

I Filtri Solari INORGANICI

Emanuele Piras



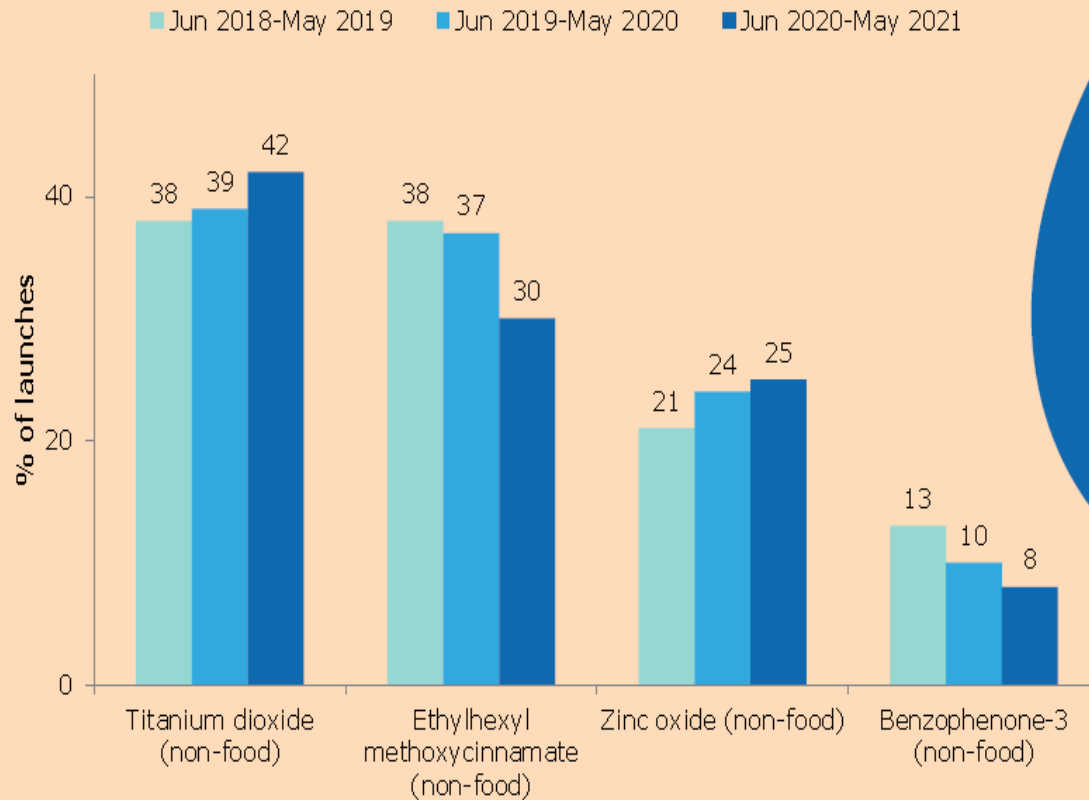
WORKSHOP SOLARI

Università di Bari, 12 Settembre 2024



Mineral suncare launches 2018 - 2021

Global: percentage of each active ingredient in new suncare launches, 2018-21



Source: *Mintel GNPD, June 2018-May 2021*

"Global brands... focus on mineral suncare as consumer demand for clean ingredients rise and reef-safe claims grow. Potentially harmful chemical actives are decreasing in new suncare launches, while greenlit mineral actives grow." (Mintel)



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Efficaci, fotostabili e **ampio spettro**

