SOREMARTEC

food science, technology and human nutrition
MASTER UNIVERSITARIO DI SECONDO LIVELLO - MICHELE FERRERO
scienza e tecnologia dell'alimentazione e nutrizione umana

Master's degree "Food Science, Technology and Human Nutrition - Michele Ferrero"

# *"Nanotechnologies & Food Products: Applications, Risk Assessment and Acceptance of Consumers"*

Università degli Studi di Torino – DSTF – 20/11/2015

Giacomo Rinaudo
giacomorinaudo@yahoo.it

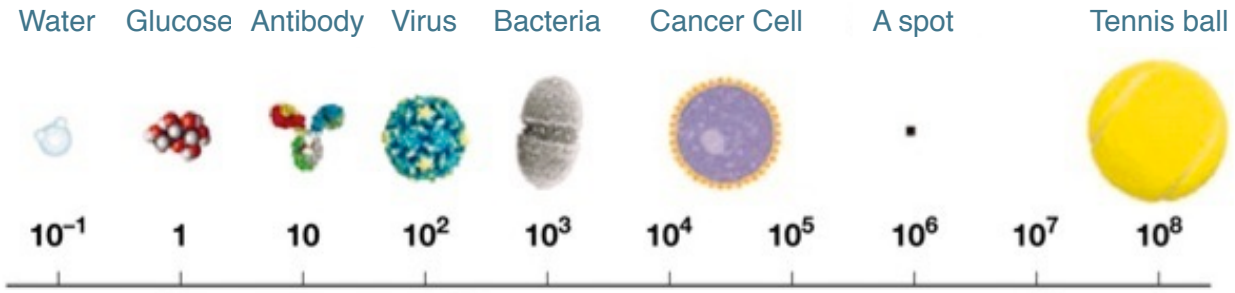
# Aim of the work

Give an overview of nanotechnologies within the food sector concerning:

- Definition & Legislation
- Applications
- Risk Assessment
- Awareness and Attitudes

In order to support the company in an appropriate orientation.

# Definition & Legislation

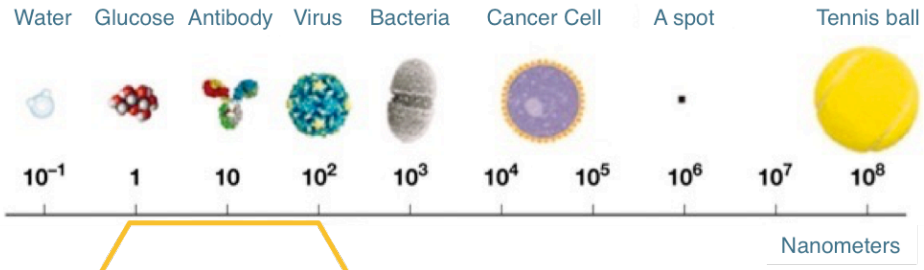


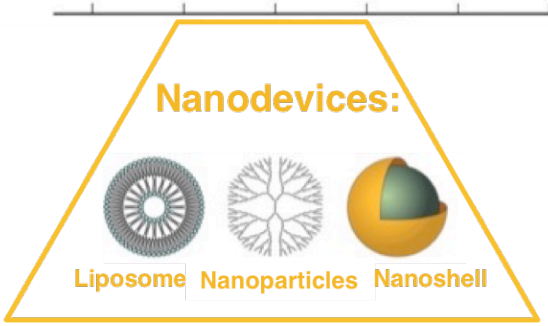

**Nanodevices:**

Liposome Nanoparticles Nanoshell

One nanometer is to a tennis ball what a tennis ball is to the Earth...

# Definition & Legislation




## Possible change of….

- Chemical reactivity
- Morphology
- Biopersistence
- Solubility
- Bioactivity

# Definition & Legislation

European Commission Recommendation 696/2011:

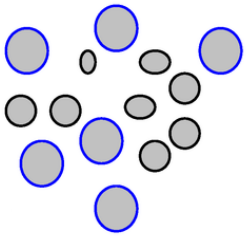
*"Nanomaterial means a **natural**, **incidental** or **manufactured** material containing particles,*

*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 **1nm-100nm**."*

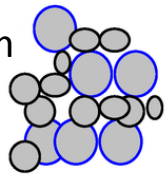
# Definition & Legislation

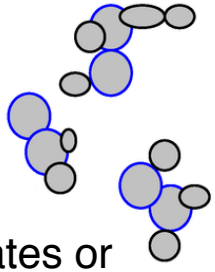
*…in an **unbound** state or as an **aggregate** or as an **agglomerate** …*



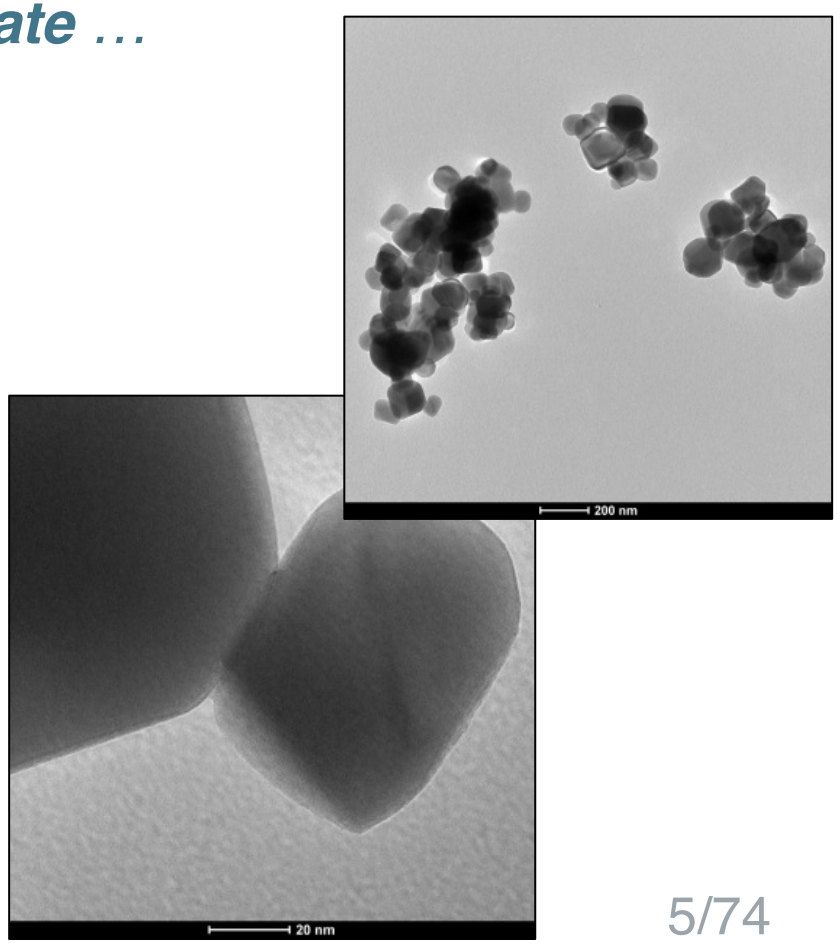
Primary nanoparticles 5-20 nm

Aggregate (chemically bound) 30-200 nm



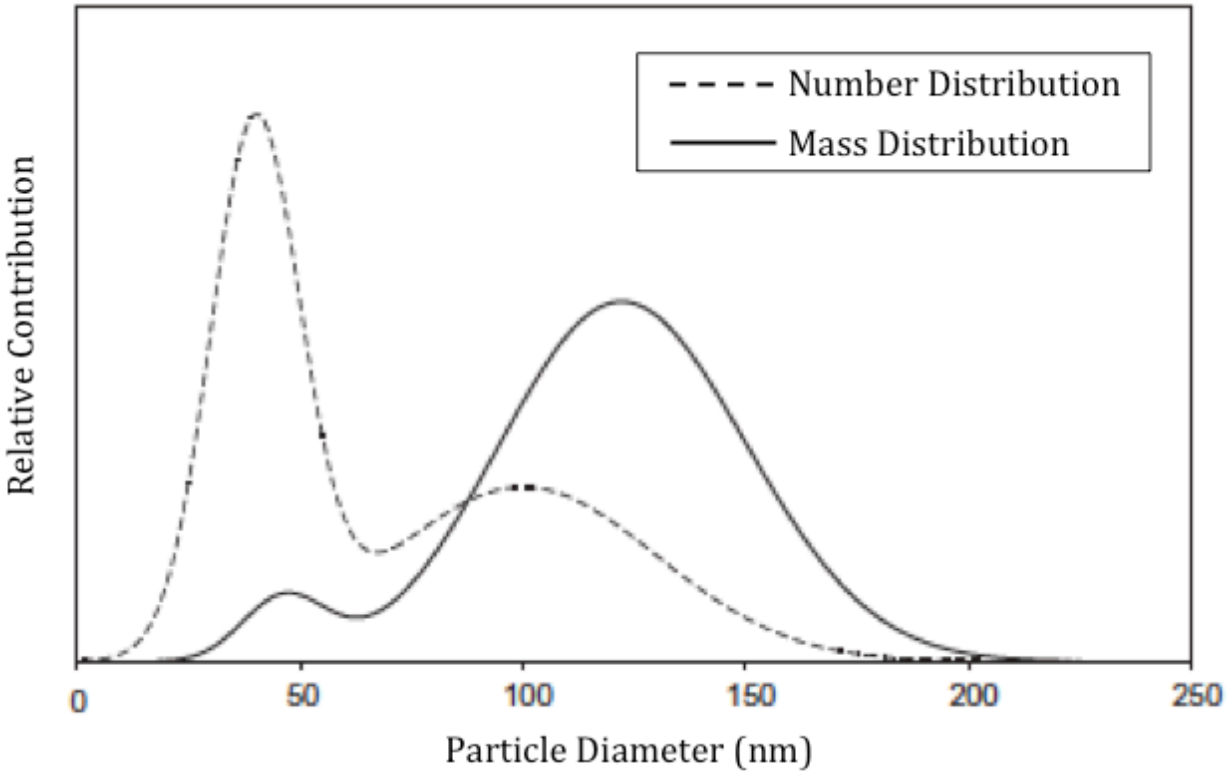


Weak Agglomerates or Flocculates 1-100 µm



# Definition & Legislation

*…for 50% or more of the particles in the **number size distribution**…*




Example of relative contribution of ideal spherical structure to particle **size distribution** expressed as **number** (broken line) and mass (full line).

(Bleeker, et al., 2013)

# Definition & Legislation

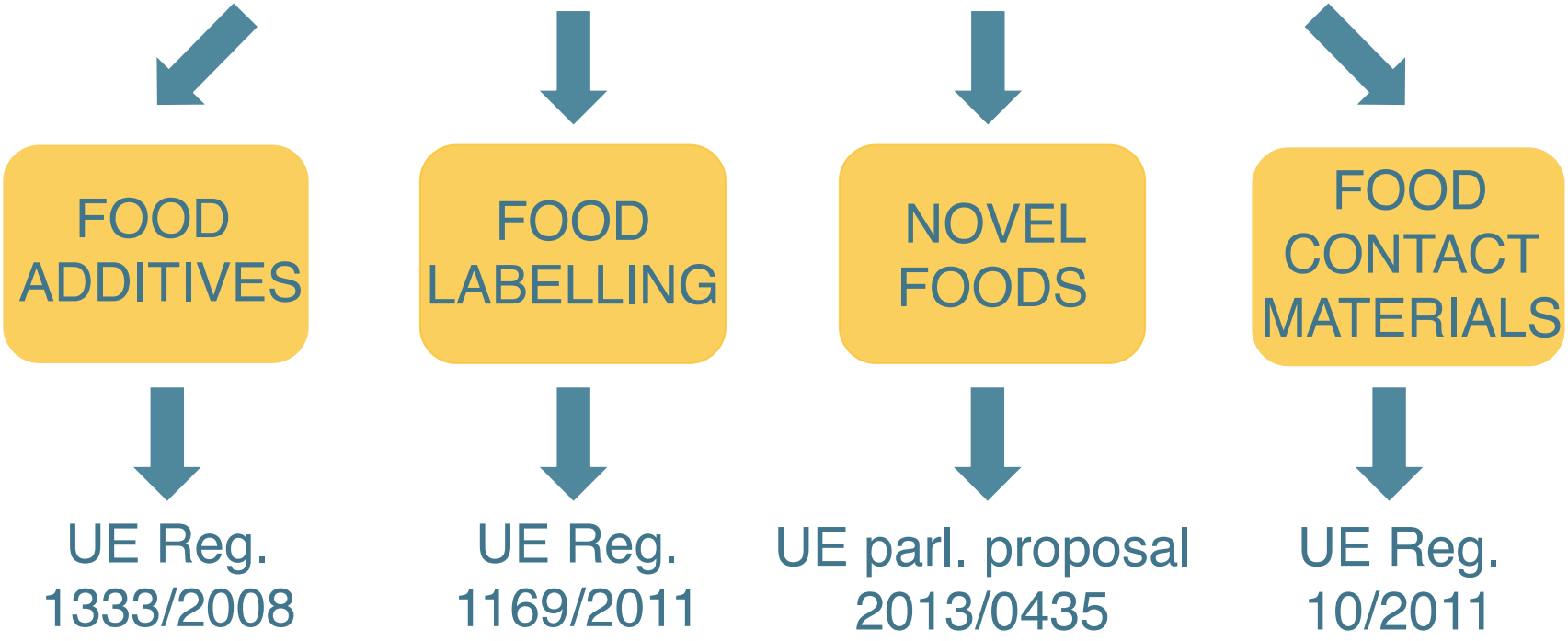
Another parameter commonly used for nanomaterial characterization is the **Volume Specific Surface Area (VSSA)** that is defined as:

