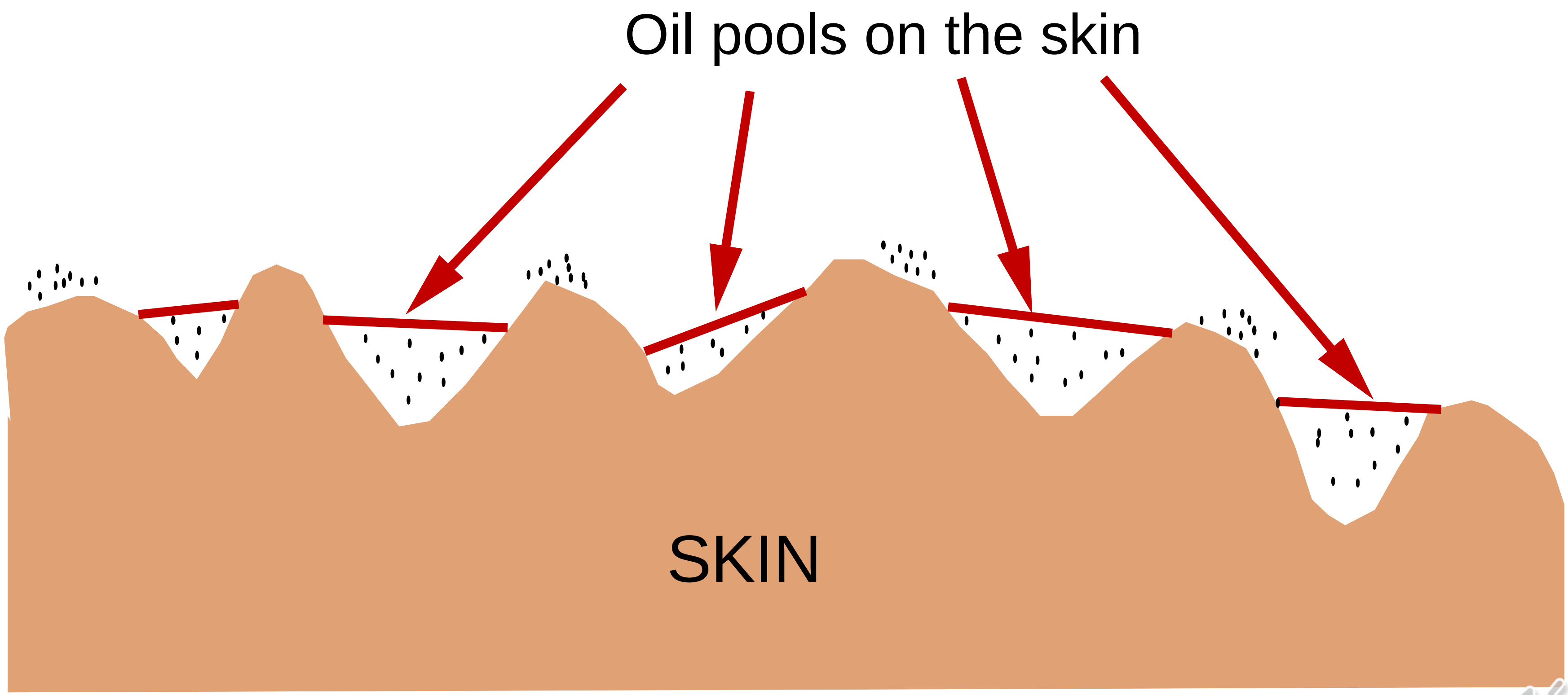


The real world?



A thin film model shows that these gaps contribute to 10% of the total skin area

Poor distribution of actives



Poor distribution of actives

Poor distribution of actives leads to poor efficacy of actives, because:

- The oil film is discontinuous, leaving some areas of the skin with no protection
- The distribution of the active particles is inconsistent
- Some of the sunscreen active is excluded from the oil film; without a dispersing medium, it will tend to aggregate