≥ 2.0 in vivo SPF / % uso

$\sim 0.3/0.9$ in vivo UVA PF / % uso

- **non penetrano** , ottima **compatibilità con la pelle**

Elevata **trasparenza** anche ad altre concentrazioni

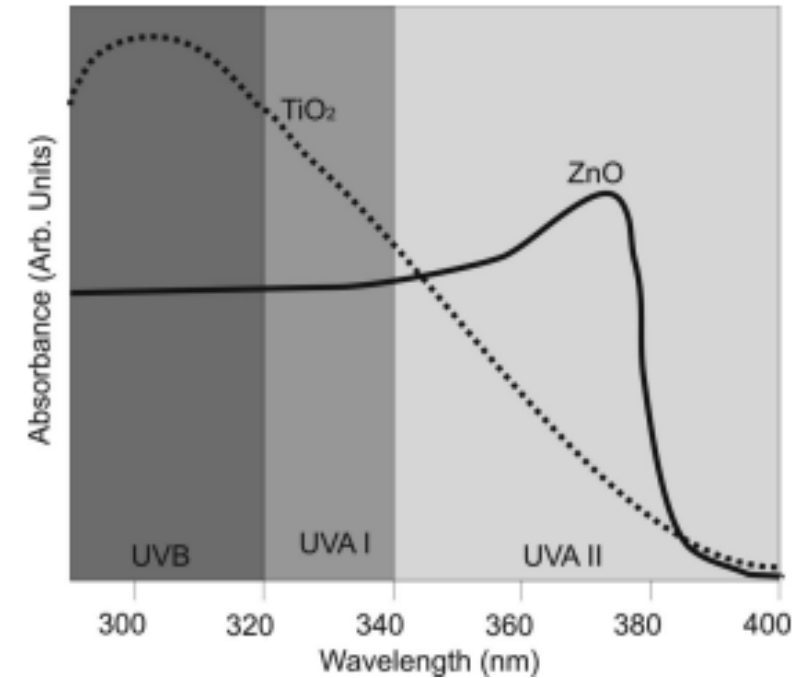
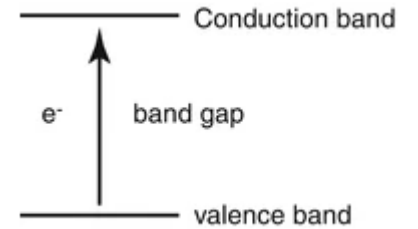
Disperdibili in **Acqua e/o Oli**

Filtri UV Globali approvati in tutto il mondo (GRASE US)

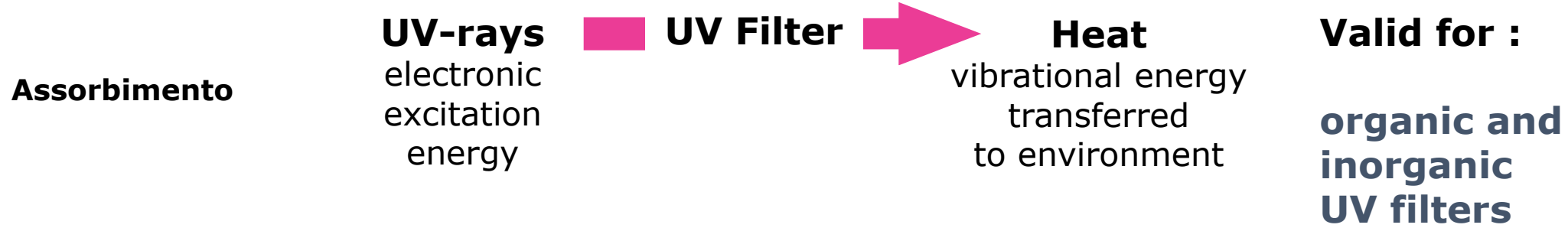


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- The two inorganic UV filters interact with UV light by two mechanisms: absorption and reflection/scattering.
- Both ZnO and TiO₂ are semiconductor materials that allow light to be absorbed.
- In fact, approximately 85 to 95 percent of UV radiation is actually absorbed by inorganic UV filters ([Cole et al., 2016](#)).
- Similar to organic UV filters, UV radiation excites an electron into a higher energy orbital state ([Smijs and Pavel, 2011](#)).
- Specifically, overlapping electron orbitals in the crystalline structure form "bands," with gaps between energy bands ("band gap").
- Electrons are excited across the band gap from a lower valence band into a higher conduction band.
- Particle size and composition influences the amount of UV radiation that is absorbed or scattered/reflected.
- Larger particles reflect/scatter more UV radiation than smaller ones, though for all particles absorption is still a dominant mechanism.
- Smaller, nanoscale particle UV filters reflect less visible light, and therefore appear nearly transparent in color, compared to the whiter appearance of larger particles. Reducing particle size also shifts the UV wavelength range that the particles are protective against



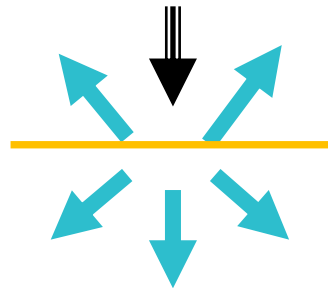
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Riflesso