"*the surface area divided by the mass of the relevant phase, when the area of the interface between two phases is proportional to the mass of one of the phases*" (IUPAC, 1972)

European Commission Recomm. 696/2011 → VSSA > $60 m^2/cm^3$

# Definition & Legislation

European Commission Recommendation 696/2011:



# Definition & Legislation

| Legislation | EU legislation | Definition[a] | Label[b] | Guidance |
|---|---|---|---|---|
| | | | | |
| **Products:** | | | | |
| Biocides | (EU) No 528/2013 | Yes | Yes | No |
| Plant protection products | (EC) No 1107/2009 | No | No | Yes |
| Cosmetics | (EC) No 1223/2009 | Yes | Yes | Yes |
| Medical devices | COM (2012) 542 final 2012/0266 (COD) | Yes | Yes | No |
| | | | | |
| **Food/Feed:** | | | | |
| Food information to consumers | (EU) No 1169/2011 | Yes | Yes | No |
| Novel foods/feeds | COM(2013) 894 final 2013/0435 (COD) | Yes | Yes | Yes |
| Plastic food contact materials | (EU) No 10/2011 | No | No | Yes |
| Active and Intelligent Materials and Articles | (EU) 450/2009 | No | No | No |
| Food additives | (EC) 1333/2008 | No | Yes | Yes |
| Feed | (EC) No 767/2009 | No | No | No |
| | | | | |
| **Chemicals:** | | | | |
| Registration, evaluation, authorisation and restriction of chemicals (REACH) | (EC) 1907/2006 | No | No | Yes |
| Classification, labelling and packaging | (EC) 1272/2008 | No | No | No |
| Occupational health and safety | 89/391/EEC: 98/24/EC: 2004/37/EC: EC 1907/2006: | No | No | No |

a): In case the specific legislation includes a definition of nanomaterial, this is indicated by "Yes".
b): In case the specific legislation requires that the use of nanomaterials is indicated on the product label, this is indicated by "Yes".

(EFSA, 2014)

# Definition & Legislation

FOOD LABELLING
UE Reg. 1169/2011

*"**Engineered nanomaterial** means any **intentionally produced** material that has one or more dimensions of the order of 100 nm or less or that is composed of discrete functional parts, either internally or at the surface, **many of which** have one or more dimensions of the order of 100 nm or less"*

# Definition & Legislation

FOOD LABELLING
UE Reg. 1169/2011

Amending Regulation 1363/2013 of December 2013

*"Engineered nanomaterial means any intentionally 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 to 100 nm"*

**One week later** the Commision itself released the 346/89 corrigendum which **nulled and voided** the publication.

# Definition & Legislation

FOOD ADDITIVES
UE Reg. 1333/2008

Although it does not contain a definition, the Reg. states that:

*"When a food additive is **already included** in a Community list and there is a significant **change in its production methods**… for example through nanotechnology, the food additive prepared by those new methods or materials shall be considered as a different additive and **shall undergo a new safety evaluation** carried out **by European Food Safety Authority** (EFSA)"*

# Definition & Legislation

FOOD ADDITIVES
UE Reg. 1333/2008

Re-evaluation program
(Reg. 257/2010)

**$TiO_2$, Ag, Au, Fe oxides within 31/12/2015**

**$SiO_2$ within 31/12/2016**

**Mg and Ca silicates within 31/12/2018**

# Definition & Legislation

FOOD ADDITIVES
UE Reg. 1333/2008

## Re-evaluation program (Reg. 257/2010)

For the moment, the only two substances with nanosized fraction presence concern that has been re-evaluated, are the **calcium carbonate** (E 170: "*the current levels of adventitious nanoscale calcium carbonate in commercial products* ***would not be an additional toxicological concern***") and **vegetable carbon** (E 153: "***the presence of nanoparticles*** *in vegetable carbon products currently on the market* ***can be excluded***").

# Definition & Legislation

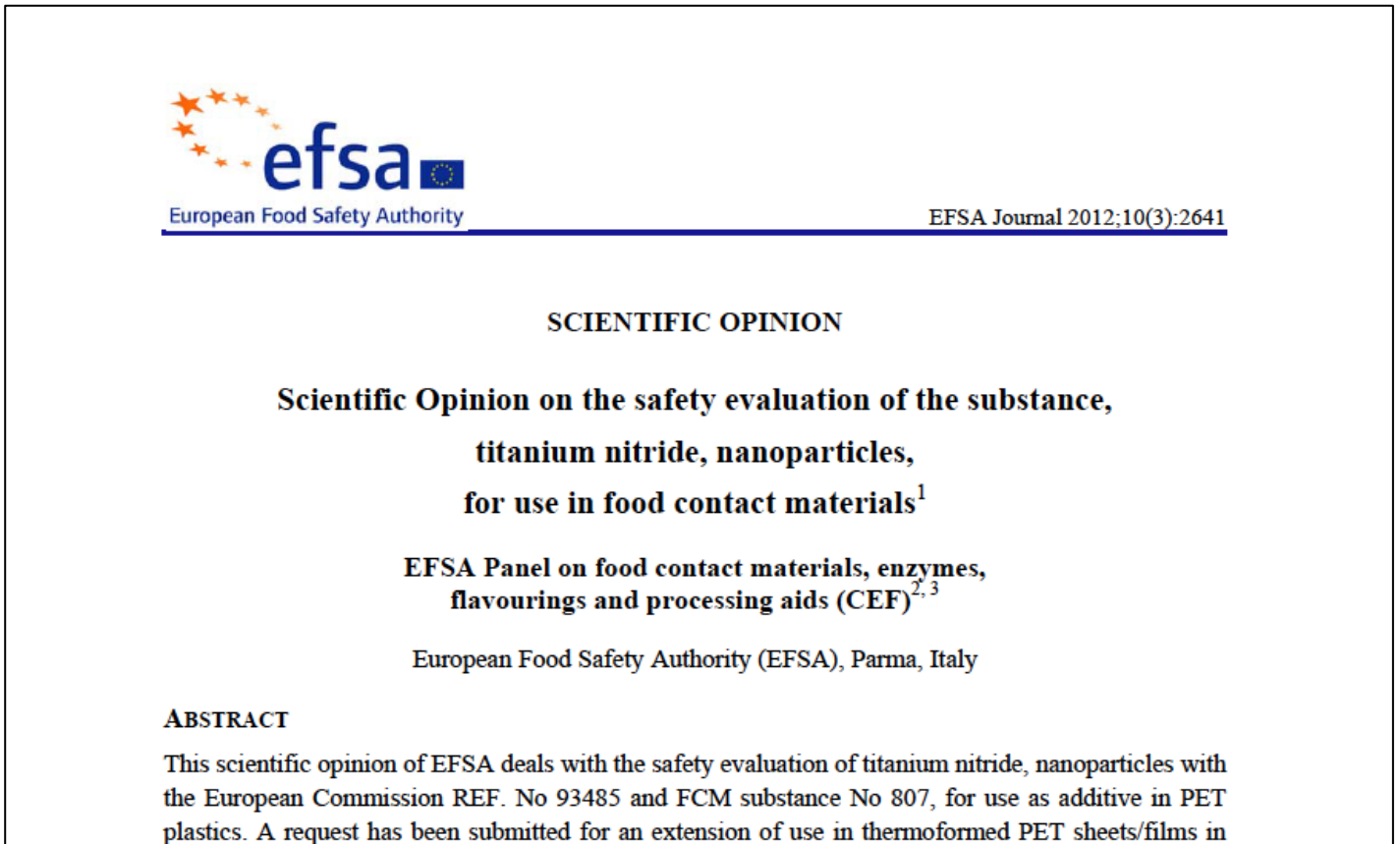
FOOD CONTACT MATERIALS
UE Reg. 10/2011

*"Substances in nanoform shall only be used if **explicitly authorised**"*

Furthermore, it states that nanoparticles should be assessed on a **case-by-case basis** as regards their risk until more information is known about such new technology.

# Definition & Legislation

## FOOD CONTACT MATERIALS
## UE Reg. 10/2011



efsa
European Food Safety Authority

EFSA Journal 2012;10(3):2641

SCIENTIFIC OPINION

**Scientific Opinion on the safety evaluation of the substance, titanium nitride, nanoparticles, for use in food contact materials**[1]

**EFSA Panel on food contact materials, enzymes, flavourings and processing aids (CEF)**[2, 3]

European Food Safety Authority (EFSA), Parma, Italy

ABSTRACT

This scientific opinion of EFSA deals with the safety evaluation of titanium nitride, nanoparticles with the European Commission REF. No 93485 and FCM substance No 807, for use as additive in PET plastics. A request has been submitted for an extension of use in thermoformed PET sheets/films in

# Definition & Legislation

## FOOD CONTACT MATERIALS
## UE Reg. 10/2011


**ABSTRACT**

This scientific opinion of EFSA deals with the safety evaluation of titanium nitride, nanoparticles with the European Commission REF. No 93485 and FCM substance No 807, for use as additive in PET plastics. A request has been submitted for an extension of use in thermoformed PET sheets/films in addition to the use in PET bottles, evaluated by the EFSA in 2008. Under the intended conditions of use, no migration of the substance into food is expected and therefore no exposure of the consumer via food is expected. Based on this, the CEF Panel concluded that there is no safety concern for the consumer if the substance is used up to 20 mg/kg in only PET plastics intended for contact with all types of foodstuffs under conditions of any duration of time and at temperatures up to and including hot-fill.



