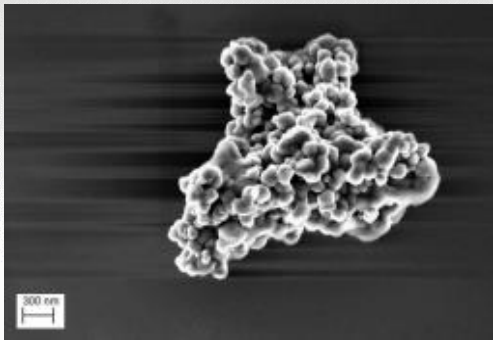
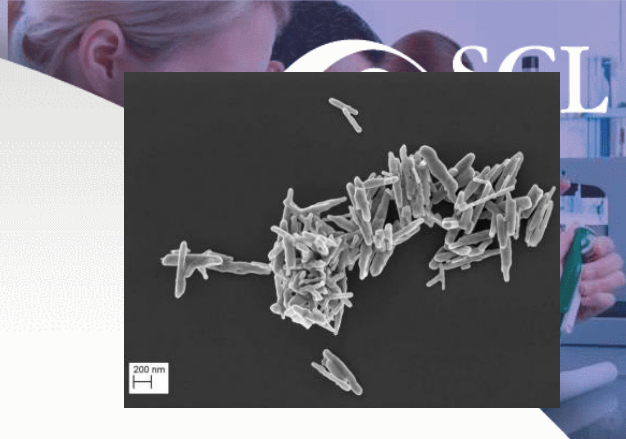


Nanomaterials Legislation and analytical strategies



Co-funded by the Horizon 2020 Framework Programme of the European Union
under the grant N° 952306



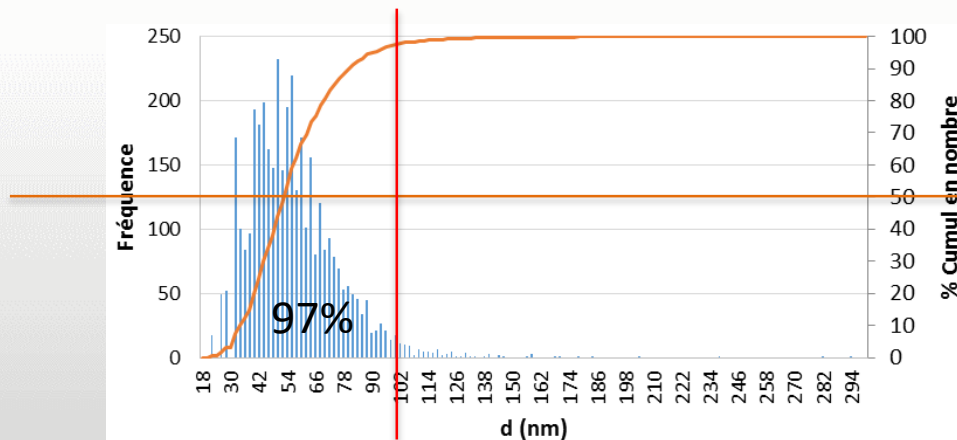


Nanomaterial definition according European Committee 2011/696/UE

- **Natural** material
- Incidental or manufactured material containing particles in an unbound state or as an **aggregate** or as an **agglomerate**



- where for **50% or more** of the particles, in the number size distribution, one or more external dimensions is in the size range **1-100 nm**



