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PHYSICAL AGING OF EMULSIONS CONTAINING COATED TiO_2 NANOPARTICLES: INTERACTION BETWEEN NANOPARTICLES AND OTHER INGREDIENTS

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INTRODUCTION

Titanium dioxide (TiO_2) nanoparticles (NP) are commonly used in cosmetics as UV filters ^{(1) (2)}.

For cosmetic grades, coatings are applied to prevent TiO_2 radical oxidation / contact with ingredients ^{(3) (4)}. These coatings procure to the NP their surface properties (polarity, charge) and impose their behavior in emulsion.

During formulation and storage, cosmetic emulsions are exposed to aggressions which can induce and/or aging. NP in emulsion may aggregate, adsorb formula's compounds or be deteriorated ⁽⁵⁾.

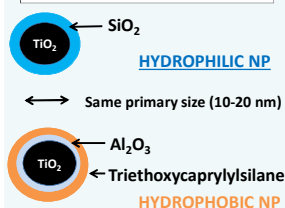
The surface modifications of the NP are here studied as they could explain the (de)stabilisation mechanisms in emulsion.

MATERIAL & METHODS

➤ Process optimization:

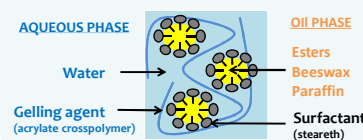
- physically stable control emulsion,
- well-dispersed NP in the continuous phase.

➤ Cosmetic grades of TiO_2 -NP



➤ Development of three model emulsions

- nanoparticle-free (control emulsion),
- with hydrophilic NP,
- with hydrophobic NP.



CHARACTERIZATION OF NP SURFACE IN USE CONDITIONS

➤ Emulsions characterization

- **Microstructure:** Optical microscopy, Laser granulometry
- **Macroscopic properties:** Rheology, Texture analyses ⁽⁶⁾, Zetametry, pH.

➤ Accelerated aging

Monitored time and temperature.

➤ NP extraction from fresh/aged emulsions

- Dilution of emulsions in methanol/pentane,
- Homogenization by sonication,
- Centrifugation of the NP powder (8000 g, 10 min).

➤ NP surface characterization

Thermogravimetric analyses (TGA): 10°C/min from 200 to 700°C

RESULTS & DISCUSSION

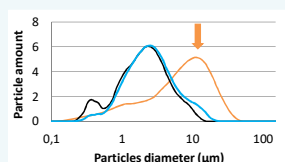
➤ FRESH EMULSIONS CHARACTERIZATION

➤ Similar microstructures:

- Homogeneous
- Fine droplets.

➤ But slight differences:

- Less flocculated with hydrophilic NP emulsion,
- Large aggregates with hydrophobic NP.

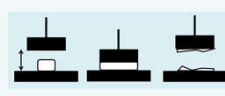


Volumetric repartitions of colloids in fresh emulsions.

➤ Macroscopic properties:

- Not affected by the presence and nature of NP and confirmed by other methods (pH, rheology...).

Fresh emulsions	Probe work (kg.s)
Control	0.17 ± 0.02
With hydrophilic NP	0.19 ± 0.03
With hydrophobic NP	0.19 ± 0.03



Compression test.

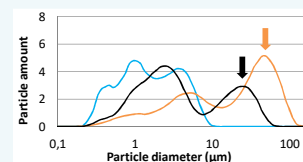
Aged emulsions	Probe work (kg.s)
Control	0.24 ± 0.05
With hydrophilic NP	0.32 ± 0.00
With hydrophobic NP	0.08 ± 0.02

➤ AGED EMULSIONS CHARACTERIZATION

➤ Emulsions not demixed.

➤ Different microstructures:

- Control emulsion: few larger droplets,
- Hydrophilic NP: enhanced stability,
- Hydrophobic NP: larger aggregates (50 μm).

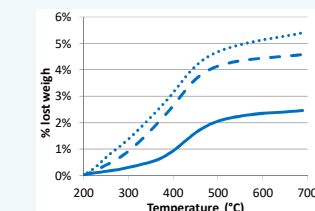


Volumetric repartitions of colloids in aged emulsions

➤ Macroscopic properties:

- Control remains unchanged,
- Emulsion with hydrophilic NP: more consistent (NP/droplets network)
- Emulsion hydrophobic NP: fall of consistency (demixion)

➤ EXTRACTED HYDROPHILIC NP FROM FRESH/AGED EMULSIONS



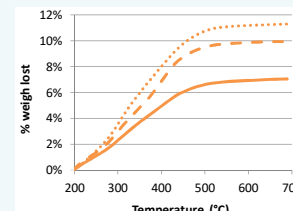
Percentage of weight lost during TGA: NP control (line), NP extracted from fresh emulsion (points), NP extracted from aged emulsion (dashes).

➤ Thermogravimetric analyses on NP:

- When extracted from fresh/aged emulsions, higher weight lost than the control.
- No difference between NP extracted from fresh/aged emulsions.

➤ In both cases, evidencing of adsorption of emulsion compounds on the NP surface.

➤ EXTRACTED HYDROPHOBIC NP FROM FRESH/AGED EMULSIONS



Percentage of weight lost during TGA: NP control (line), NP extracted from fresh emulsion (points), NP extracted from aged emulsion (dashes).

CONCLUSION

In this work, two natures of coated TiO_2 NP were studied in cosmetic emulsions. This leads to innovative characterizations of particles in complex media. Whereas hydrophilic NP stabilize emulsion by steric hindrance, during aging, hydrophobic NP form large aggregates that make the emulsion less homogenous and alters the emulsion macroscopic properties (spreading quality,...).

Innovative protocols for NP extraction from the fresh/aged emulsions were developed. Characterizations by TGA proved that emulsion compounds quickly adsorbed the NP surface which modified the NP chemistry and properties. Hence, the observed mechanisms in emulsions are linked to the surface nature of the NP and moreover, these surface modifications have to be taken into account.

PERSPECTIVES

In order to clarify the role of NP surface modifications on the mechanisms in emulsion, the chemistry of the adsorbed molecules have to be explored by further methods for chemical analysis. Moreover, studying the impact of adsorbed species on the surface properties (polarity, charge) will allow understanding these complex phenomena.

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