Product film composition

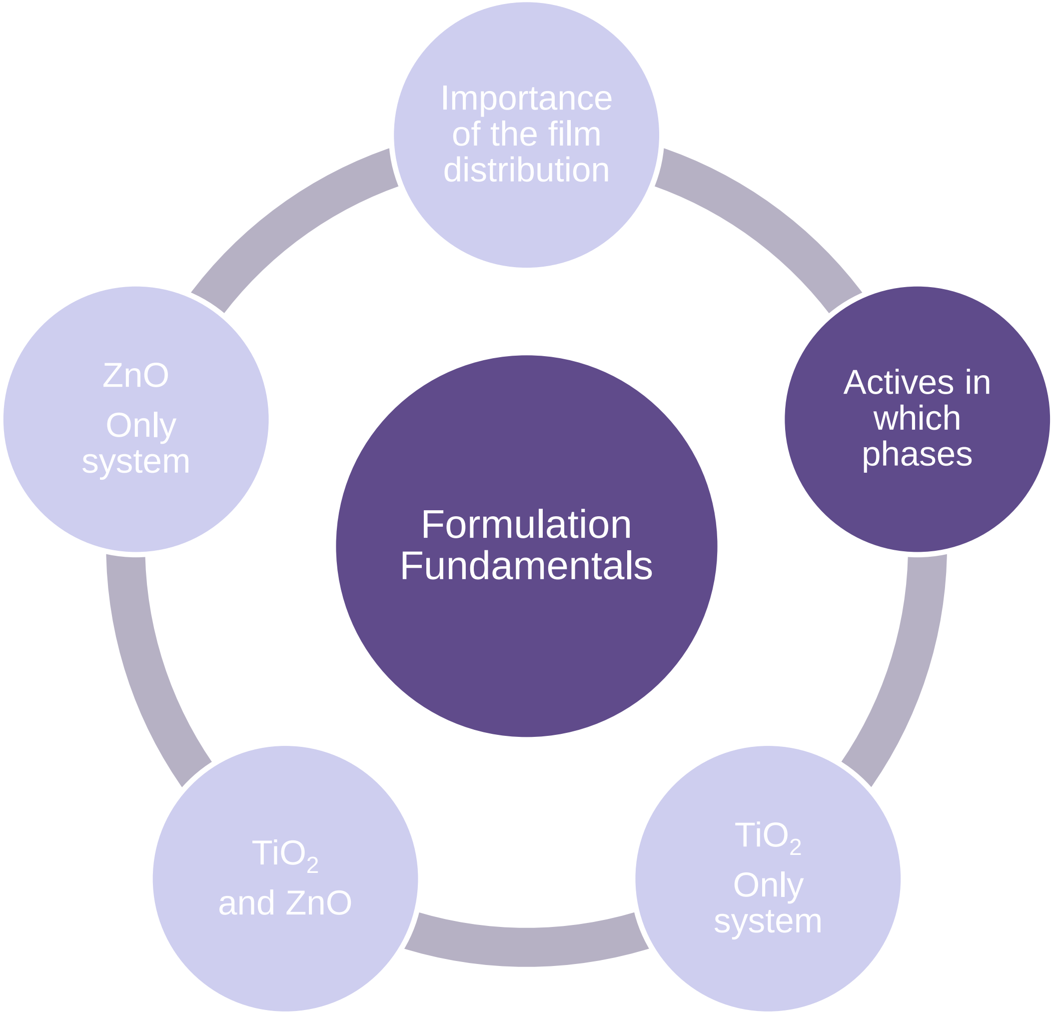
- Depends on the type of emulsion:
  - W/O - evaporation of water is relatively slow, so the film can be considered as consisting of the emulsion itself
  - O/W - more rapid evaporation of water, the film consists of oils, emulsifiers, active, and any other non-volatile ingredients
- In either case, the film should be as continuous and even as possible
- Achieving such an even film depends critically on the rheology of the product

Achieving "The Right Film"

Depends on:

- Product rheology
  - product must spread well to give good initial coverage of the skin (a low viscosity under high shear conditions)
  - then rapid recovery of structure after spreading to maintain an even film (once shear is removed)
- De-emulsification / coalescence
  - in O/W emulsions, oil droplets should ideally coalesce quickly to form a film