Nanomaterials omnipresence in daily life



Food

- Candies
- Ornament cake
- Frosting



Cosmetics

- Sunscreens
- Moisture
- Make-up



Contact materials

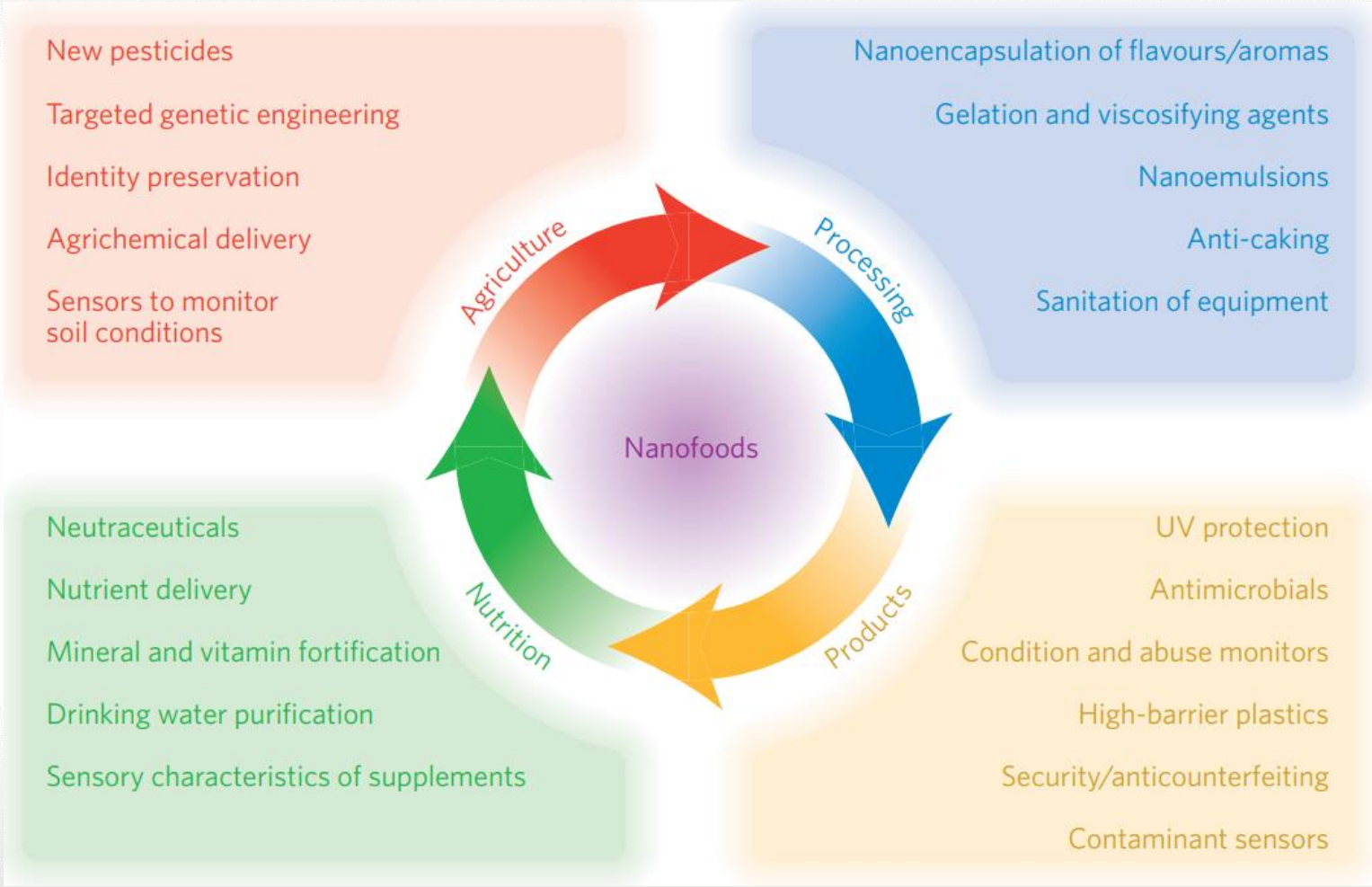
- Plastics
- Cardboard
- Ceramics



Biocides

- Disinfection

Nanotechnology and benefits to food industry





« Classic » Food colouring agents



micrometric powders containing a more or less significant fraction of fine particles



Titanium dioxide

- Confectionery
- Pastry
- Cream
- Yoghurt
- Ready meals




Iron oxides

- Charcuterie
- Confectionery
- Biscuits





Silver or Gold

- Decoration



Not designed to enhance fine particle fraction properties
BUT

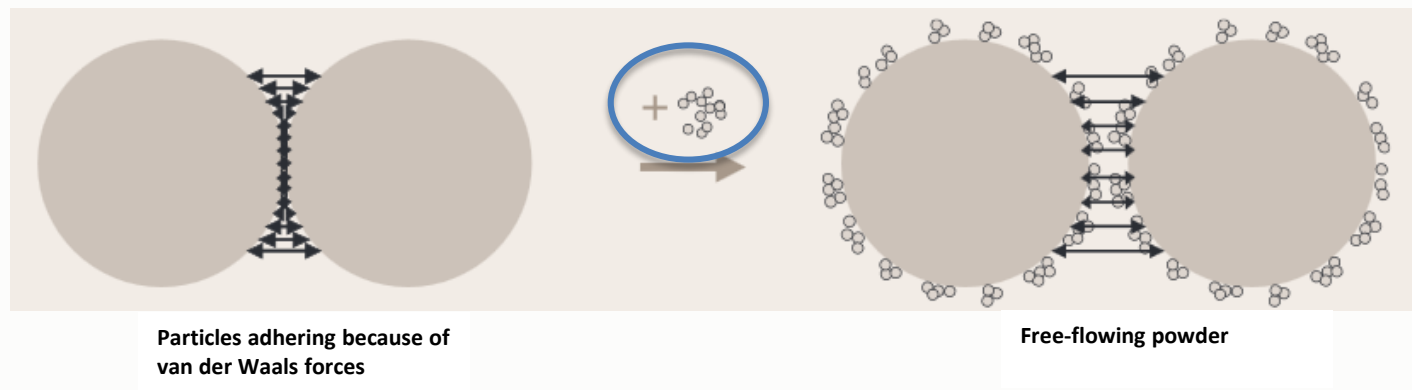
Presence of fine particle = « **nanometric** » character



« Classic » Texturizing agents



SiO_2 :Used as **anti-caking agent** or to improve texture/smoothness



Silice SiO_2 (E551)
Calcium carbonate (E170)
Magnesium oxide



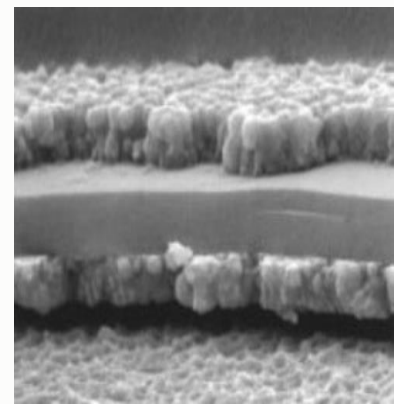
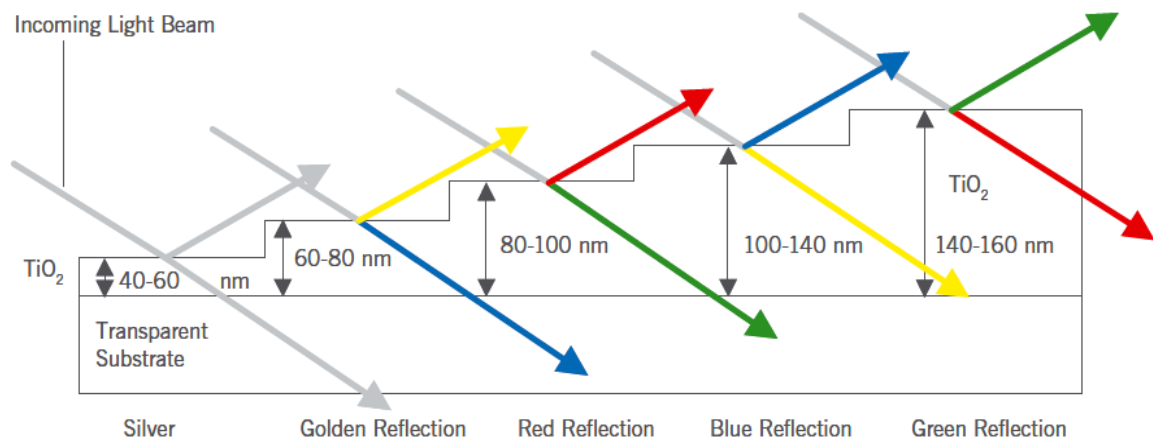