**ABSTRACT**

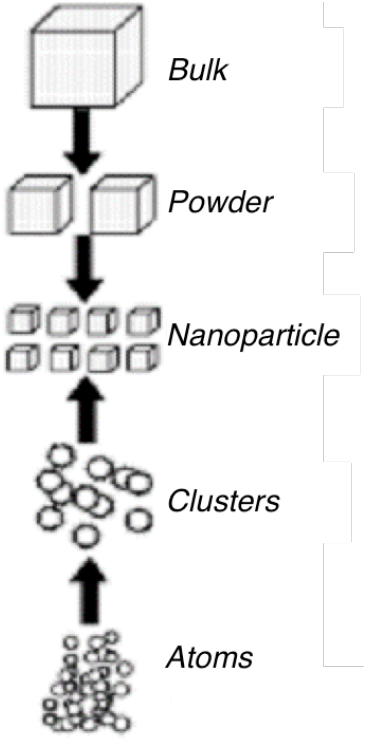
This scientific opinion of EFSA deals with the safety evaluation of titanium nitride, nanoparticles with the European Commission REF. No 93485 and FCM substance No 807, for use as additive in PET plastics. A request has been submitted for an extension of use in thermoformed PET sheets/films in

# Production & Applications

**Intentional Production** **V.S.** **Accidental Production**

# Production & Applications

## Intentional Production




**Top Down** ➡
- Mechanical milling
- High-pressure homogenisation
- Ultrasound emulsification

**Bottom up** ➡
- Self assembling
- Salting out
- Sol-gel synthesis

# Production & Applications

## Accidental Production

*Accidental results of the common production processes*

- Mechanical milling
- Hydrolysis in acidic solution
- Emulsification

→ $TiO_2$, $SiO_2$, Mg and Ca silicates

# Production & Applications

## FOOD INGREDIENTS:

**Nanoemulsions**

Top Down

Nanoencapsulates

Bottom up

$SiO_2$

$TiO_2$

# Production & Applications

## FOOD INGREDIENTS:

Nanoemulsions

Top Down

**Nanoencapsulates**

Bottom up

$SiO_2$

$TiO_2$


# Production & Applications

## FOOD INGREDIENTS:

Nanoemulsions

Top Down

Nanoencapsulates

Bottom up

**$SiO_2$**



$TiO_2$

# Production & Applications

## FOOD INGREDIENTS:

Nanoemulsions

Top Down

Nanoencapsulates

Bottom up

$SiO_2$

**$TiO_2$**

# Production & Applications

## FOOD CONTACT MATERIALS:

Top Down

Bottom up

**TiN**


efsa
European Food Safety Authority
EFSA Journal 2012;10(3):2641

SCIENTIFIC OPINION

Scientific Opinion on the safety evaluation of the substance, titanium nitride, nanoparticles, for use in food contact materials[1]

EFSA Panel on food contact materials, enzymes, flavourings and processing aids (CEF)[2, 3]

Nanoclays

$TiO_2$

Ag

# Production & Applications

## FOOD CONTACT MATERIALS:

Top Down

Bottom up

TiN

**Nanoclays**

$TiO_2$

Ag


# Production & Applications

## FOOD CONTACT MATERIALS:

Top Down

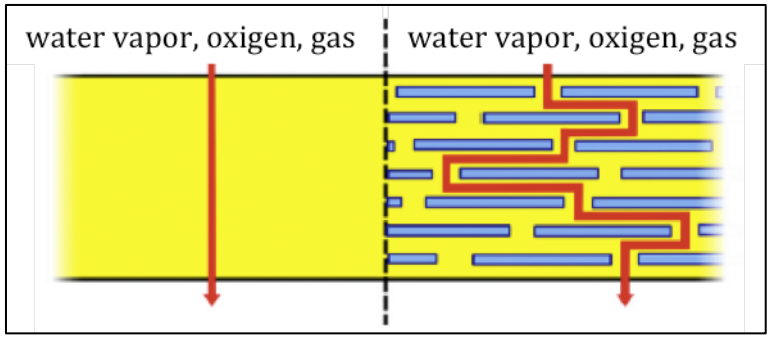
**Nanoclays**

Bottom up

TiN

$TiO_2$

Ag



# Production & Applications

## FOOD CONTACT MATERIALS:

Top Down

Bottom up

TiN

Nanoclays

$TiO_2$

Ag

# Production & Applications

## FOOD CONTACT MATERIALS:

Top Down

Bottom up

TiN

Nanoclays

$TiO_2$

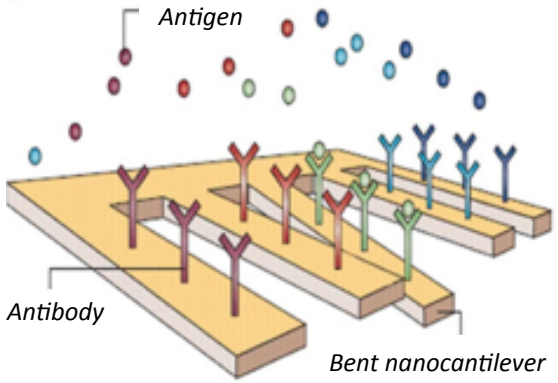
**Ag**

# Production & Applications

## FOOD PROCESSING:

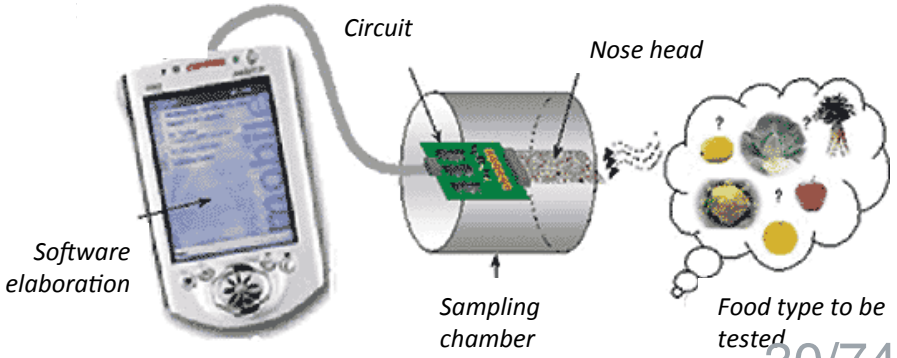
Top Down

**Nanocantilevers**




Bottom up

Electronic nose/tongue

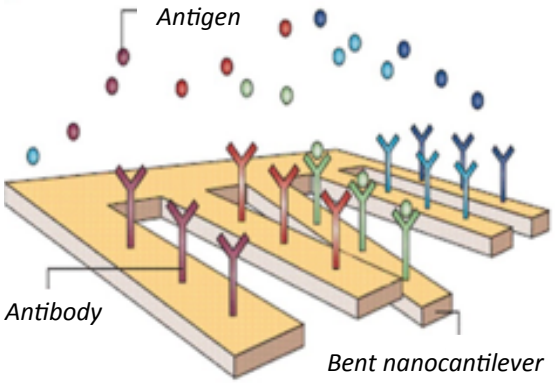


# Production & Applications

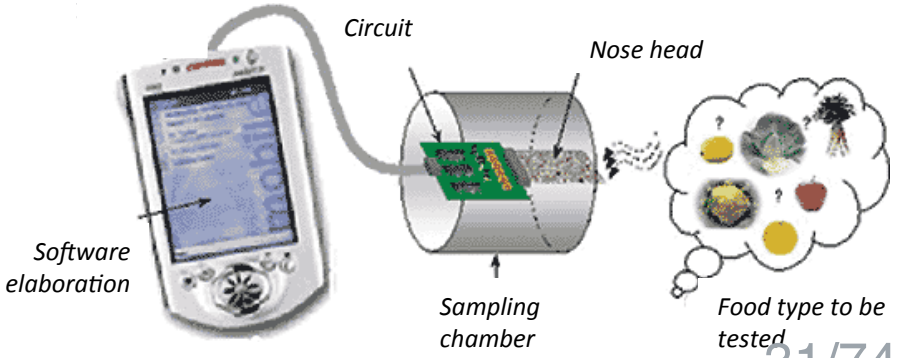
## FOOD PROCESSING:

Top Down

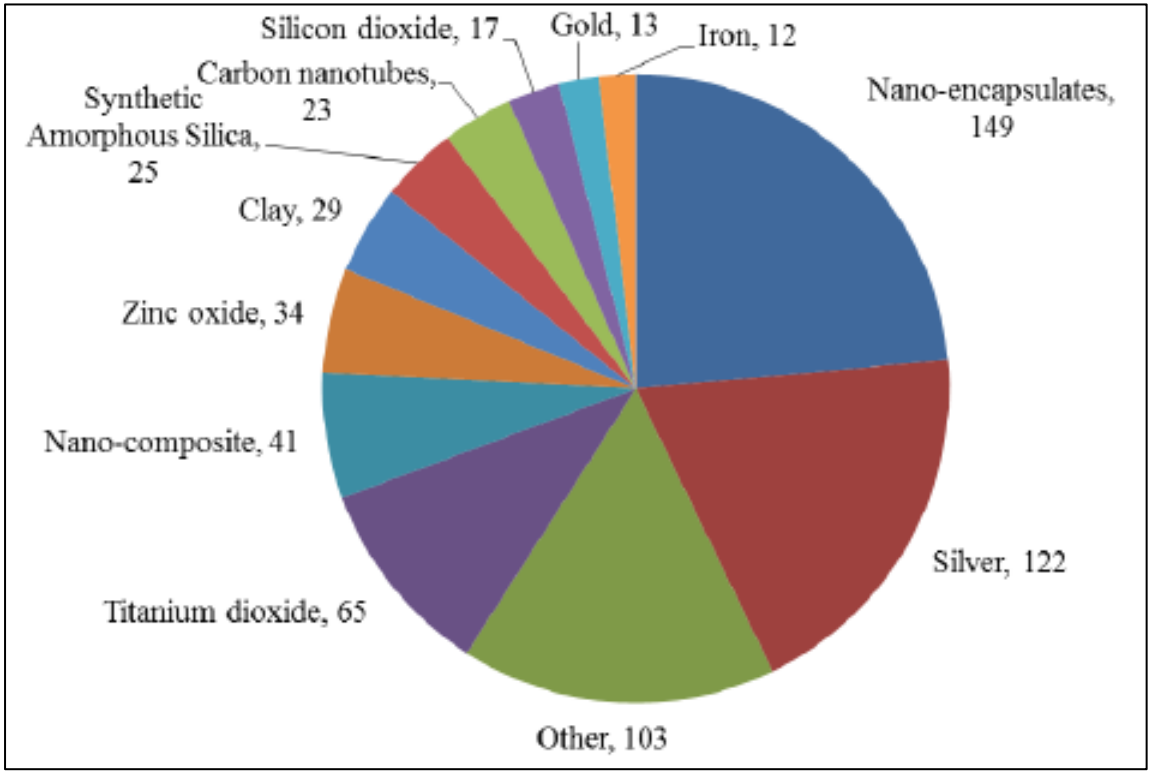
Nanocantilevers




Bottom up → **Electronic nose/tongue**



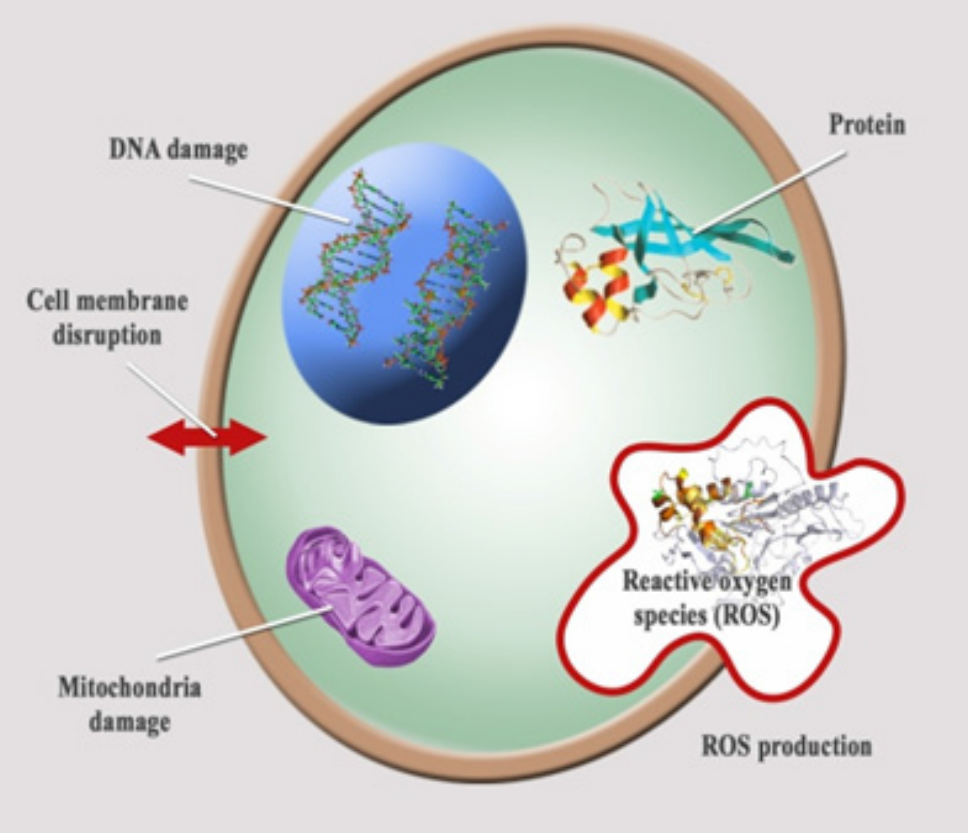
# Production & Applications




Nanomaterials mentioned in the Nano Invetory (EFSA, 2014).