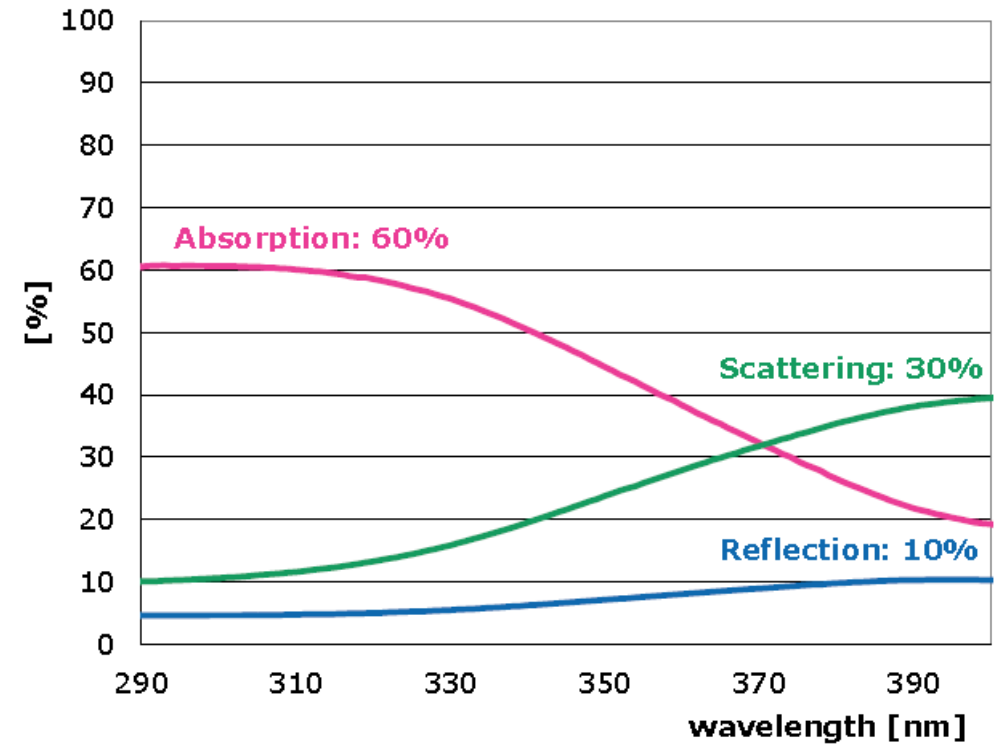
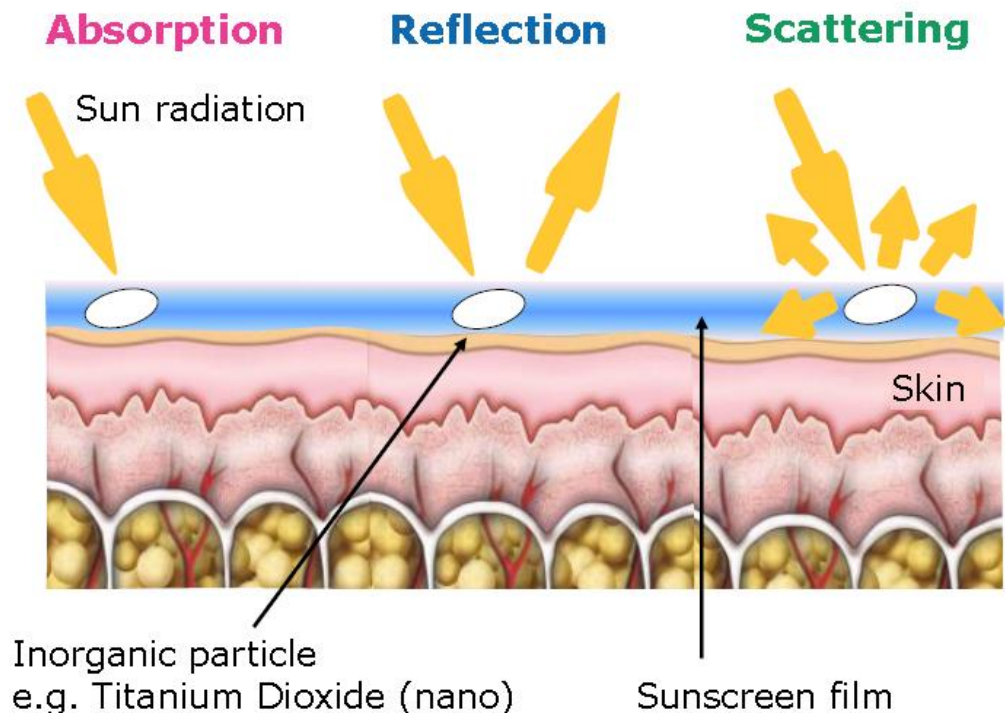
Scattering/Diffusione