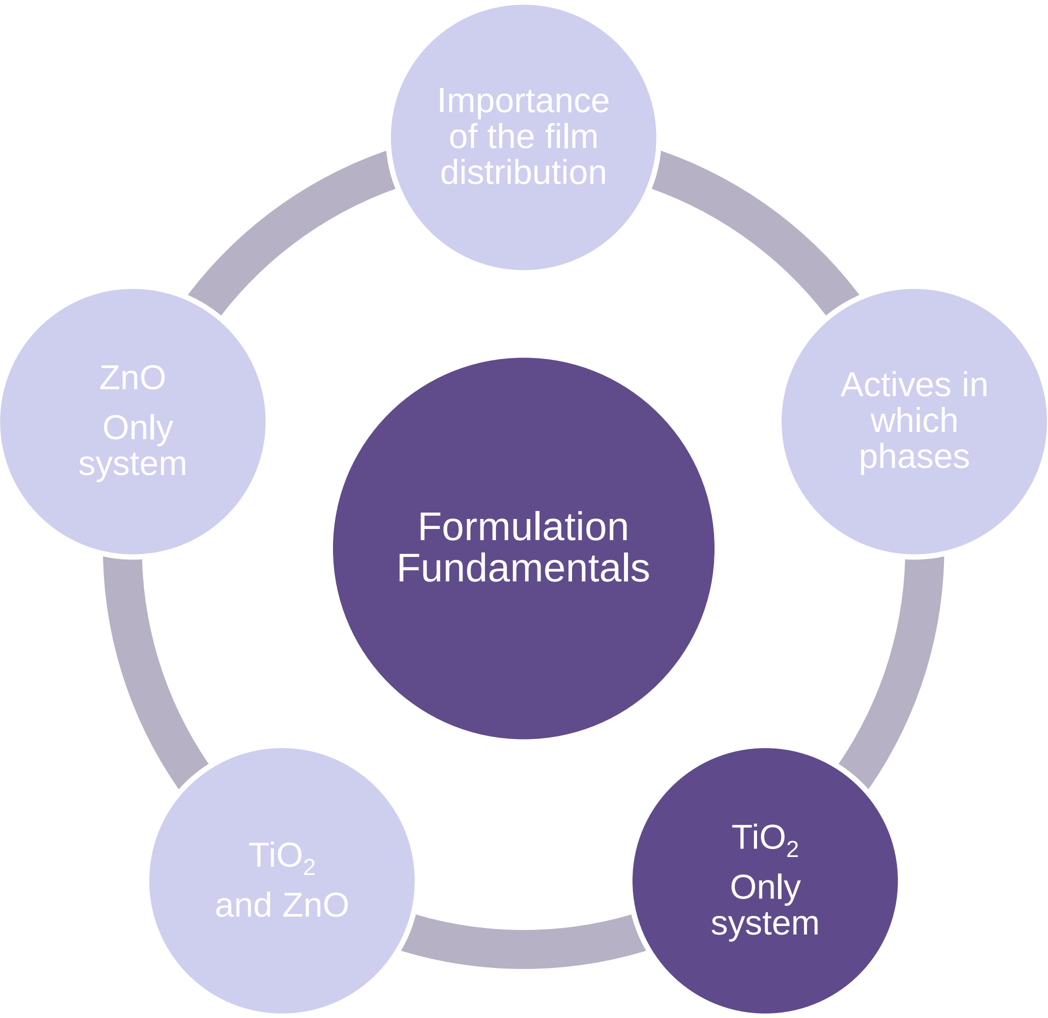
Formulation fundamentals



Actives in which phase?

- Croda has a range of dispersions with different carrier fluids
- Therefore actives can be included in the internal or external phase or both phases of emulsions
- The most versatile systems tend to be when the active is in the external phase
- **Water-based** dispersions tend to be most suited to the water phase of **O/W emulsions**
- **Oil-based** dispersions tend to be most suited to the oil phase of **W/O emulsions**
- Can achieve synergy when dispersion is used in both phases, plus a higher loading of solids is possible

Formulation Fundamentals



TiO_2 with extra UVA

- To meet global UVA regulations using TiO_2 as the **single** UV filter system, you need to use a TiO_2 with improved UVA
  - Solaveil SpeXtra or Solaveil Harmony
- TiO_2 without UVA enhanced will not meet the UVA European regulation when used as a sole active
- TiO_2 is most commonly available as oil dispersion or powder, but also as water dispersions

Water TiO_2 dispersions

- Water dispersions, like Solaveil XT-40W, offer formulation flexibility
- Incorporation into the water phase of an O/W emulsion means the oil phase can be manipulated to:
  - Provide the skin feel of choice
  - Allow the solubilisation of actives (solid organic UV filters)
  - Provide more freedom in the choice of oils (easier to make COSMOS formulations)
  - Offer better spreadability and hence reduce whitening appearance on skin