INNOVATION

« New » Food colouring agents

New physico-chemical properties at the nanoscale such as : glitter/shiny effect

E171 + E172
(+E555)



- ← Titanium dioxide
- ← Mica (E555)
- ← Titanium dioxide

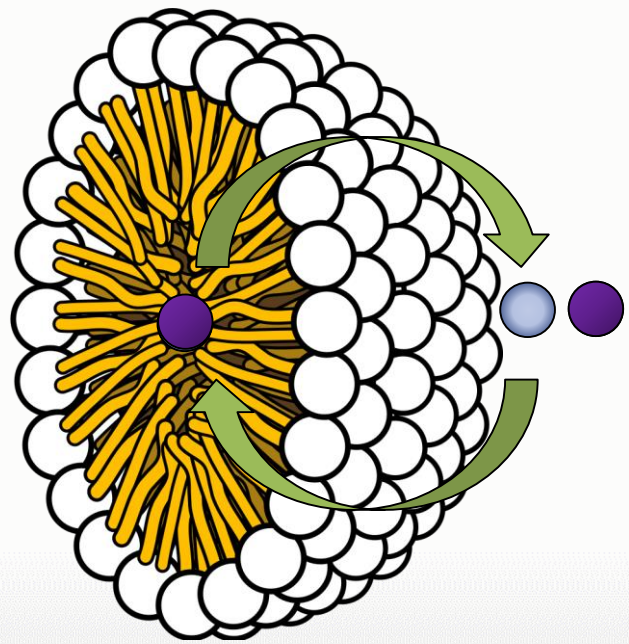


INNOVATION

R&D – Food nanotechnologie

Encapsulation of substances/food additives to :

- Improve their stability and bioavailability
- Improve their taste, nutritional quality or retention of aromas
- Reduce the quantity needed



- Ligand
- Food additives
- Complexe ligand-food

Enhancement of physico-chemical properties by selectively developing certain types of interactions, always in order to limit the quantities to be introduced into the formulation

Food contact materials

Nanomaterials	Properties	Application field
Titanium nitride	Improvement of « barrier » properties	Plastic packaging
Titanium dioxide	UV filter	Plastic and glass packaging
Calcium carbonate	Charge - Improvement of « barrier » properties	Plastic packaging
Carbon black	Black pigment	Printing
Magnesium silicate	Moisture absorber	Container
Silver	Anti-microbial agent	Food contact work surface/storage, packaging
Starch	Antistatic agent	Plastic film
Clay, aluminum and aluminum oxide	Charge - Improvement of « barrier » properties	Plastic packaging