# Risk Assessment

## Mechanism of toxicity of nanomaterials




(Nikodinovska et al., 2015)

# Risk Assessment

The risk assessment paradigm

Hazard identification

Hazard characterization

Exposure assessment

# Risk Assessment

The risk assessment paradigm

*THROUGH…*

Definition of the:

- CHEMICAL COMPOSITION
- PHYSICOCHEMICAL PROPERTIES
- INTERACTIONS WITH TISSUES
- POTENTIAL EXPOSURE SCENARIOS

# Risk Assessment

## Parameter and methodologies for an appropriate characterization and identification of nanomaterials

| Parameter | Requirements | Currently available methods |
|---|---|---|
| Surface charge | Essential | Electrophoresis, e.g. CE, LDE (Laser Doppler Electrophoresis) |
| Redox potential | Essential for inorganic ENMs | Potentiometric methods |
| Solubility and partition properties | Essential | Standard tests for water solubility (e.g. OECD TG 105), and log kow (OECD TG 107, 117) can be used. Dissolution rate constants. |
| pH | Essential for liquid dispersions | |
| Viscosity | Essential for liquid dispersions | Methods such as OECD TG 114. |
| Density and pour density | Essential for granular materials | DIN ISO 697, EN/ISO 60 |
| Dustiness | Essential for dry powders | Methods such as EN 15051:2006, DIN 33897-2. |
| Chemical reactivity/catalytic activityb | Essential | Kinetic measurements of the chemical, biochemical and/or catalysed reactions |
| Photocatalytic activity | Essential for photocatalytic materials | Kinetic measurements of the chemical, biochemical and/or catalysed reactions |

(EFSA, 2011)

# Risk Assessment

## Parameter and methodologies for an appropriate characterization and identification of nanomaterials

| Parameter | Requirements | Currently available methods |
|---|---|---|
| Chemical composition/ identity | Essential | Elemental analysis: OES, AAS, XPS, EDX, NMR, Mass Spectrometry (MS) in particular ICP-MS, TXFX, etc.<br>Molecular composition: Mass spectrometry (ToF, QqQ) using suited ionisation techniques (e.g. MALDI, ESI), coupled with separation methods (e.g. HPLC, GC, CE etc), NMR, FT-IR<br>Shell/core composition (for encapsulates, micelles): by a suitable method given above, after disintegration of the particles and separation of the components by a suitable method (e.g. HPLC, SEC, CE, HDC etc) |
| Particle size (Primary/ Secondary) | Essential (two methods, one being electron microscopy) | Microscopy methodsb - e.g. TEM, SEM, STEM, AFM, STXM.<br>Separation methods: Flow separation, chromatography methods – e.g. FFF, HDC, SEC, RP/NP-HPLC; DMA/IMS (ultra)Centrifugation methods.<br>Spectroscopy methods – e.g. XRD (for crystal size, crystallite size)<br>Light (laser) scattering methodsc – e.g. DLS, MALS, SLS; PCCS, NTA |
| Physical form and morphology | Essential | Microscopy methods (TEM, SEM, STXM, AFM), X-ray diffraction |
| Particle and mass concentration | Essential for dispersions and dry powders | Mainly light scattering methodsc (for dispersions). Particle concentration (in puredry powders) may also be calculated from particle size, mass concentration and density of the material.<br>Suited methods from those listed under chemical composition e.g. mass spectrometry (ICP-MS) AEM, CFM; Gravimetric methods; centrifugal sedimentation (for suspensions) |
| Specific surface area | Essential for dry powders | BET method |
| Surface chemistry | Essential (for ENM with surface modifications) | Any of the suitable chemical characterisations methods listed above |

(EFSA, 2011)

# Risk Assessment

Abbreviations: AAS: Atomic Absorption Spectroscopy; AEM: Analytical Electron Microscopy; AFM: Atomic Force Microscopy; BET: Brunauer Emmett Teller; CE: Capillary Electrophoresis; CFM: Chemical Force Microscopy; DLS: Dynamic Light Scattering; DMA: Differential Mobility Analysis; EDX: Energy Dispersive X-ray Spectroscopy; FFF: Field Flow Fractionation; HDC: Hydrodynamic Chromatoghrapy; IMS: Ion Mobility Spectroscopy; LDE: Laser Doppler Electrophoresis; MALS: Microwave Absorption Line-Spectra; NTA: Nanosecond Transient Absortion; OES: Optical Emission Spectroscopy; PCCS: Photo Cross Correlation Spectroscopy; SAXS: Small-Angle X-ray Scattering; SEC: Size Exclusion Chromathography; SedFFF: Sedimentation Field Flow Fractionation; SLS: Static Light Scattering Microscopy; SMPS: Single Mobility Particle Sizing; STM: Scanning Tunnelling Microscopy; XPS: X-ray Photoelectron Spectroscopy; XRD: X-ray Diffraction

# Risk Assessment

Qualitative evaluation of the relative advantages and disadvantages for different techniques to measure the size of nanoparticles.

| | SEM | TEM | FFF | DLS | SP-ICP-MS |
|---|---|---|---|---|---|
| Minimum size | ++ | +++ | +++ | +++ | + |
| Dynamic range | +++ | ++ | ++ | +++ | ++ |
| Accuracy of measure | ++ | ++ | + | + | + |
| Suitable for mixtures | + | + | ++ | − | ++ |
| *In-situ* measure | − | − | + | ++ | ++ |
| Ease of use | − | − | + | ++ | + |
| Cost | − | − | ++ | +++ | + |

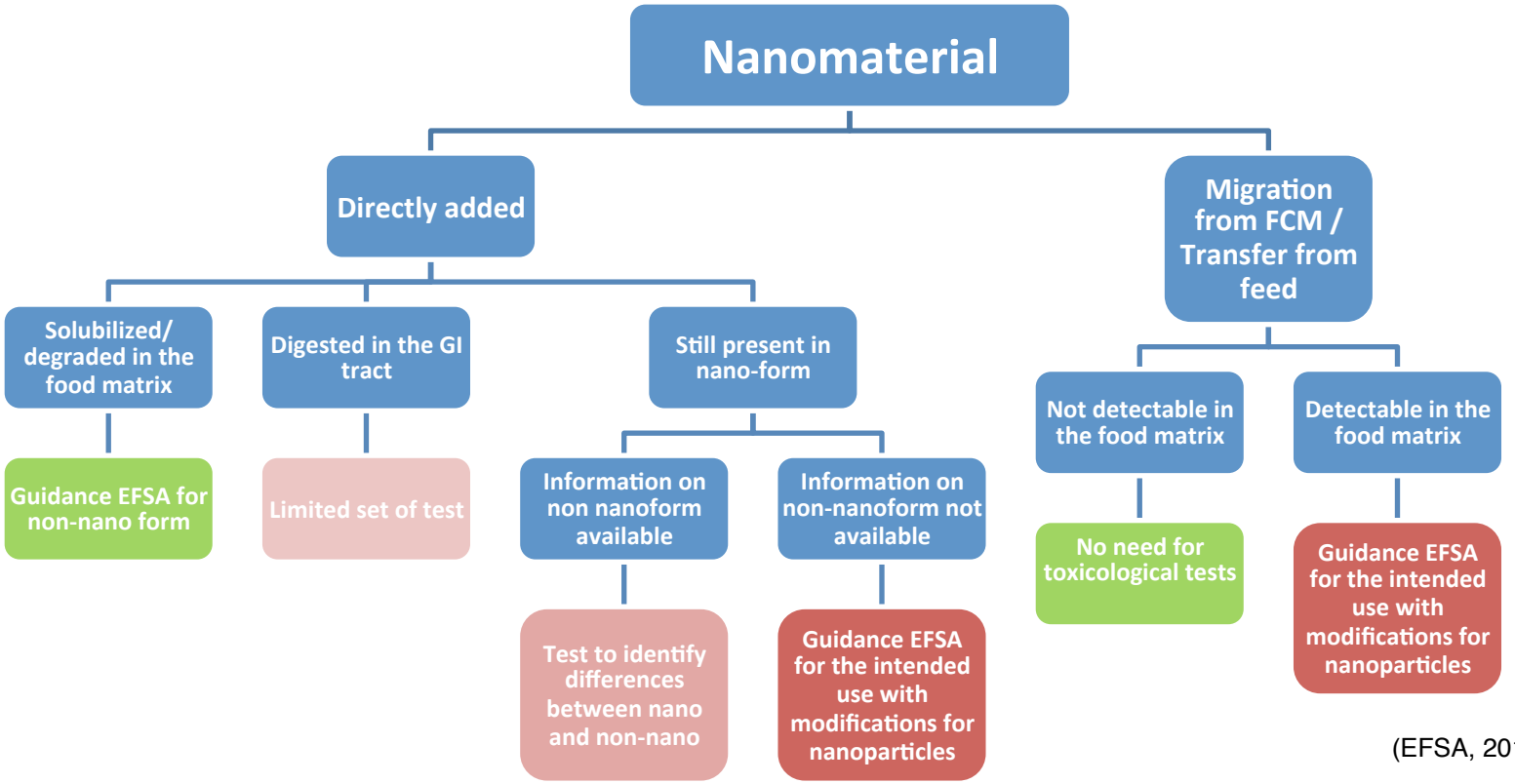
(Calzolai, Gilliland, & Rossi, 2012).

DLS, dynamic light-scattering; FFF, field flow fractionation;
SEM, scanning electron microscopy; SP-ICP-MS, single particle inductively coupled plasma;
TEM, transmission electron microscopy.

excellent (+++), good (++), fair (+) and insufficient (-)

# Risk Assessment

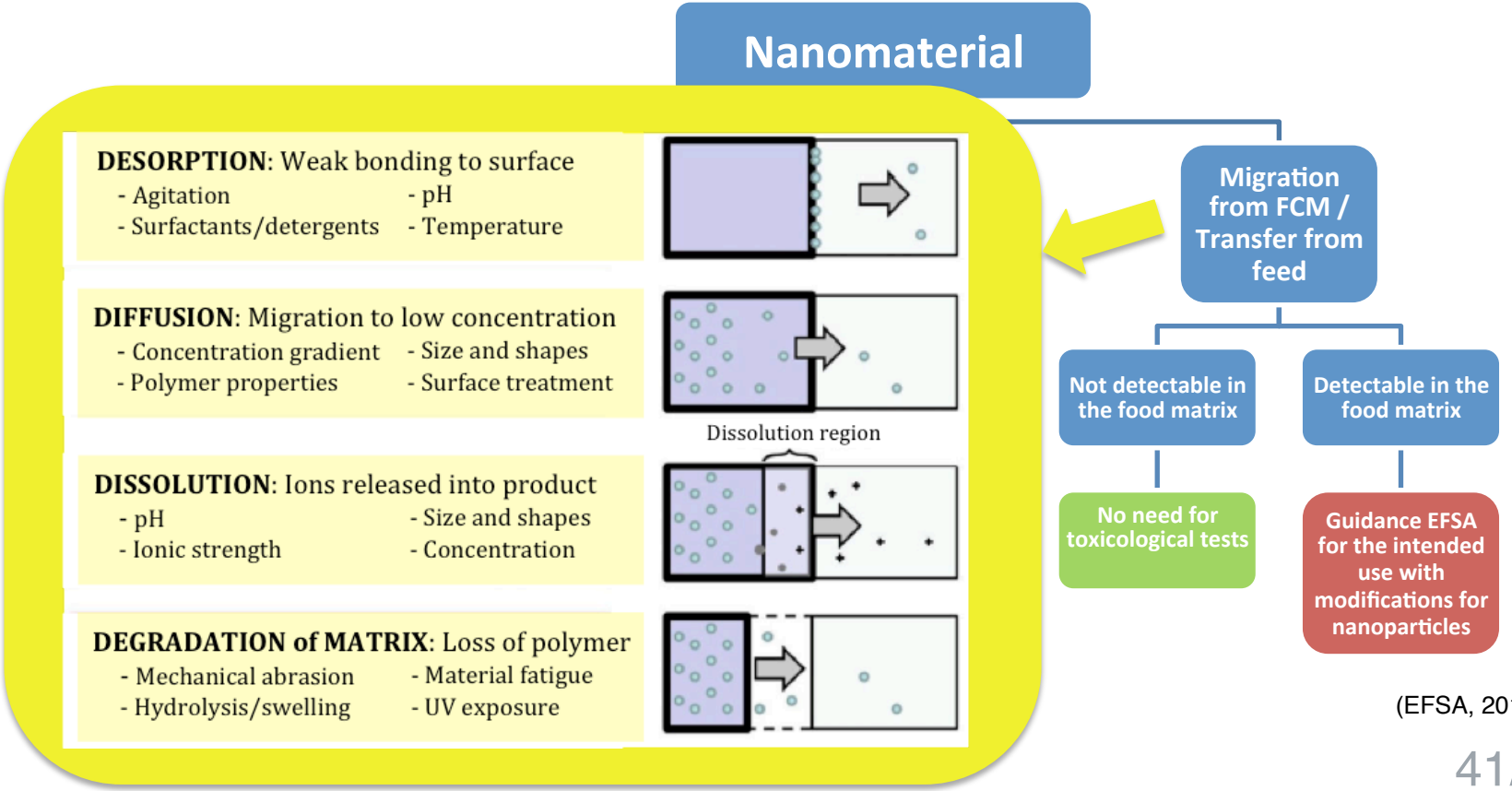
EFSA *Guidance on the risk assessment of the application of nanotechnologies in the food and feed chain* (2011)