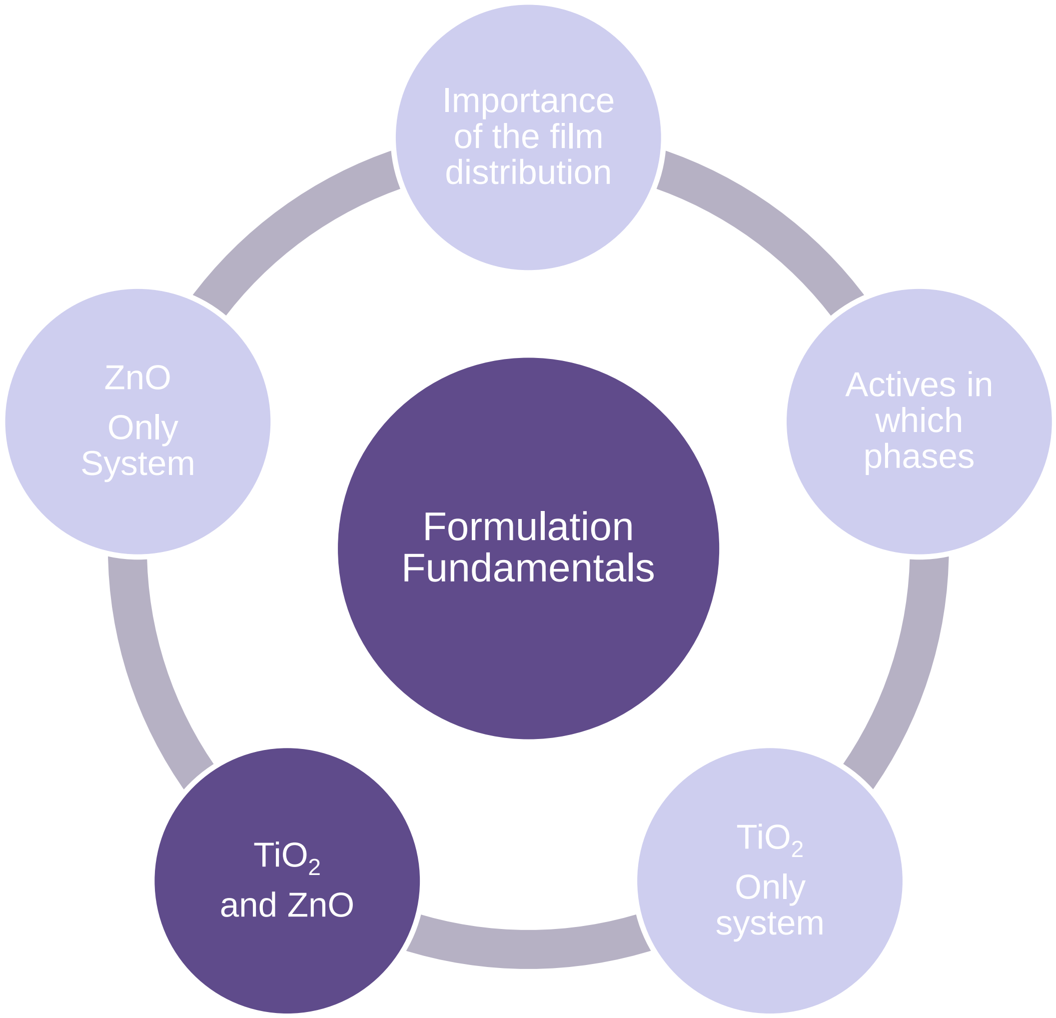
Using TiO_2 powders

- TiO_2 powder can have the benefit of lower "cost" but a pre-dispersion made with homogenisation, or high shear specialist equipment, is required to ensure efficacy

1. Combine oil (or silicone) phase ingredients, including the emulsifier and any solid materials such as fatty alcohol or wax, and heat if necessary
2. Add powder to the oil (or silicone) phase whilst homogenising for 3 – 5 minutes at 10,000rpm using an Ultra Turrax homogeniser
3. Reheat (if applicable) then continue to emulsification
4. Following emulsification, homogenise once more for 3-5 minutes at 10,000rpm