+

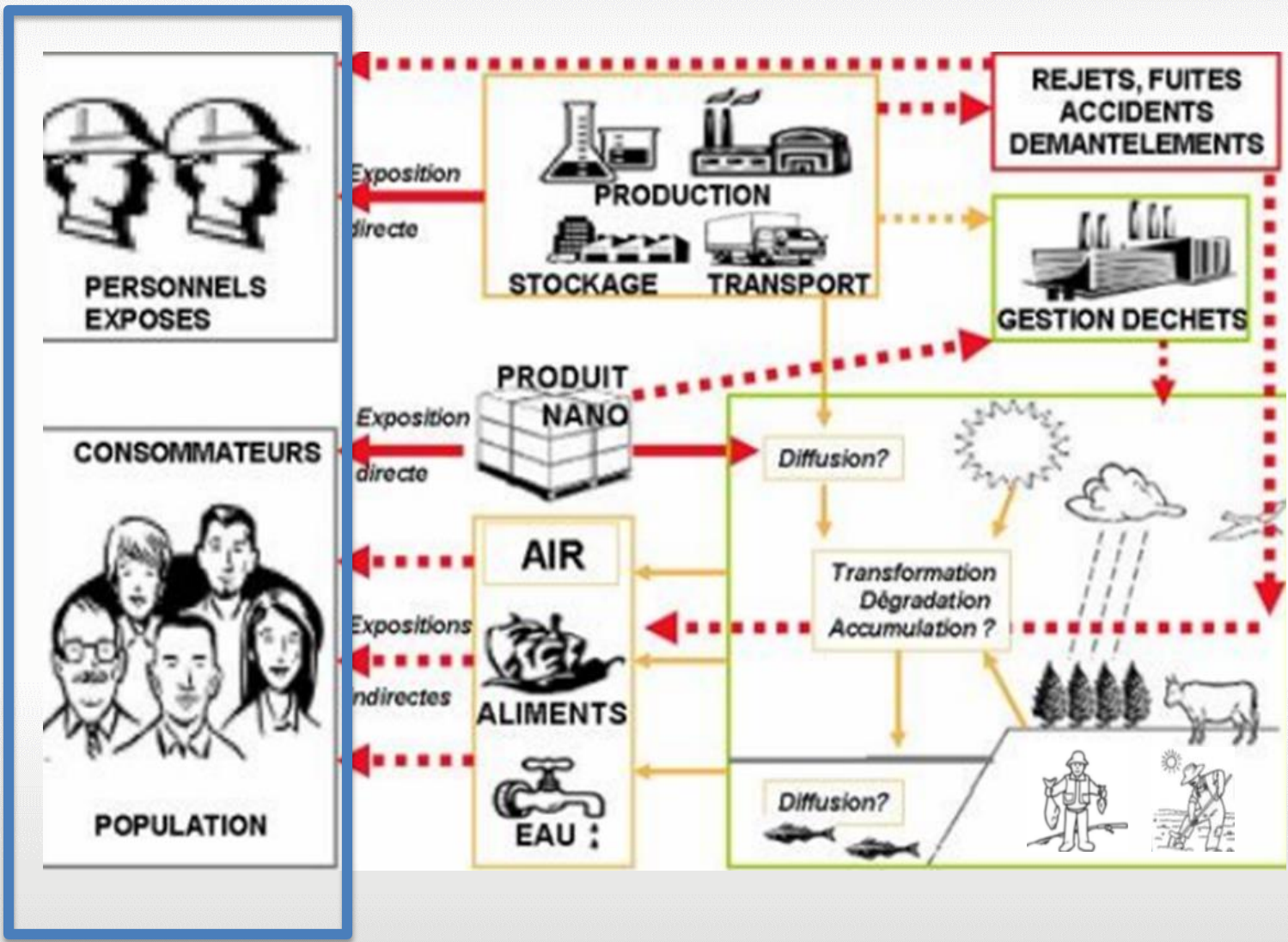
Intelligent packaging :
traceability, nanosensors



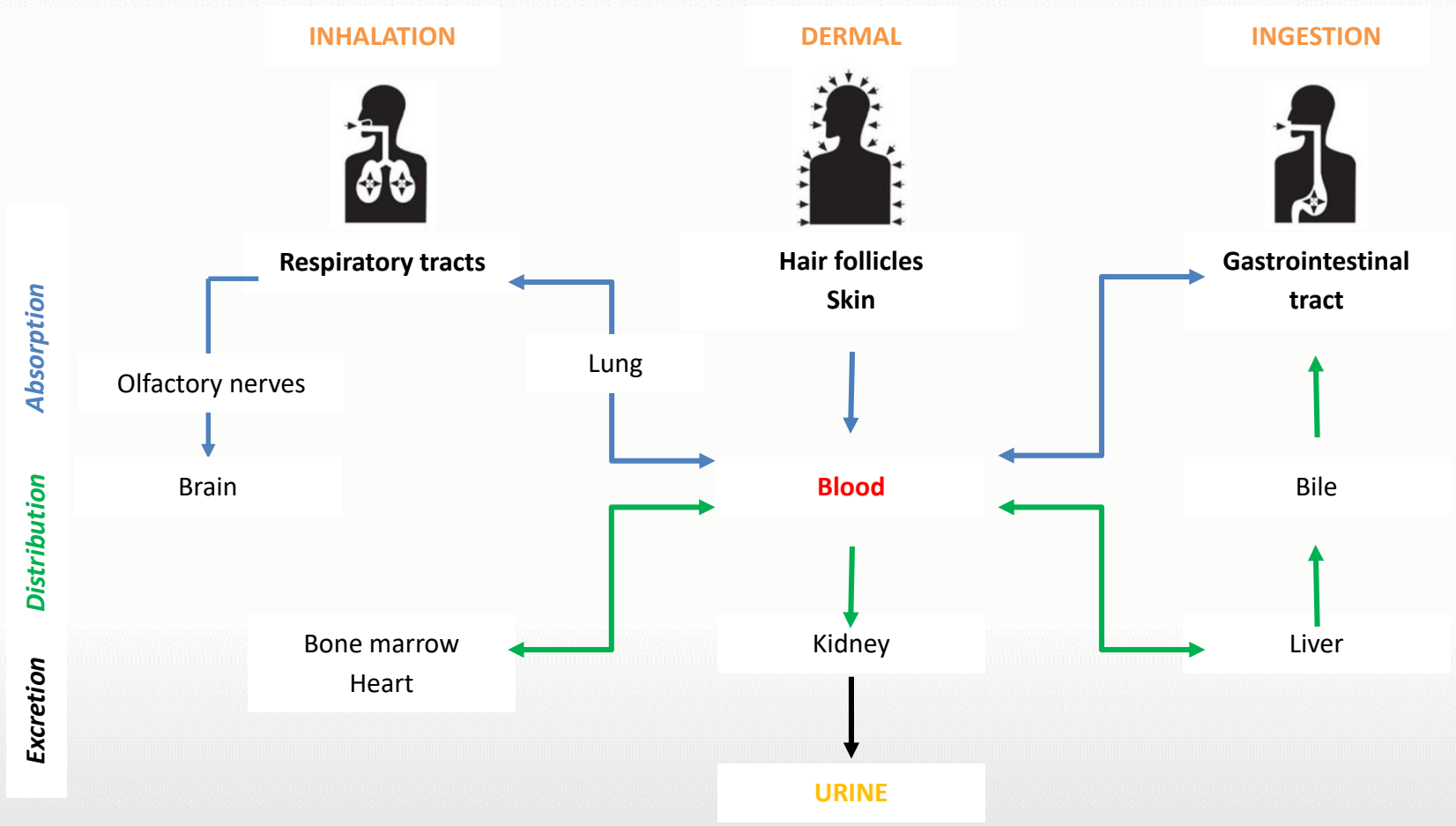
Active
ripeSense™
sensor

Sensor changing color according to the maturity of the fruit
(Source [site Ripesense](http://site.Ripesense))

Nanomaterials : environment exposition and human hasards



Human exposure



Essential regulations for consumer protection



'Nanomaterial' means a **natural, incidental or manufactured** material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm.