inorganic UV filters

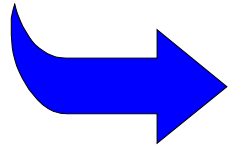
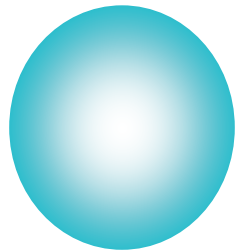


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Pigment



Down-Scaling

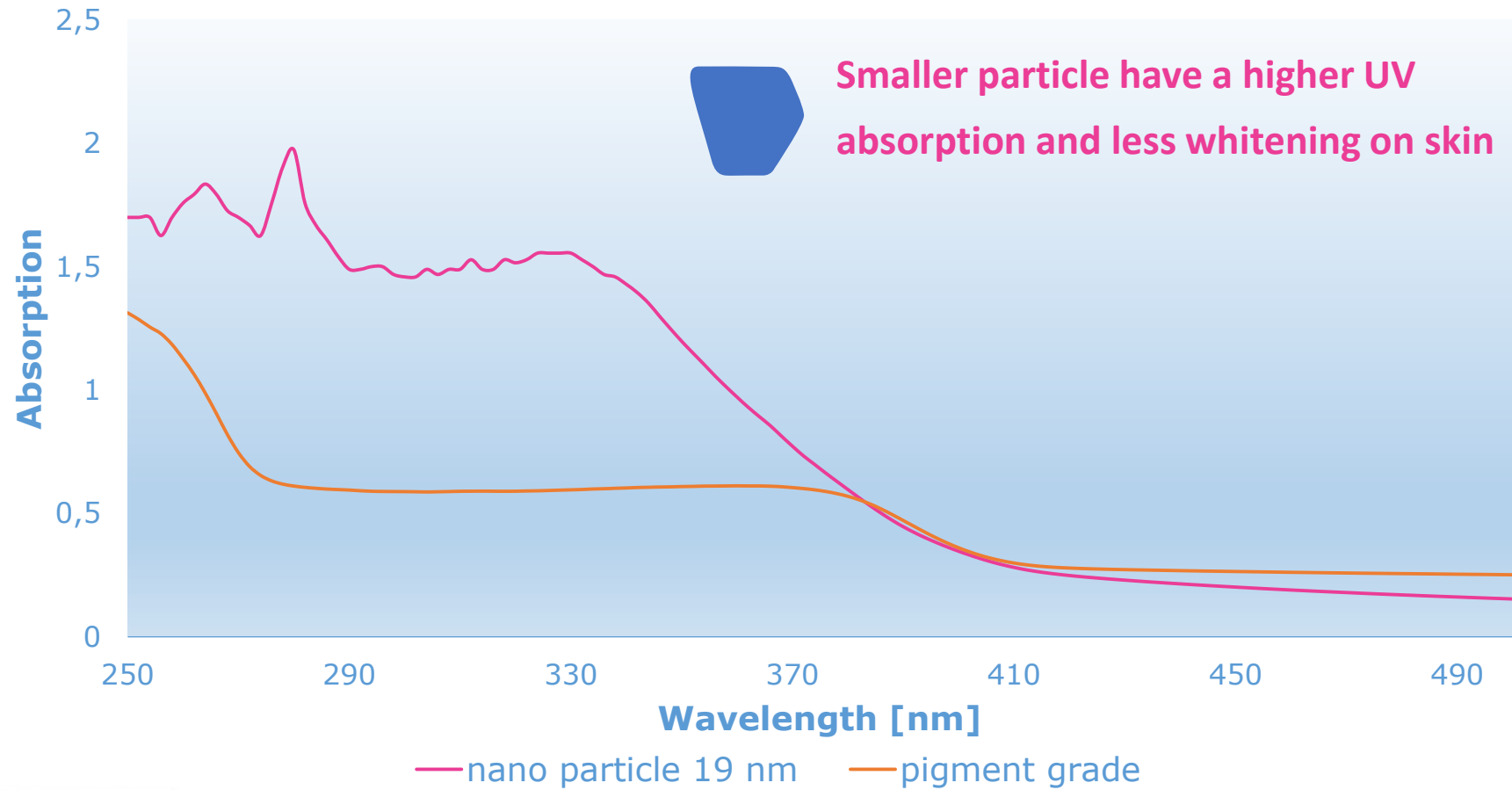


Microfine particle, "nano"

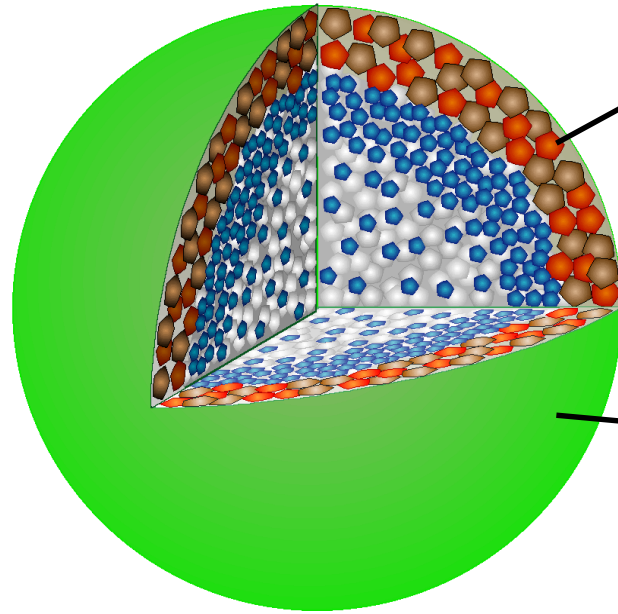
- Crucial influence on
 - light scattering / whiteness on skin
 - absorption of UV radiation and efficiency
 - specific surface
 - surface coverage on skin
 - dispersibility
 - flocculation stability



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Inorganic Coatings

- Alumina
- Silica
- Manganese Dioxide
- Sodium Metaphosphate
- ...

Organic Treatments

- Stearic Acid
- Glycerin
- Dimethicone, Hydrogen Dimethicone, Simethicone
- Tri(m)ethoxycaprylylsilane
- Cetyl Phosphate
- ...



Adjustment of specific surface to induce:

- passivation
- dispersability in media
- flocculation stability etc.



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TiO ₂ Crystalline Form	Coating Material*	Doping Material	Form	Bulk density (g/cm ³)	VSSA (m ² cm ⁻³)
> 98 % Rutile, < 2 % Anatase	16 % Silica, 6 % Cetyl Phosphate	None	Hydrophobic powder	0.2	150
> 95 % Rutile, < 5 % Anatase	7 % Alumina, 0.7 % MnO ₂	1000 ppm Fe	Hydrophilic powder	0.16	370
100 % Rutile	3 % Alumina, 9 %Triethoxycaprylsilane	None	Hydrophobic powder	0.48	95