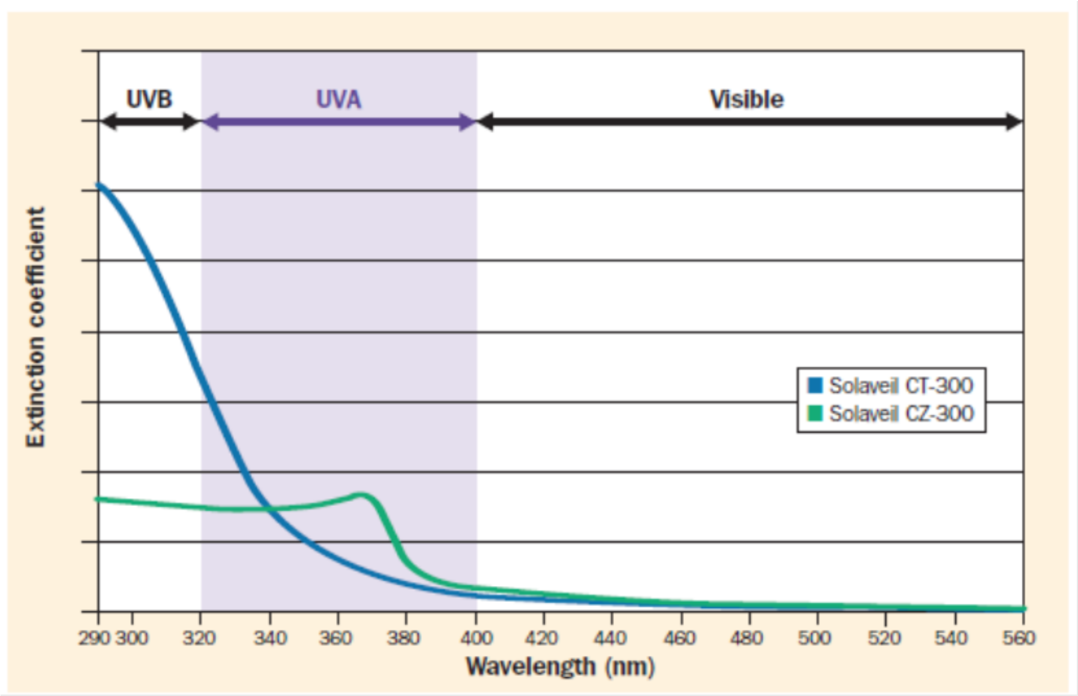
- For colour cosmetics, combine TiO_2 powder with powder pigments then triple roll mill with oil/dispersant then add to formulation

Formulation fundamentals



Combining TiO_2 and ZnO

- When the use of a more transparent TiO_2 is necessary, there is the need to combine with an UVA active.