(EFSA, 2011)

# Risk Assessment

EFSA *Guidance on the risk assessment of the application of nanotechnologies in the food and feed chain* (2011)




(EFSA, 2011)

# Risk Assessment

## Indicators of a potential for high exposure, of prospective toxicity or of reduced likelihood of adverse effects for NM used in food applications

| | |
|---|---|
| Indicators of a potential for high exposure | High production volume for the field of application<br>High mobility of the nanoform in organisms (probability of internal exposure) (e.g., transport via macrophages; transport through cell membranes, blood–brain barrier and/or placenta; drug delivery systems) and mobilization potential (e.g., infiltration, sorption, complex formation)<br>Targeted or controlled release<br>Persistence/stability (e.g., in water, fat, and body fluids, lack of solubility/degradation)<br>Bioaccumulation |
| Indicators of potential toxicity | High level of reactivity (e.g., catalytic, chemical, biological)<br>Complex morphology (e.g., rigid, long tubes or fibres, high aspect ratio nanomaterials, fullerenes, crystal structure, porosity). ENM with cores and shells of different biopersistence (e.g., multifunctional ENM)<br>Interactions with biomolecules such as enzymes, DNA, receptors, 'Trojan horse' effect<br>Complex transformations (e.g., aging, changes of surface properties, porosity) or metabolites (e.g., changes to or loss of coating, 'dynamic corona')<br>ENM intended to be used as antimicrobials (e.g., unintended consequences on the gut flora) |
| Indicators of reduced likelihood of adverse effects and/or loss of nano-properties | Increased rate of dissolution (e.g., in water, food/feed matrix or body fluids)<br>Increased rate of degradability (e.g., biological or photocatalytic) to non-nanoform degradation products<br>Presence of strongly bound aggregates (e.g., determined by conditions of production), fixed, permanent bonding in matrices (e.g. stability of matrix, type of bond, end-of-life behavior) |

(EFSA, 2011)

# Risk Assessment

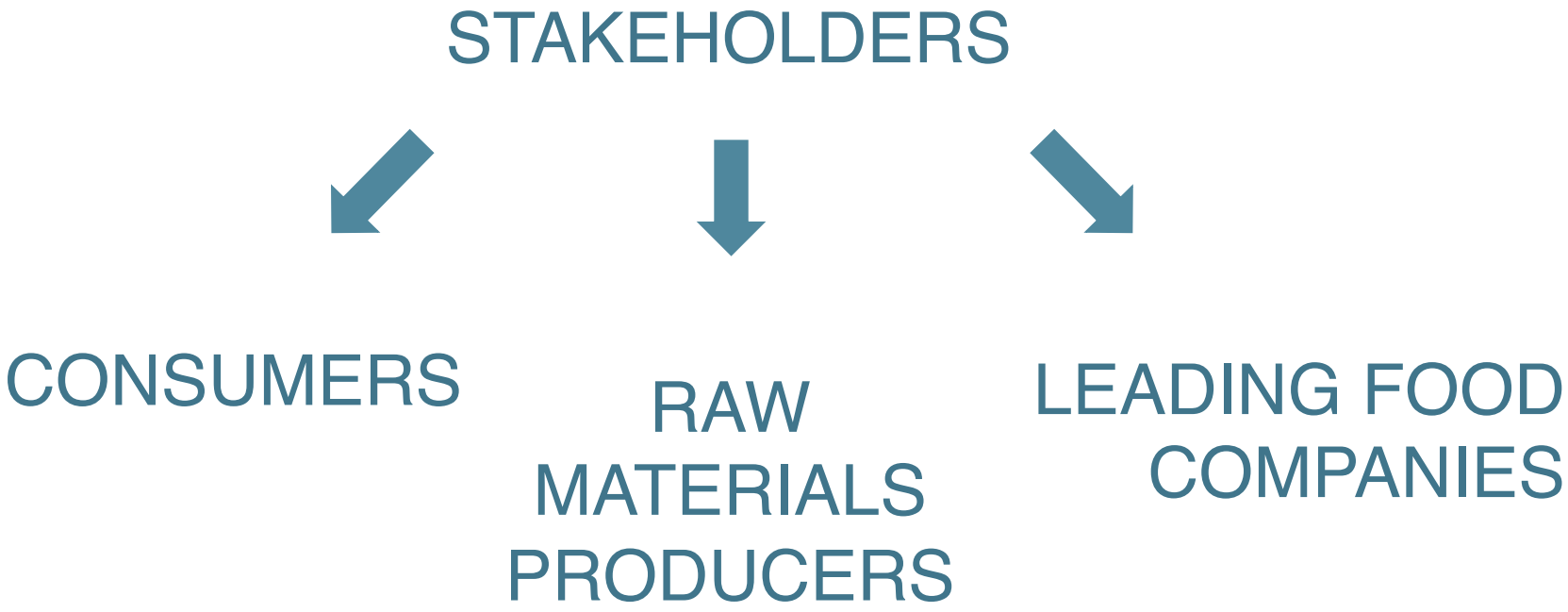
## Oral exposure of rodents to metal and oxide nanoparticles and related effects

| Particle (primary size) | Duration | Dose (species)[a] | Results | Reference |
|---|---|---|---|---|
| Ag (60 nm) | 28 days | 30, 300, 1000 mg/kg bw/day (r) | Changes in ALP and cholesterol indicating mild liver damage | Kim *et al.*, 2008 |
| Ag (56 nm) | 90 days | 30, 125, 500 mg/kg bw/day (r) | Changes in ALP and cholesterol indicating mild liver damage, bile-duct hyperplasia | Kim *et al.*, 2010 |
| Ag (22-42-71-323 nm) | 14 days (28 days for 42 nm-NPs) | 1 mg/kg bw/day (m) | Inflammatory responses, liver and kidney toxicity | Park *et al.*, 2010 |
| $SiO_2$ (7, 15–20 nm) | 28 days (84 days highest dose) | 100, 500, 1000, 2500 mg/kg bw/day (r) | Liver fibrosis, differences between the two pyrogenic SAS types studied | van der Zande *et al.*, 2014 |
| $SiO_2$ (~20 nm) | 5 days | 20 mg/kg bw/day (r) | Distribution in liver and spleen, differences between the precipitated and pyrogenic SAS studied | Cubadda *et al.*, in preparation |
| $TiO_2$ (5–6 nm) | 90 days | 2, 5, 10 mg/kg bw/day (m) | Chronic spleen injury and reduction of immune capacity | Sang *et al.*, 2012 |
| $TiO_2$ (5–6 nm) | 90 days | 10 mg/kg bw/day (m) | Ovarian damage, imbalance of mineral elements and sex hormones, decreased fertility/pregnancy rate and oxidative stress | Gao *et al.*, 2012 |
| $TiO_2$ (5–6 nm) | 90 days | 2, 5, 10 mg/kg bw/day (m) | Testicular lesions, spermatogenesis suppression, sperm malformations, and alterations in serum sex hormone levels | Gao *et al.*, 2013 |
| $TiO_2$ (5–6 nm) | 90 days | 2, 5, 10 mg/kg bw/day (m) | Deposition in ovary, fertility reduction and ovary injury associated with alteration of inflammation-related or follicular atresia-related | Zhao *et al.*, 2013 |

[a] Animal species: mice (m) or rats (r).

(Rossi et al., 2014)

# Awareness & Attitudes



# Consumers

- Limited knowledge

- Differences amongst EU

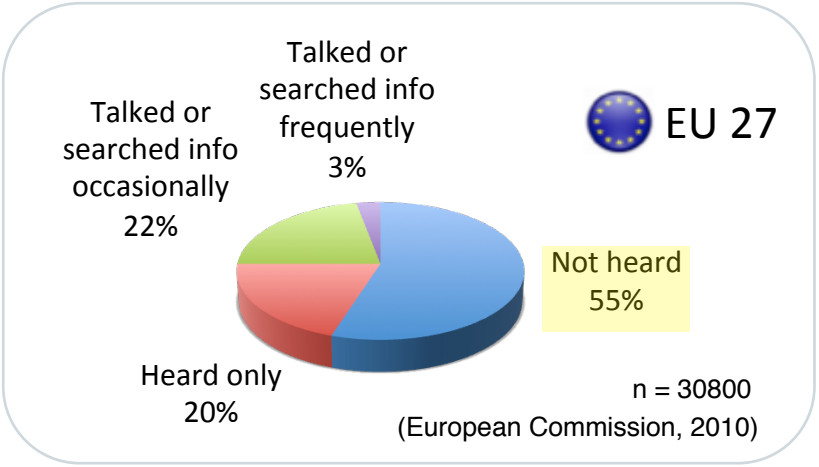
- Low concern

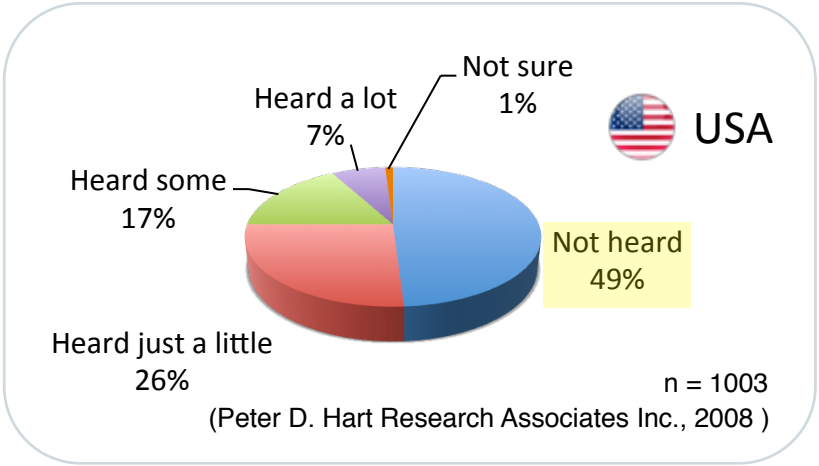
- Nano outside vs. inside

- Trust in food industries

# Consumers

- **Limited knowledge**
- Differences amongst EU
- Low concern
- Nano outside vs. inside
- Trust in food industries