COMMISSION RECOMMENDATION
of 18 October 2011
on the definition of nanomaterial
(Text with EEA relevance)
(2011/696/EU)

Biocides

R(UE)n°528/2012

≠ Active or non active substance

Alimentation

R(UE)n°1169/2011
(INCO)

≠ **Intentionally** produced material
+ Aggregates/Agglomerates > 100 nm but retains nanoscale properties :

- Large specific surface area
- Different physico-chemical properties from the non-nanoform

Cosmetics

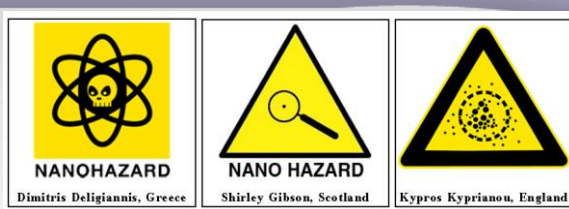
R(UE)n°1223/2009

≠ Insoluble or biopersistent and intentionally manufactured material
≠ **List of authorized nanoparticles**
+ Internal structure in the size range 1-100 nm

Contact materials

R(UE)n°10/2011

≠ **List of authorized nanoparticles**
+ Aggregates/Agglomerates > 100 nm with nanosize properties



R(UE)n°528/2012

R(UE)n°1169/2011 (INCO)

R(UE)n°1223/2009

[Nano] mandatory labelling



Ingrédients pour 2 à 4 Gélules
 Contenu: Extrait sec de pépins de Pamplemousse(300/600 mg),
 Curcuma (200/400 mg),
 Extrait sec de graines de Courge* (100/200 mg),
 Cumin (100/200 mg),
 Dioxyde de silicium [nano] E551.

INGRÉDIENTS : CAPRYLIC/CAPRINIC TRIGLYCERIDE, [NANO] ZINC OXIDE, AQUA, ALCOHOL*, [NANO] TITANIUM DIOXIDE, GLYCERIN, MENTHA PIPERITA WATER*, DICAPRYLYL CARBONATE, POLYGLYCERYL-2 DIPOLYHYDROXYSTEARATE, LAURYL GLUCOSIDE, PONGAMIA GLABRA SEED OIL, GLYCERYL ISOSTEARATE, POLYHYDROXYSTEARIC ACID, POLYGLYCERYL-2 STEARATE, BENZYL ALCOHOL, COCOS NUCIFERA OIL, GARDENIA TAHITENSIS FLOWER, CITRIC ACID, XANTHAN GUM, TOCOPHEROL, DEHYDROACETIC ACID, POTASSIUM SORBATE, SODIUM BENZOATE, PARFUM, LINALOOL

*Ingrédients issus de l'agriculture biologique
 **Transformé à partir d'ingrédients biologiques

98,98 % du total des ingrédients sont d'origine naturelle.
 100 % des ingrédients végétaux sont certifiés Bio.
 10,97 % du total des ingrédients sont issus de l'Agriculture Biologique.

COSMÉTIQUE ÉCOLOGIQUE et BIOLOGIQUE certifié par ECOCERT Greenlife selon le référentiel ECOCERT disponible sur <http://cosmetiques.ecocert.com>

A utiliser de préférence avant fin : voir sur le haut du tube.

National databases and registers

- Consumer information
- Sample targeting



R-Nano register:

Compulsory annual declarations (decrees n° 2012-232 et 2012-233) allow the authorities to better understand substances at nanoscale, their uses and quantities handled on national territory.

→ **Substances traceability** (from manufacturer or importer to the distributor)

→ **Better knowledge of the market.**

→ **Annual study report published on the R-Nano site** : general informations (declaration number, declared quantities, product families)

→ **Lack of accessible and precise datas** regarding properties and uses of these substances.

→ **« Nanomaterial » definition : Commission recommandation!**

Inventaires et sources d'information de produits contenant des nanomatériaux



www.nanodb.dk

The Nanodatabase

SEARCH DATABASE NEWS ANALYSIS NANORISKCAT REPORT PRODUCT ABOUT US

LOGIN ENGLISH

FRUITS SKITTLES

Home / Product

Fruits Skittles

Manufacturer: Mars Nanomaterial: Titanium dioxide Category: Food and Beverage

Nano Risk Category (See how this is generated)

EXPOSURE: Professional, Consumers, Environment

EFFECT: Humans

Product Information

Fruit candy

Manufacturer's description

INGREDIENTS:
Sugar, Corn Syrup, Hydrogenated Palm Kernel Oil; less than 2% of: Citric Acid, Tapioca Dextrin, Modified Corn Starch, Natural and Artificial Flavors, Colors (Titanium Dioxide, Red 40 Lake, Yellow 6 Lake, Yellow 5 Lake, Blue 2 Lake, Blue 1 Lake, Yellow 6, Red 40, Yellow 5, Blue 1), Sodium Citrate, Carnauba Wax.
<http://www.wrigley.com/global/brands/skittles.aspx#panel-3>