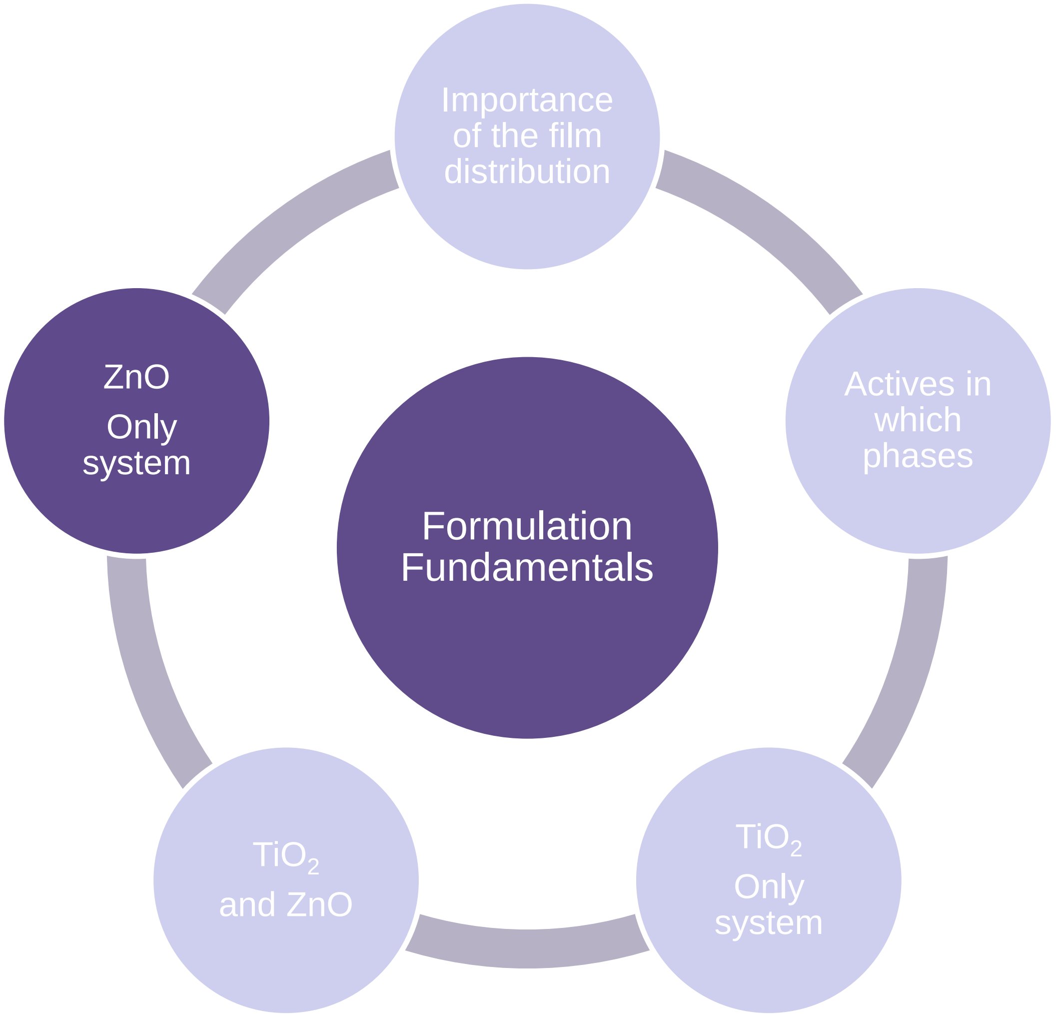
- TiO_2 tends to have high attenuation in the UVB and lower in the UVA.
- ZnO tends to have high attenuation in the UVA region of the UV spectrum and lower attenuation in the UVB

Solaveil™ physical shield

Emulsion choice

- Emulsions, whether lotions, creams, sprays, are the most common form for sunscreens
- Emulsions have the best rheology to form a good film on the skin
- They allow oily products to be applied to the skin in an elegant manner
- They allow incompatible ingredients and actives to be brought together
- As emulsions contain large amounts of water they are cheaper
- Emulsions provide formulation flexibility as the viscosity, skin feel, appearance can easily be modified

Formulation fundamentals



Formulating with Zinc Oxide

Solaveil™ physical shield

- Notoriously difficult to formulate with!
- O/W can suffer from pH drift and separation
- W/O can suffer from thickening
- Anhydrous can be a good option

ZnO only

Formulation problems

- Migration of ZnO is characterised by:
  - Increase in pH (via the formation of alkaline complexes)
  - Increase in electrolyte concentration
  - Agglomeration of ZnO in the water phase
- Therefore a successful formulation must:
  - Prevent migration
  - Enhance redispersion of ZnO if it does migrate
  - Ensure that emulsion system is tolerant to high electrolyte and high pH
- Most important factor to control is pH 6.5-7.5

Formulation tips

Solaveil™ physical shield

Non polar oils – stronger barrier between oil and water phase and ensure that dispersants coat the ZnO effectively

Strengthen interface with 0.5-1.5% liquid hydrophobic emulsifier Span™ 80 or Arlacel™ 1690

EDTA in water phase to chelate any ZnO

If liquid crystal system use 0.2% anionic surfactant to strengthen in presence of electrolyte – sodium cetearyl sulfate

Xanthan gum 0.25% in water phase to re-disperse ZnO

Propylene glycol 3-5% in oil phase to re-disperse ZnO

If using carbomer partially pre-neutralise prior to addition

Maintain pH>6.0 after mixing oil and water

Ideally add the buffering agent/pH adjuster in the water phase prior to emulsification

Solaveil™
physical shield

Anhydrous formulations

- Very easy to use ZnO dispersions in an anhydrous system
- No water phase, so no migration
- No thickening
- Can be low viscosity fluids or high viscosity sticks
- Good water resistance

Formulation evaluation

When formulating sunscreen the following evaluations are extremely relevant to achieve a stable and unique formulation

- Stability testing (accelerated stability protocols)
- SPF and UVA performance
- Sensory
- Microscopy

Most of the follow evaluations are very well known by the industry, but one in particular is not always routinely used, that is microscopy