# Consumers

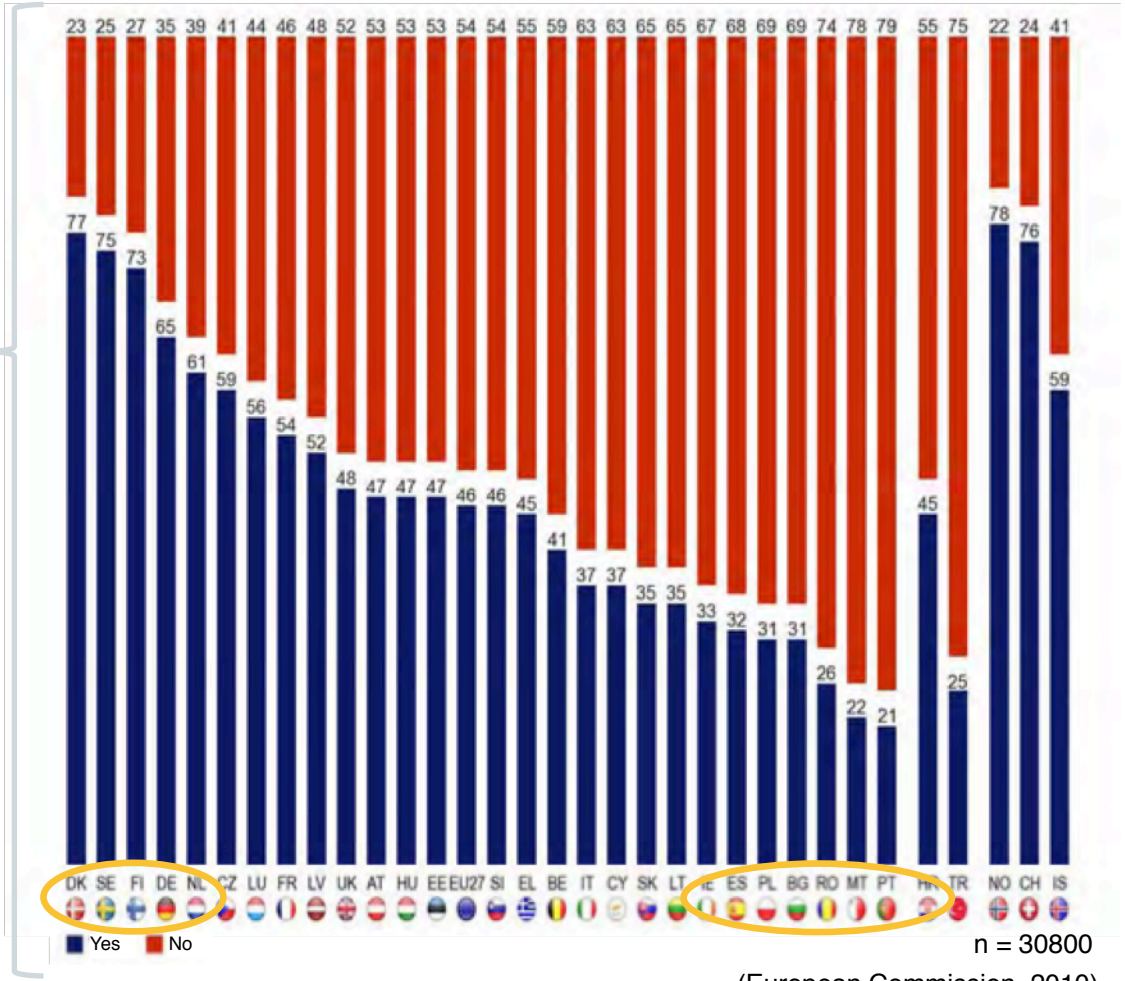
- Limited knowledge

- **Differences amongst EU**

- Low concern

- Nano outside vs. inside

- Trust in food industries

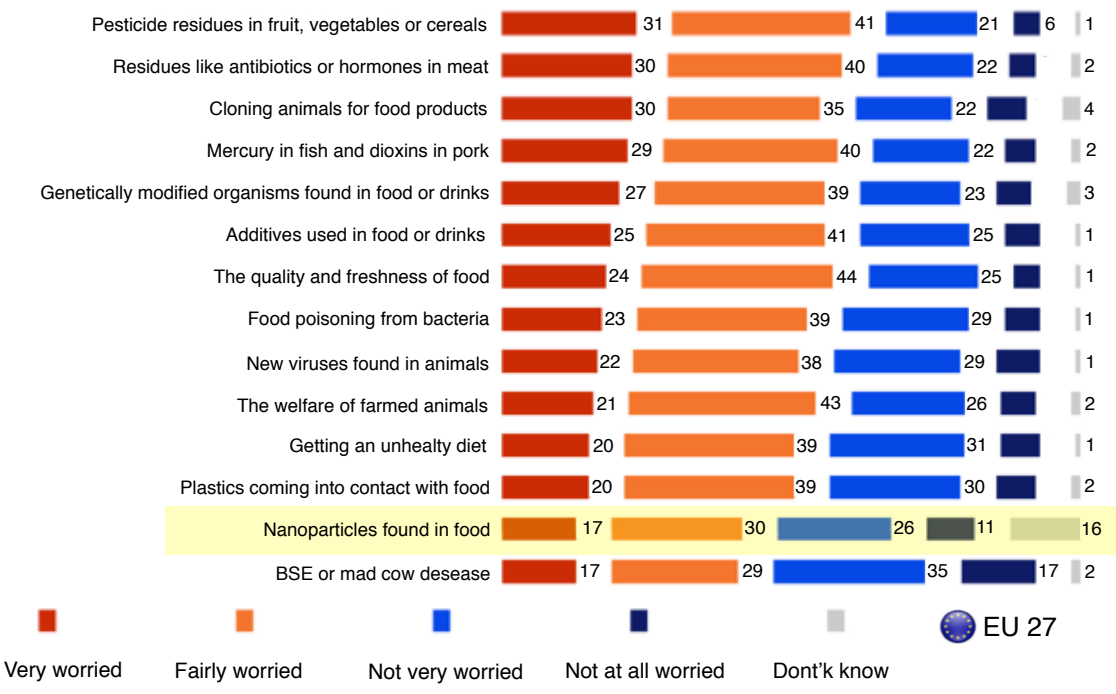



n = 30800

(European Commission, 2010)

# Consumers

- Limited knowledge
- Differences amongst EU
- **Low concern**
- Nano outside vs. inside
- Trust in food industries

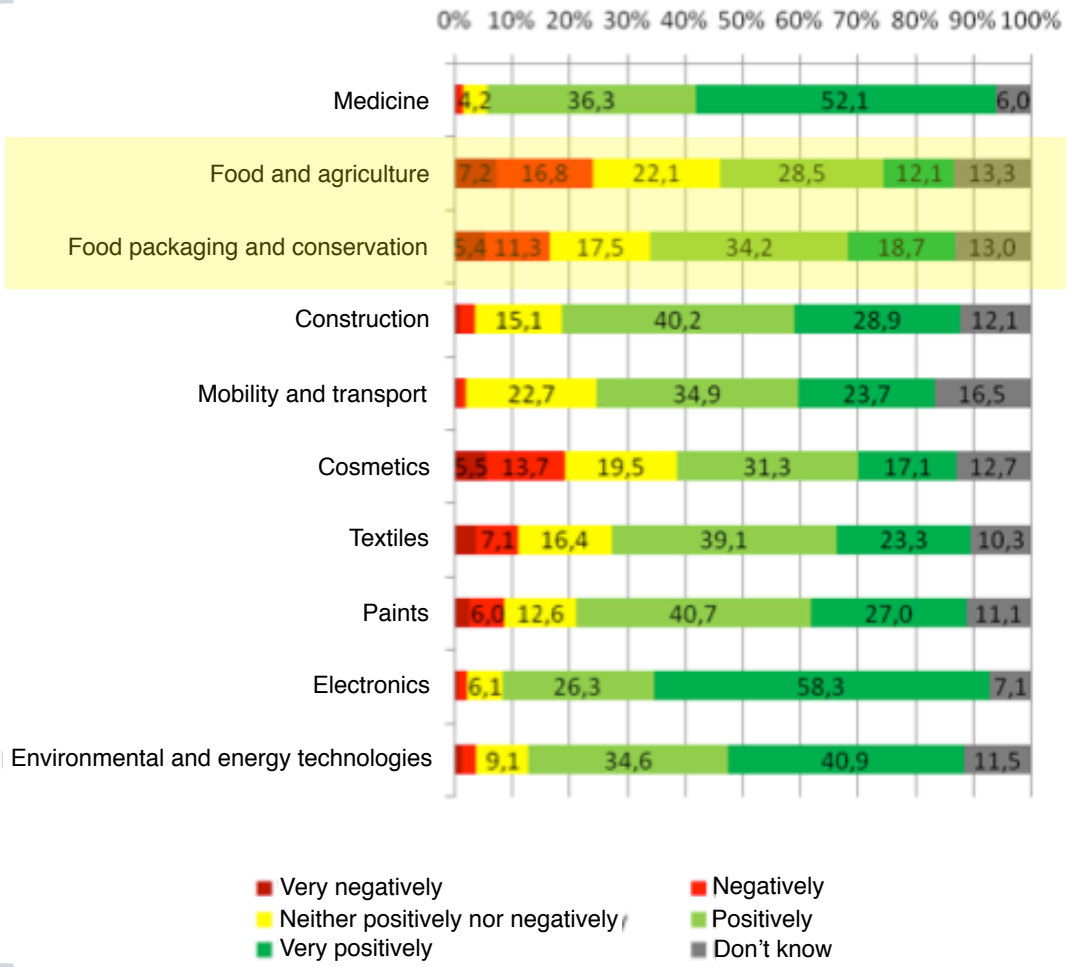



n = 26691

(European Commission, 2010)

# Consumers

- Limited knowledge
- Differences amongst EU
- Low concern
- **Nano outside vs. inside**
- Trust in food industries




n = 1500
(NanoDiode Project, 2014)

# Consumers

- Limited knowledge

- Differences amongst EU

- Low concern

- Nano outside vs. inside

- **Trust in food industries**

| | Food manufacturers | | |
|---|---|---|---|
| | Total 'Confident' | Total 'Not confident' | Don't know |
| EU27 | 35% | 62% | 3% |
| BE | 39% | 60% | 1% |
| BG | 27% | 67% | 6% |
| CZ | 51% | 47% | 2% |
| DK | 31% | 68% | 1% |
| DE | 22% | 76% | 2% |
| EE | 49% | 49% | 2% |
| EL | 18% | 82% | 0% |
| ES | 50% | 47% | 3% |
| FR | 25% | 72% | 3% |
| IE | 40% | 56% | 4% |
| IT | 38% | 56% | 6% |
| CY | 34% | 64% | 2% |
| LT | 26% | 73% | 1% |
| LV | 34% | 64% | 2% |
| LU | 30% | 69% | 1% |
| HU | 34% | 64% | 2% |
| MT | 31% | 65% | 4% |
| NL | 30% | 69% | 1% |
| AT | 51% | 46% | 3% |
| PL | 26% | 69% | 5% |
| PT | 54% | 41% | 5% |
| RO | 37% | 60% | 3% |
| SI | 37% | 62% | 1% |
| SK | 54% | 43% | 3% |
| FI | 64% | 34% | 1% |
| SE | 32% | 67% | 1% |
| UK | 42% | 55% | 3% |

n = 26691

(European Commission, 2010)

# Raw materials producers

| | YES | Currently NOT, but envisaged or under development | NO and not planned | Don't Know | Refuses to answer |
|---|---|---|---|---|---|
| Does your company produces or imports raw materials containing constituents with dimensions within 1nm and 100nm? | | | | | |
| | | | | | |
| Does your Company uses technological procedures designed to produce or exploit intentionally materials with typical properties of the nanoscale (1nm-100nm)? | | | | | |
| | | | | | |
| Would you be able to ensure the absence of manufactured, engineered or accidental nanomaterials in your products? | | | | | |
| **IF YES,** are you able to provide certificate or instrumental analysis wich confirm the absence? | | | | | |
| | | | | | |
| **IF YOU ARE USING NANOMATERIALS**, are you able to provide documentation relating the physico chemical characterization or the safety assessment of the material? | | | | | |
| **IF YES**, please report which document/s: | | | | | |
| | | | | | |
| Have you ever been questioned previously about the use or production of nanomaterials by customers, institutions, consumer organizations, press, private? | | | | | |
| **IF YES**, could you please report the category (i.e. Press, Customers) of the applicant/s: | | | | | |

# Raw materials producers

| | YES | Currently NOT, but envisaged or under development | NO and not planned | Don't Know | Refuses to answer |
|---|---|---|---|---|---|
| Does your company produces or imports raw materials containing constituents with dimensions within 1nm and 100nm? | 2 | / | 4 | / | 2 |
| Does your Company uses technological procedures designed to produce or exploit intentionally materials with typical properties of the nanoscale (1nm-100nm)? | / | / | 6 | / | 2 |
| Would you be able to ensure the absence of manufactured, engineered or accidental nanomaterials in your products? | 3 | 1 | / | 1 | 3 |
| **IF YES,** are you able to provide certificate or instrumental analysis wich confirm the absence? | / | 1 | 2 | / | 3 |
| **IF YOU ARE USING NANOMATERIALS**, are you able to provide documentation relating the physico chemical characterization or the safety assessment of the material? | 2 | / | / | / | 3 |
| **IF YES**, please report which document/s: | Answer 1: Silicon dioxide (E 551) permitted as food additive according to 1333/2008/EC<br>Answer 2: Association of synthetic amorphous silica producers | | | | |
| Have you ever been questioned previously about the use or production of nanomaterials by customers, institutions, consumer organizations, press, private? | 5 | / | / | / | 3 |
| **IF YES**, could you please report the category (i.e. Press, Customers) of the applicant/s: | **Customers** | | | | |