Others Say

This product was labeled as containing "Colours (171)". The E171 food designation represents TiO₂. Particles in the nanoscale range were observed by TEM and point analysis using EDX of the particles indicated they contained titanium and oxygen, at ratios consistent with TiO₂.
<http://emergingtech.foe.org.au/vp-content/uploads/2015/09/foe-aus-report-final-web.pdf>

GO TO WEBSHOP

- Online database developed by the “Danish Consumer Council” & the “Danish Ecological Council in cooperation” with the Technical University of Denmark (DTU) Environment
- Reports 3036 products (au 08/10/2018) including:
 - 127 in « food and beverage »
 - 981 in « cosmetics and personal care »

Evaluation of the conformity

Manufacturers : know if the product meets regulatory requirements

Control authority : whether or not to accept the classification made by the manufacturer

Consumer : ensure that the product is properly labeled



Legislation

Regulation (CE) n°1169/2011



Conformity ?

Application in daily life





Control authority :

« Is the product properly labeled ? »

- Presence of particles ?
- Particles composition ?
- « Nano » particles ? Which distribution ?



- Analytical strategy for the numerical characterization in size of inorganic nanoparticles additives in food products and cosmetics (DLS,TEM,SP-ICP...)

- Development of analytical methods suitable for regulatory purposes (robust, rapid, not expensive)



Reference method: MEB (+EDX)

Recommendations

TiO₂

EFSA statement
(sept. 2016)

The Panel recommended that:

- The EU specifications for TiO₂ (E 171) should include a characterisation of particle size distribution using appropriate statistical descriptors (e.g. range, median, quartiles) as well as the percentage (in number and by mass) of particles in the nanoscale (with at least one dimension < 100 nm) present in TiO₂ (E 171) used as a food additive. The measuring methodology applied should comply with the EFSA Guidance document (EFSA Scientific Committee, 2011).



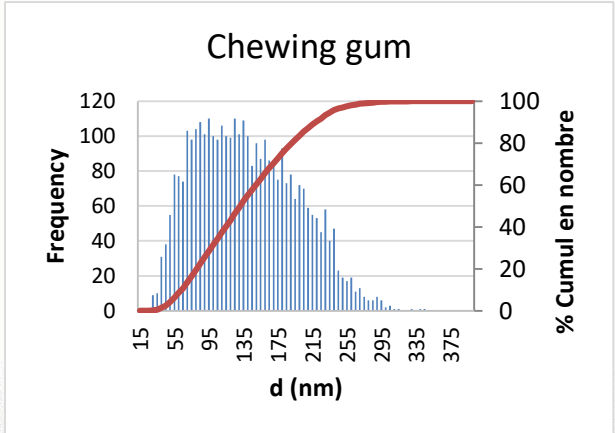
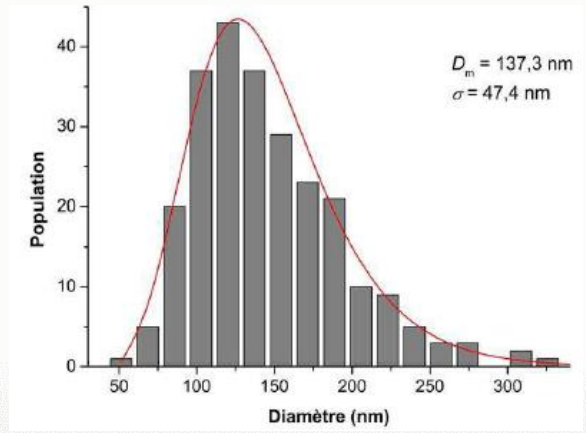
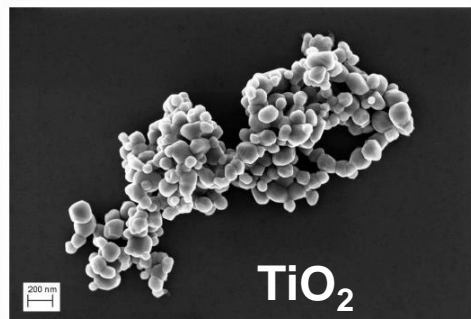
Guidance for risk assessment of engineered nanomaterials

Table 1: Parameters for characterisation and identification of ENM (see appendix A for methods)

Parameter	Requirements	Description
Chemical composition/ identity	Essential	Information on chemical composition of the ENM – including purity, nature of any impurities, coatings or surface moieties, encapsulating materials, processing chemicals, dispersing agents and/or other formulants e.g. stabilisers.
Particle size (Primary/ Secondary)	Essential (two methods, one being electron microscopy)	Information on primary particle size, size range and number size distribution (indicating batch to batch variation – if any). The same information would be needed for secondary particles (e.g. agglomerates and aggregates) if present. .