Summary

Formulation of mineral only sunscreens guarantees simple and global filter systems, but can present challenges

Key requirement is to maintain good dispersion of particles in the emulsion and when applied on skin

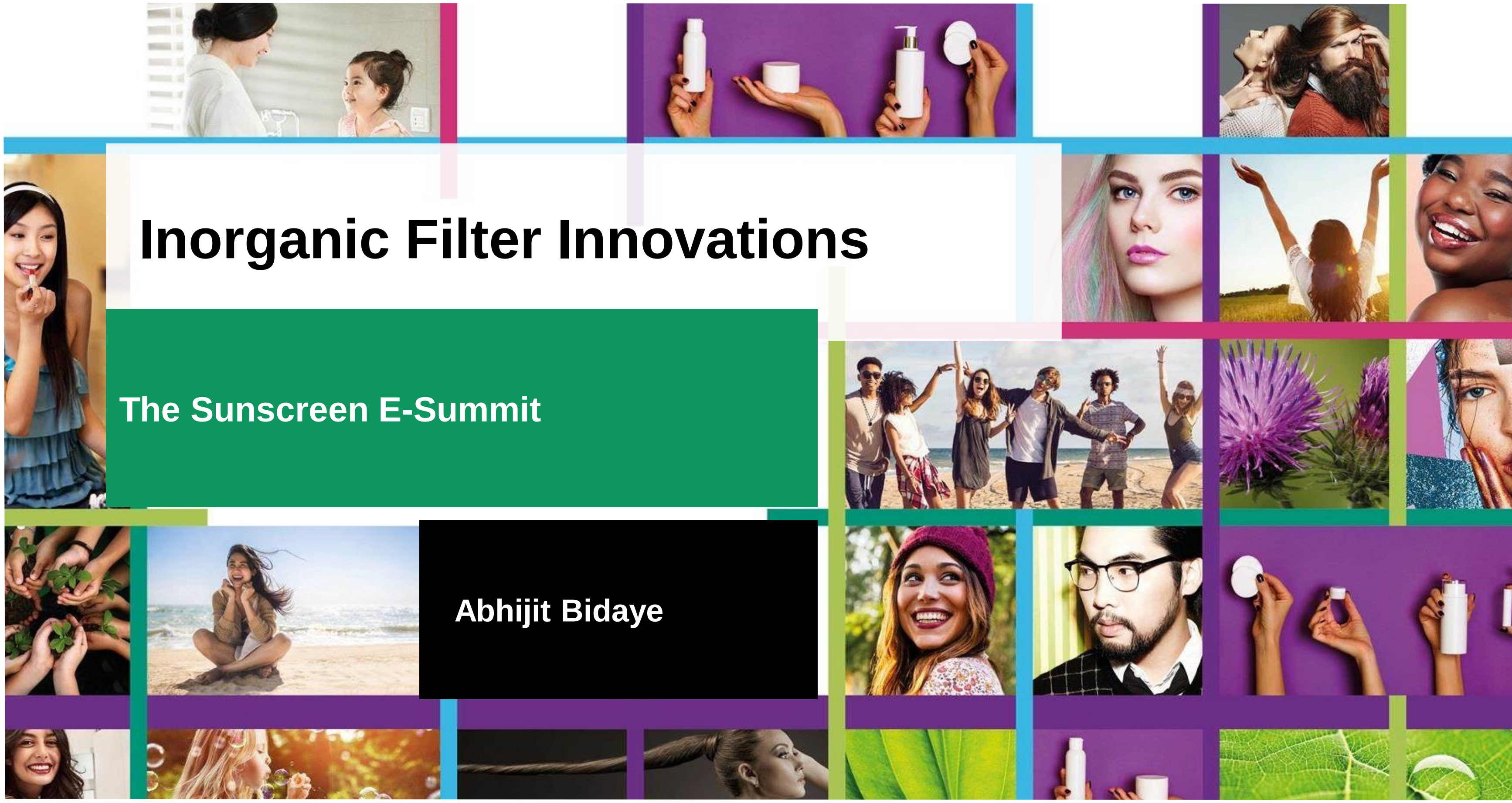
Most versatile systems tend to be those where active is in external phase

Use predominantly non-ionic emulsifiers

In W/O systems, pay particular attention to rheology and phase volume fraction

With ZnO in O/W systems, take steps to prevent migration or mitigate its effects

Solaveil™ physical shield



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