# Food Companies

Mondelēz International

*"Currently we're not using nanotechnology. But we need to understand the potential of this technology…especially regarding packaging materials"*

# Food Companies

Mondelēz International

Coca-Cola

*"Currently we're not using nanotechnology. But we need to understand the potential of this technology…especially regarding packaging materials"*

# Food Companies

Mondelēz International

Coca-Cola

*"We believe that there is considerable potential for nanotechnology applications… decision to apply in our products will be taken on the basis of safety evaluations and regulations"*

Unilever

# Food Companies

Mondelēz International

Coca-Cola

***2012**: "We monitor all nanotechnologies developments…We make limited use of NMs in packaging"*
***2014**: NO STATEMENT*

Unilever

Nestlé

# Food Companies

Mondelēz International

Coca-Cola

***2012**: "We monitor all nanotechnologies developments…We make limited use of NMs in packaging"*
***2014**: NO STATEMENT*

Unilever

Kellogg's®

Nestlé

# Food Companies

Mondelēz International

Coca-Cola

McDonald's

***2011**: "We are working to understand NMs and their application …but actually we do not support their use"*
***2015**: NO STATEMENT*

Unilever

Kellogg's

Nestlé

# Case history 1

## Titanium Dioxide (E171)





# Case history 1

## Titanium Dioxide (E171)

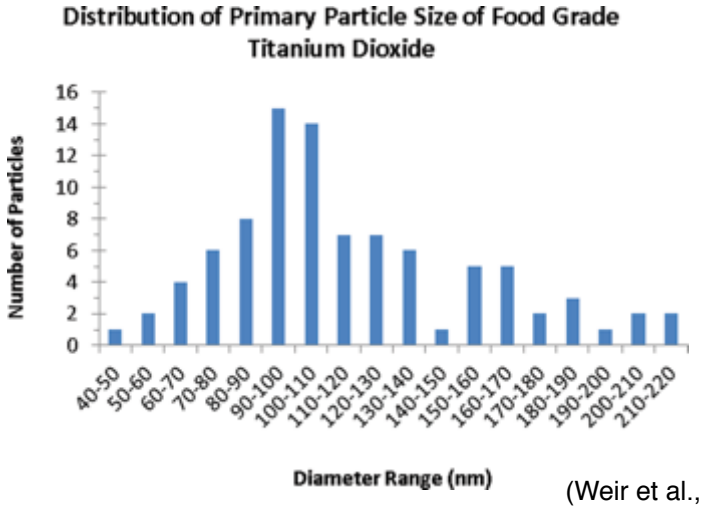




ENVIRONMENTAL Science & Technology
Article
pubs.acs.org/est

**Titanium Dioxide Nanoparticles in Food and Personal Care Products**

Alex Weir,[†] Paul Westerhoff,*[,†] Lars Fabricius,[‡,§] Kiril Hristovski,[∥] and Natalie von Goetz[‡]




(Weir et al., 2012)

# Case history 1

AS YOU SOW

## ARE NANOMATERIALS IN OUR FOODS?

Whether and to what degree nanomaterials are currently in our foods remains a murky issue. A study by American, Swiss, and Norwegian researchers entitled *Titanium Dioxide Nanoparticles in Food and Personal Care Products* estimates and quantifies the human exposure resulting from nanoparticle sized titanium dioxide ($TiO_2$) found in processed foods.[6] The study measured nanoparticles in food-grade $TiO_2$ and derived estimates of nano $TiO_2$ in foods including M&M's, Betty Crocker Whipped Cream Frosting, Jell-O Banana Cream Pudding, Mentos, Trident and Dentyne gums, Vanilla Milkshake Pop Tarts, and Nestlé Original Coffee Creamer. The authors state that "electron microscopy and stability testing of food-grade $TiO_2$ [...] suggests that approximately 36% of the particles are less than 100nm in at least one dimension."

# Case history 1

AS YOU SOW

## Donut Products Tested for $TiO_2$

Two of the donut products in which titanium concentrations were found—Hostess Donettes and Dunkin' Donuts Powdered Cake Donut-were subsequently tested for the presence of nanoparticle sized titanium dioxide. Titanium dioxide materials of less than 10 nm were found in both of the donuts tested, as set forth in more detail below. While there are varying definitions of what constitutes a nanoparticle, our testing assessed a conservative particle size of less than 10 nm. The test results underscore that the low-end of the nanoparticle-sized spectrum (<10 nm) titanium dioxide is present in our food supply.

DUNKIN' DONUTS®

AMERICA RUNS ON DUNKIN

| Product | $TiO_2$ Listed as Ingredient | Total Ti PPM |
|---|---|---|
| Conchitas – Fine Pastry | | Not Detected |
| Dolly Madison – Donut Gems | • | 58 |
| Dunkin' Donuts – Powdered Cake Donut | • | 19 |
| Entenmann's – Pop'ems Donuts | | 73 |
| Hostess Brand – Donettes | • | 75 |
| Kroger – Sugared Cake Donut Holes | • | 43 |

# Case history 1

theguardian
Winner of the Pulitzer prize 2014

## Dunkin' Donuts to remove titanium dioxide from donuts

The baked goods giant says it will remove whitening agent from its powdered donuts over fears it might contain toxic nanomaterials

Food Safety News
Breaking news for everyone's consumption

## Dunkin' Donuts Plans to Phase Out Whitening Agent

...Y NEWS DESK | MARCH 10, 2015

...response to a shareholder request, the parent company of Dunkin' Donuts is reportedly testing alternatives to ...anium dioxide as a whitening agent in the powdered sugar used to top some of its doughnuts.

...mitting the request was the group As You Sow, a non-profit foundation based in Oakland, CA, which focuses ...nvironmental and social corporate responsibility issues. According to a March 5 statement on its website, the ... has withdrawn the request in response to the commitment from Canton, MA-based Dunkin' Brands Group

...a groundbreaking decision. Dunkin' ...onstrated strong industry ... ...ving this pot...

CNN Money Business Markets Tech Personal Finance Small Business Luxury

## Dunkin' Donuts to remove titanium dioxide from donuts

# Case history 1

## Titanium Dioxide (E171)

| Product | OLD Ingredient list | NEW Ingredient list |
|---|---|---|
|   | (2013) Edulcoranti: xilitolo (30%), sorbitolo, mannitolo, sciroppo di maltitolo, aspartame; gomma base, fosfato dicalcico diidrato (6,9%) aromi, stabilizzante: glicerolo), **coloranti (E171), carminio,** addensanti: gomma arabica, E466, maltodestrine, amido di mais, emulsionanti lecitine (SOIA) olio vegetale, fluoruro di potassio, agente di rivestimento (cera di carnauba), antiossidante: E320. | (2015) Edulcoranti: xilitolo (30%), sorbitolo, mannitolo, sciroppo di maltitolo, aspartame; gomma base, fosfato dicalcico diidrato (6,9%), aromi, maltodestrine, stabilizzante: glicerolo; addensanti: gomma arabica, E466; emulsionanti: lecitine (SOIA), E473; fluoruro di potassio, agente di rivestimento: cera di carnauba, antiossidante: E321. |
|   | (2013) Sweeteners (xylitol, maltitol, mannitol, sorbitol, maltitol syrup, aspartame, acesulfame K, sucralose), base gum, thickener (arabic gum, E466), flavourings, maltodextrin, stabilizer (glycerol), **colourings (E171, E133)**, corn starch, vegetable oil, emulsifier (soy lecithin), coating agent (carnauba wax), antioxidant (E320). | (2015) Sweeteners (xylitol, maltitol, mannitol, sorbitol, maltitol syrup, aspartame, acesulfame K, sucralose), base gum, maltodextrin, thickener (arabic gum, E466), flavourings, stabilizer (glycerol), emulsifier (soy lecithin, E473), palm kernel oil, **colourings (E133)**, antioxidant (E321). |
|   | (2013) Sweeteners (xylitol, sorbitol, mannitol, maltitol syrup, maltitol, aspartame, acesulfame K, sucralose), gum base, stabilizer (glycerol), flavourings, thickening agents (gum arabic, xanthan gum), **colours (titanium dioxide, brilliant blue FCF)**, emulsifier (soy lecithin), green tea extract (0.1%), glazing agent (carnauba wax), antioxidant (E320). | (2015) Sweeteners (xylitol, mannitol, sorbitol, maltitol syrup, maltitol, aspartame, acesulfame K, sucralose), gum base, stabilizer (glycerol), flavourings, maltodextrine, thickening agents (gum arabic, E466, E451), emulsifier (soy lecithin, E473), green tea extract (0.1%), **colours (E133),** glazing agent (carnauba wax), antioxidant (E320). |

# Case history 1

## Titanium Dioxide (E171)

| Product | OLD Ingredient list | NEW Ingredient list |
|---|---|---|
|   | (2007) Sweetener: sorbitol, isomalt, mannitol, xylitol, maltitol syrup, aspartame, acesulfame K, gum base, thickener: arabic gum, liquorice extract, flavouring, stabiliser: glycerol**; colouring: E171, E104, E133,** emulsifier: soy lecithin, coating agent: carnauba wax, antioxidant: E320. | (2015) Sweetener: sorbitol, isomalt, mannitol, maltitol syrup, xylitol, aspartame, acesulfame K, gum base, thickener: arabic gum, E466; flavouring, stabiliser: glycerol, liquorice extract, vegetable oil (palm kernel), maltodextrine, emulsifier: soy lecithin, E473, **colouring: curcumine, E133**; coating agent: carnauba wax, antioxidant: E321. |
|   | (2007) Sweeteners: maltitol, sorbitol, mannitol, maltitol syrup, aspartame, acesulfame-k; gum base, stabiliser: glycerol; flavouring, fruit juice: lemon (3%); acidifier: malic acid, citric acid, tartaric acid; food gelatine, **colouring: E110, E171, E120, E104, E131**; thickener: arabic gum, E466; vegetable extracts, emulsifier: soya lecithin; E473; coating agent: carnauba wax; antioxidant: E320 | (2015) Sweeteners: isomalt, maltitol, maltitol syrup, sorbitol, aspartame, acesulfame-k, sucralose; gum base, fruit juice: strawberry, lemon (3%), stabiliser: glycerol; acidifier: malic acid, citric acid, maltodextrine, thickener: arabic gum, E415; flavouring, vegetal oil (palm, palm kernel), emulsifier: soya lecithin, E473; vegetable extracts (paprika), **colouring (carmine, curcumin, E133)**; coating agent: carnauba wax; antioxidant: E321. |
|   | (2002) Sweetener (xylitol, sorbitol, mannitol, maltitol syrup, aspartame, acesulfame-K), gum base, thickener (arabic gum), stabiliser (glycerol), flavouring, **colouring (E171)**, sodium bicarbonate, coating agent (carnauba wax), antioxidant (E320). | Sweetener (xylitol 25%, sorbitol, mannitol, maltitol syrup, aspartame, acesulfame-K), gum base, flavouring, thickener (arabic gum), stabiliser (glycerol), **colouring (E171)**, sodium bicarbonate (0.4%), emulsifier (soy lecithin), coating agent (carnauba wax), antioxidant (E320). |

# Case history 2

## Silicon Dioxide (E551)

MARS food

US005741505A

**United States Patent** [19]

**Beyer et al.**

[11] **Patent Number: 5,741,505**

[45] **Date of Patent: Apr. 21, 1998**

[54] **EDIBLE PRODUCTS HAVING INORGANIC COATINGS**


[75] Inventors: **Daniel L. Beyer**; **Theodore E. Jach**, both of Netcong, N.J.; **Dennis L. Zak**, Doylestown, Pa.; **Ralph A. Jerome**, Blairstown, N.J.; **Frank P. DeBrincat**, Tobyhanna, Pa.