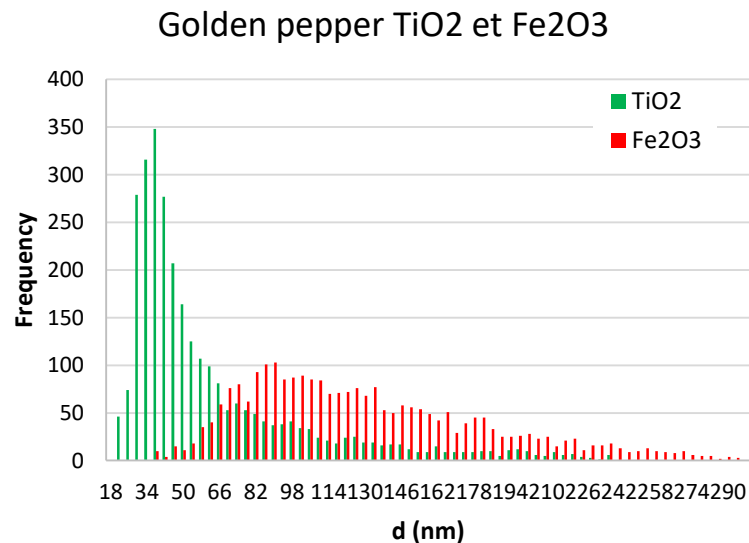
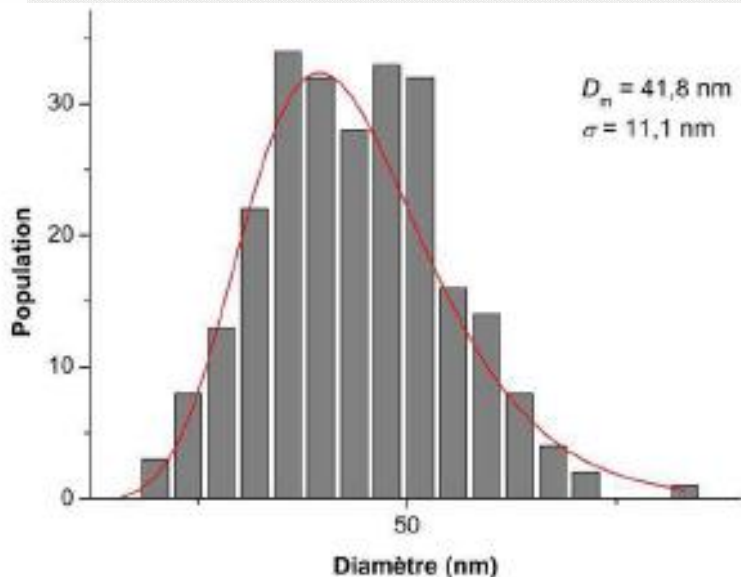
Analytical strategies & methods – Conformity

Method	MEB	SP-ICP-MS
Size	✓	✓
Size range	✓	✓
Number size distribution	✓	✓
Agglomeration/Aggregation states	✓	✓



	MEB	SP-ICP-MS
Average	137 nm	140 nm
Median	127 nm	135 nm
Mode	120 nm	114 nm
<100 nm	23%	29%

Analytical strategies & methods – Conformity



	MEB	SP-ICP-MS TiO ₂	SP-ICP-MS Fe ₂ O ₃
Average	42 nm	69 nm	134 nm
Median	42 nm	46 nm	121 nm
Mode	36 nm	38 nm	70 nm
<100 nm	100 %	83 %	34 %

- ✗ No distinction between E171/E172
- ✗ 250 NP - Manual counting

- ✓ Differentiation E171/E172
- ✓ 3000 NP/60s
- ✓ **Selectivity & specificity**

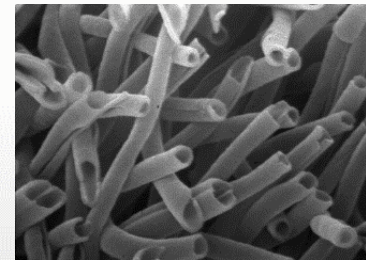
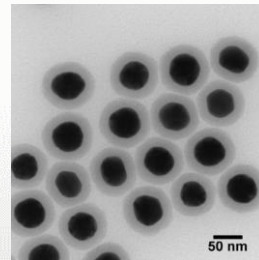
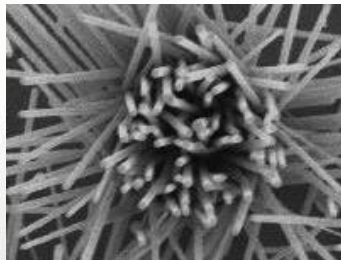
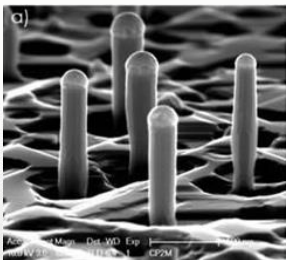
Analytical strategies & methods – Complementarity

Method	MEB	SP-ICP-MS
Size	✓	✓
Size range	✓	✓
Number size distribution	✓	✓
Agglomeration/Aggregation states	✓	✓



- Ferret diameter
- Various shapes
- No discrimination
- Expensive

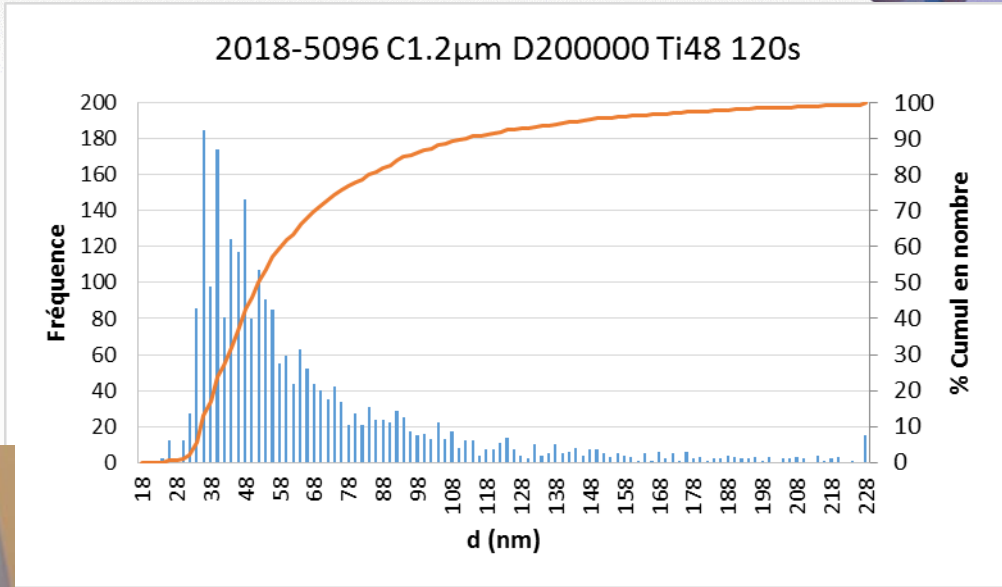
- Sphere of equivalent diameter
- Spherical
- Selectivity and specificity
- Rapid-Routine