Material code	TiO ₂ crystalline form	Coating material	Doping material	Form	Bulk density (g/cm ³)	VSSA (m ² cm ⁻³)
S75-A	> 99.5% Rutile	6% silica, 16% alumina	None	Oil dispersion	0.35	460
S75-B	> 99.5% Rutile	6% silica, 16% alumina	None	Aqueous dispersion	0.35	460
S75-C	> 99.5% Rutile	7.5% alumina, 9.5% aluminium stearate	None	Oil dispersion	0.31	220
S75-D	> 99.5% Rutile	10% alumina, 13.5% stearate	None	Oil dispersion	0.58	300
S75-E	> 99.5% Rutile	10% alumina, 13.5% stearate	None	Aqueous dispersion	0.58	300
S75-F	Anatase 85%, Rutile 15%	7.5% trimethoxycaprylsilane	None	Hydrophobic powder	0.2	192
S75-G	Anatase 85%, Rutile 15%	None	None	Hydrophilic powder	0.13	213
S75-H	> 99,5% Rutile	6% alumina, 1% glycerin	None	Hydrophilic powder	0.31	260
S75-I	> 99,5% Rutile	7% alumina 10% stearic acid	None	Hydrophobic powder	0.28	300
S75-J	> 99,5% Rutile	6% alumina 1% dimethicone	None	Hydrophobic powder	0.31	260
S75-K	> 94% Rutile	6-8% aluminium hydroxide, 3.5-4.5% dimethicone/methicone copolymer	None	Hydrophobic powder	0.12-0.28	426
S75-L	> 94% Rutile	6.5-8.5% hydrated silica, 2.5-4.5% aluminium hydroxide, 4.5-6.5% dimethicone/methicone copolymer	None	Hydrophobic powder	0.07-0.2	426
S75-M	> 98% Rutile, <2% anatase	17% silica	None	Hydrophilic powder	0.09	260
S75-N	> 95% Rutile, <5% anatase	Alumina 10% dimethicone 2%	1000 ppm Fe	Amphiphilic powder	0.16	400
S75-O	100% Anatase	Dimethicone 5%	None	Hydrophobic powder	0.75	400



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 - Informazioni utili

Caution if you adapt existing formulations, difficulties may arise (instability, change in viscosity, ...):

- when changing the **load of ZnO/TiO₂**
- when **replacing** an inorganic filter by another grade having a different coating and herewith different product properties

- **Use appropriate level of emulsifiers** (adsorption of emulsifiers on TiO₂ surface)
- **Non ionic emulsifiers** are to be preferred
(interaction of TiO₂ with ionic emulsifiers can not be totally excluded)

- Ensure a **good dispersion** of the inorganic filter in the formulation - use dispersing aids if necessary - and check homogeneity by **microscopic examination**
- Needed **energy input** depends on the **ZnO/TiO₂ type** and **coating**
- ZnO may lead to **pH change** in formulation during storage
- Emulsions of low viscosity: Use stabilization systems to avoid sedimentation, e.g. **microcristalline cellulose**



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• Suggestimenti Utili

o/w formulations

Glyceryl Stearate & PEG 100 Stearate	(e.g.Arlacel165)
Steareth-10, Steareth-7, StearylAlcohol	(e.g.Emulsifier E 2155, Volpo-S10...)
Hexadecyl-& octadecylglucoside + Cetyl/stearylalcohol	(e.g.EmulgadePL 68/50)
Polyglyceryl-3 MethylglucoseDistearate	(e.g.TegoCare 450)
Sodium CetearylSulfate, CetearylAlcohol, PEG-40 Castor Oil	(e.g.EmulgadeF)
DimethiconeCopolyolPhosphate	(e.g.PecosilPS-100)
Phosphate based emulsifiers	(e.g.AmphisolK, Emulsiphosor Crodafos)

w/o and w/siformulations

PEG-30 Dipolyhydroxystearate	(e.g.ArlacelP135 for w/si, w/o & w/si-o)
Polyglyceryl-4-Isostearate & Cetyldimethiconecopolyol& Hexyl Laurate	(e.g.AbilWE 09)
Lauryl methiconecopolyol	(for w/si)
Cyclomethicone& Dimethiconecopolyol	(for w/si)

Disperdenti

CetylDimethicone, PolyhydroxyStearic Acid, Polyglyceryl-3 Polyricinoleate

Filmanti

PVP/EicoseneCopolymer, TricontanylPVP

Viscosizzanti

Xanthan Gum (0.1 -0.3%)

Carbomers/ Acrylate based copolymers(without agglomeration generally 0.1% possible)



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- Suggestimenti Utili

Metal oxides, TiO_2 or ZnO in combination with Carbomers in formulations can cause Aggregated structures or inelegant textures („cottage cheese“ effect)

Strategies to avoid Carbomer- TiO_2 agglomerates:

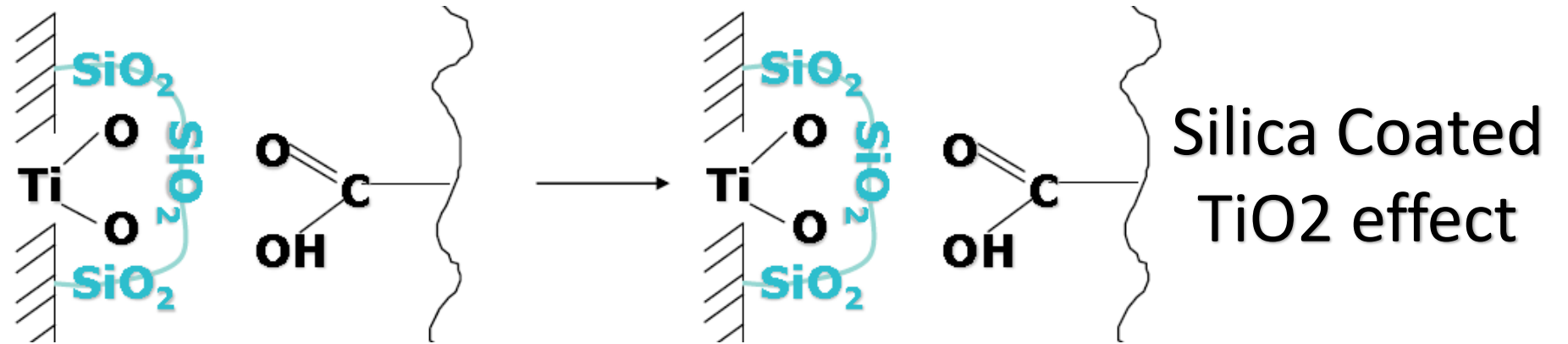
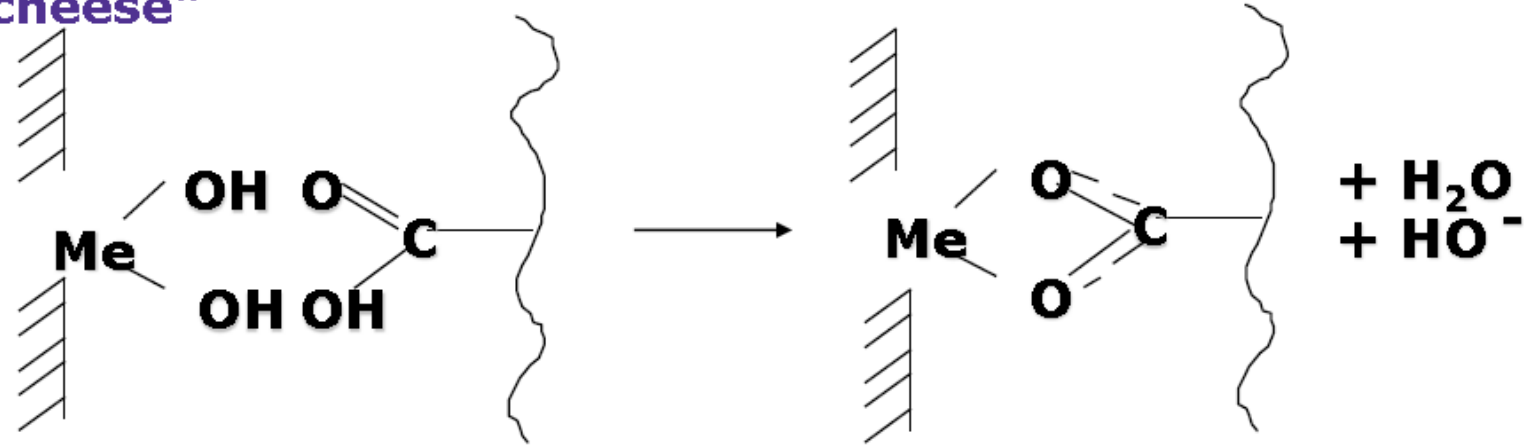
Use of low concentrations Xanthan Gum (0.1 –0.3%) in the water phase to achieve small droplets and / or Stabilize the produced emulsion at 35 –40°C by means of a Carbomer-Pemulen/ oil phase dispersion (0.1 –0.2% Carbomer/ Pemulen) and additional homogenizer step Or use **Silica Coated TiO_2**



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- Suggestimenti Utili

Metal oxides hydrates + Carbomer = „Cottage cheese“



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- Suggestioni formulativi