Analytical strategies & methods – Conformity

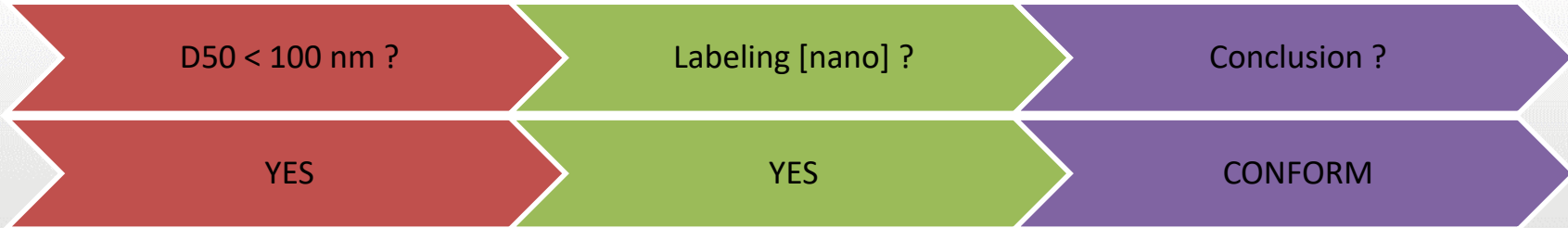


Cosmetics Real sample

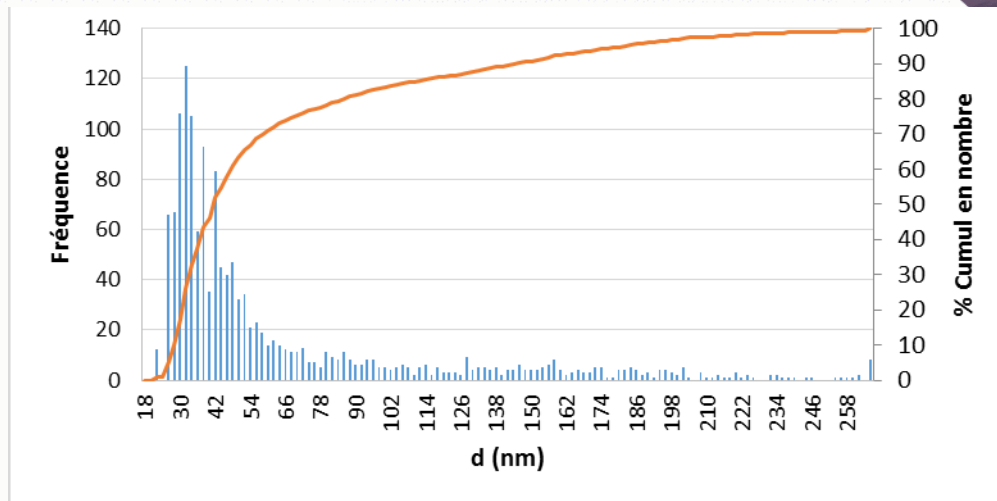
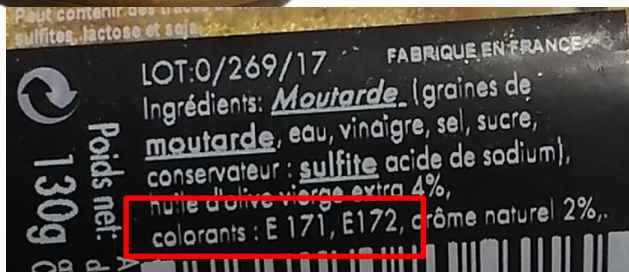


INGRÉDIENTS : Aqua (Water), Octocrylene, Ethylhexyl Salicylate, Butyl Methoxydibenzoylmethane, Diisopropyl Sebacate, Glycerin, Ethylhexyl Methoxycinnamate, C12-15 Alkyl Benzoate, Phenylbenzimidazole Sulfonic Acid, Acrylates Copolymer, **Titanium Dioxide [nano]**, Triethanolamine, Coco-Glucoside, Cetearyl Alcohol, Glyceryl Stearate, PEG-100 Stearate, Tocopheryl Acetate, Hydroxyethyl Acrylate/Sodium Acryloyldimethyl Taurate Copolymer, Caprylyl Glycol, Coconut Alcohol, Phenoxyethanol, Chlorphenesin, Xanthan Gum, Stearic Acid, 1,2-Hexanediol, Alumina, Disodium EDTA, Palmitic Acid, Silica, Polysorbate 60, Sorbitan Isostearate, Sodium Laureth Sulfate, Glucose.

Parameters	TiO2 (E171)
Median (D50)	50 nm



Food Real sample



Parameters	TiO2 (E171)
Median (D50)	49 nm