[73] Assignee: **Mars, Incorporated**, McLean, Va.



[21] Appl. No.: **376,029**

[22] Filed: **Jan. 20, 1995**

[51] **Int. Cl.**[6] ..... **A61K 47/00**

[52] **U.S. Cl.** ..... **424/439**; 424/474; 426/94;



| | | | |
|---|---|---|---|
| 5,298,273 | 3/1994 | Ito | 426/549 |
| 5,328,705 | 7/1994 | Wilhoit et al. | 426/113 |

FOREIGN PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| 43-71016507 | 6/1968 | Japan . | |

OTHER PUBLICATIONS

J.J. Kester and O.R. Fennema, "Edible Films and Coatings: A Review", *Food Technology*, pp. 49–59 (Dec. , 1986).

Ratner et al., "Plasma Deposition and Treatment for Biomaterial Applications", *Plasma Deposition, Treatment and Etching of Polymers*, Academic Press, San Diego, pp. 465–515 (1990).

Greener and Fennema, "Evaluation of Edible, Bilayer Films for Use as Moisture Barriers for Food", *Journal of Food Science*, vol. 54, No. 6, pp. 1400–1406 (1989).

# Case history 2

## Silicon Dioxide (E551)

MARS food

[57] **ABSTRACT**

An edible product having a thin inorganic coating on at least a portion of its surface. The coating preferably forms a moisture/oxygen barrier to result in a coated edible product having an improved shelf-life. The edible products include foods and pharmaceuticals. The inorganic materials used for the coating include $SiO_2$, SiO, MgO, CaO, $TiO_2$, ZnO and MnO. Processes and apparatuses for depositing a thin film of inorganic material onto an edible substrate are also disclosed. The preferred processes include sputtering and vapor deposition. The preferred apparatus provides for the continuous production of coated edible products.

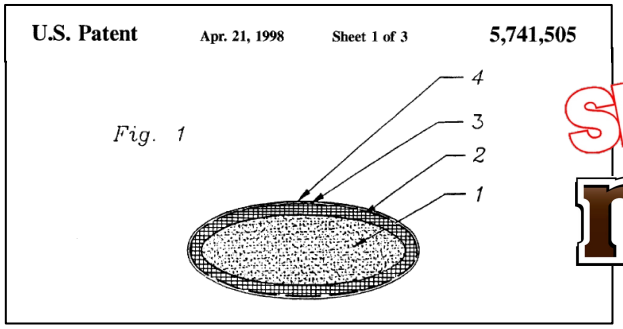

U.S. Patent Apr. 21, 1998 Sheet 1 of 3 5,741,505

Fig. 1



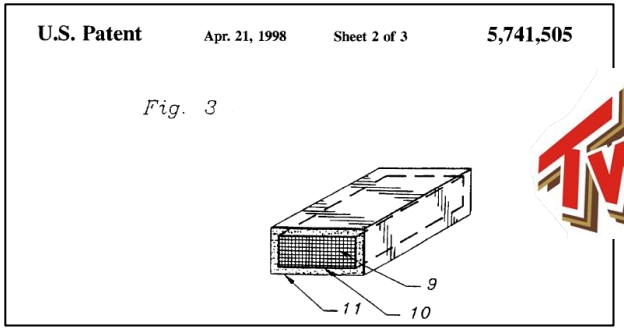

U.S. Patent Apr. 21, 1998 Sheet 2 of 3 5,741,505

Fig. 3



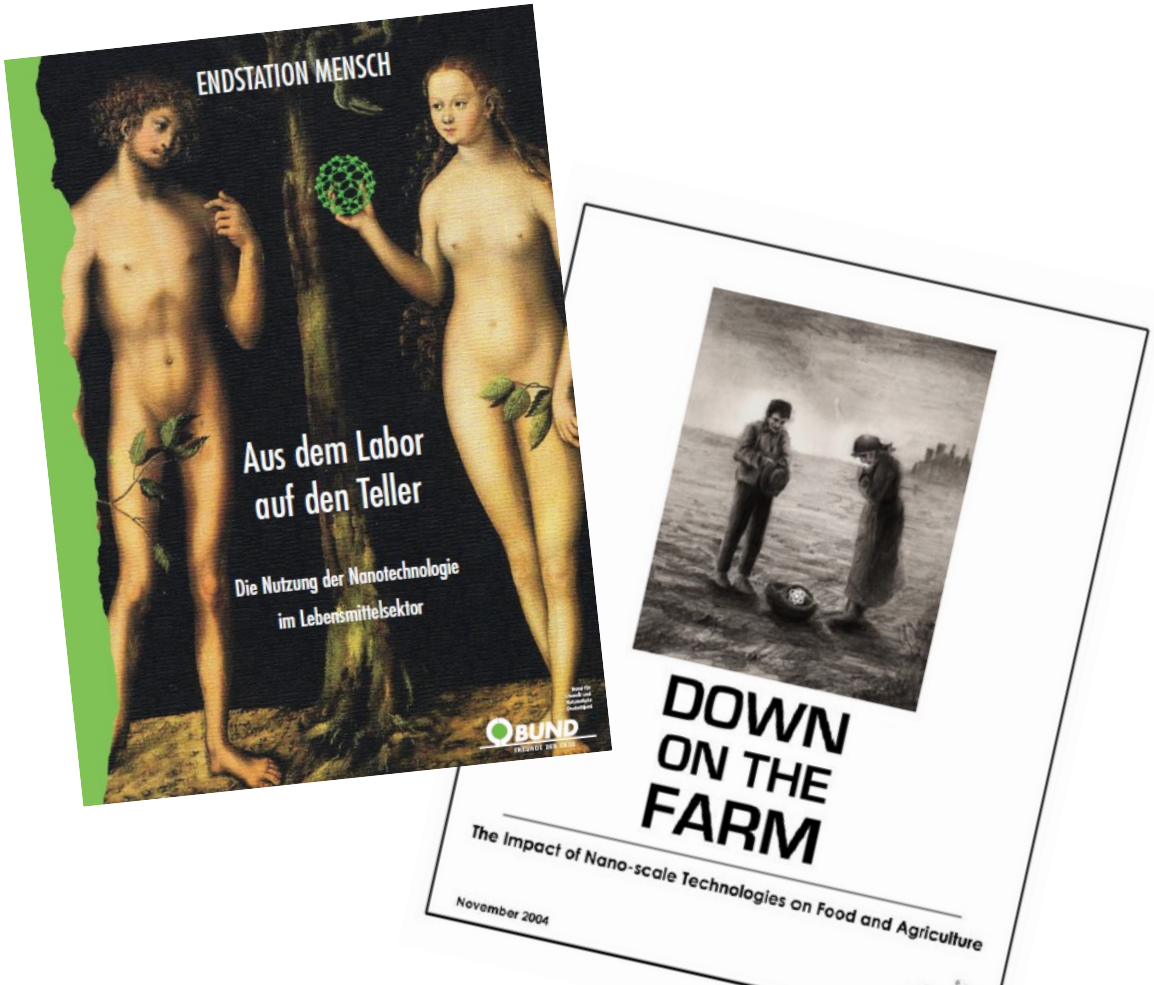
Skittles

m&m's

TWIX

# Case history 2

## Silicon Dioxide (E551)




*"This technique is no longer used and the patent is to be phased out in different Countries and will not be renewed"*

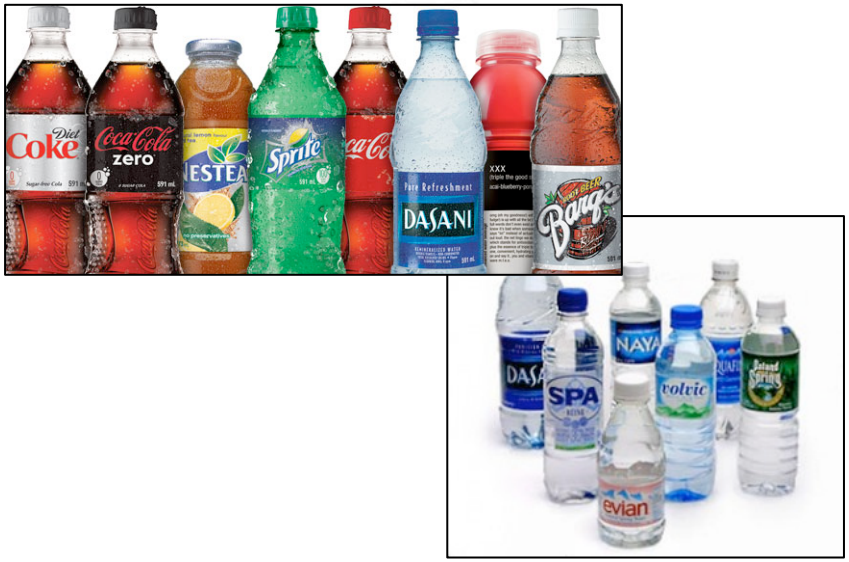
Mars Inc. 2007

# Case history 3

## Food Packaging

## PLASTIC MATERIALS

YES

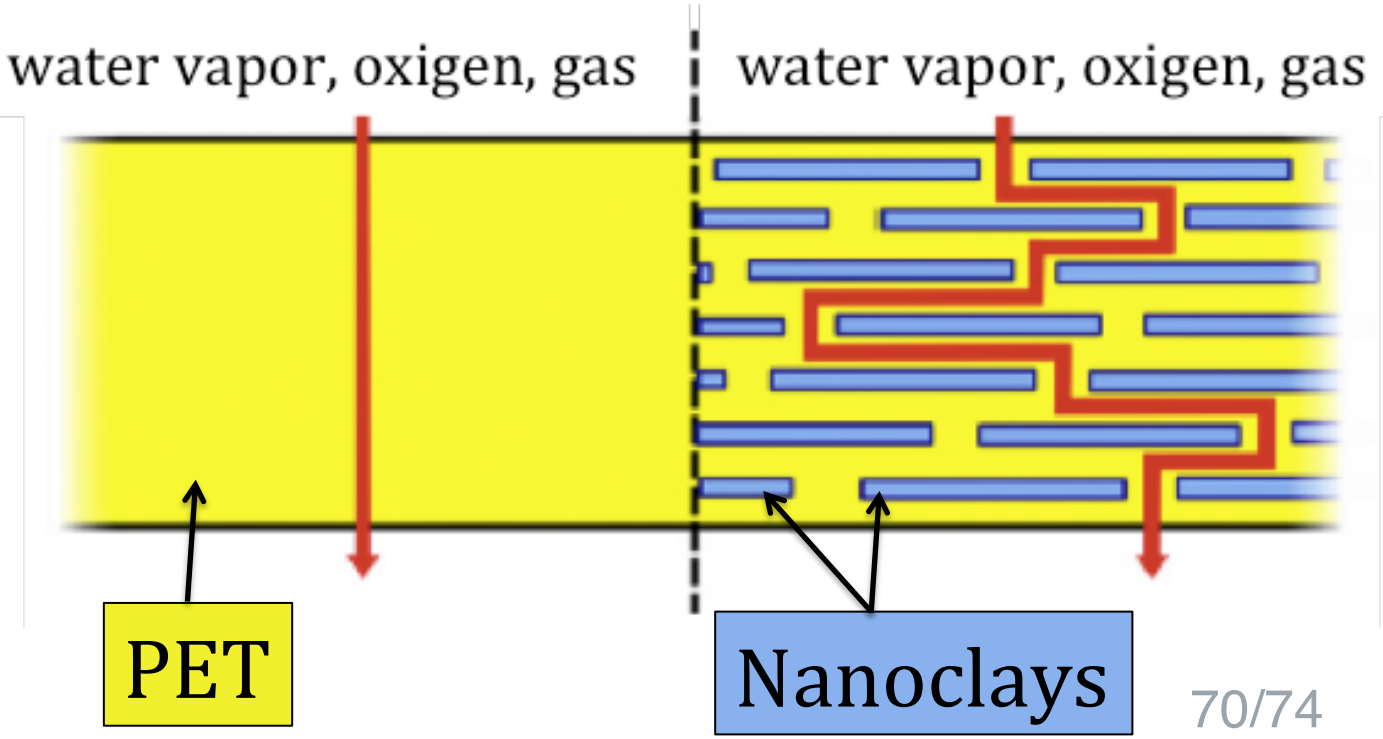



NO


# Case history 3

## Food Packaging

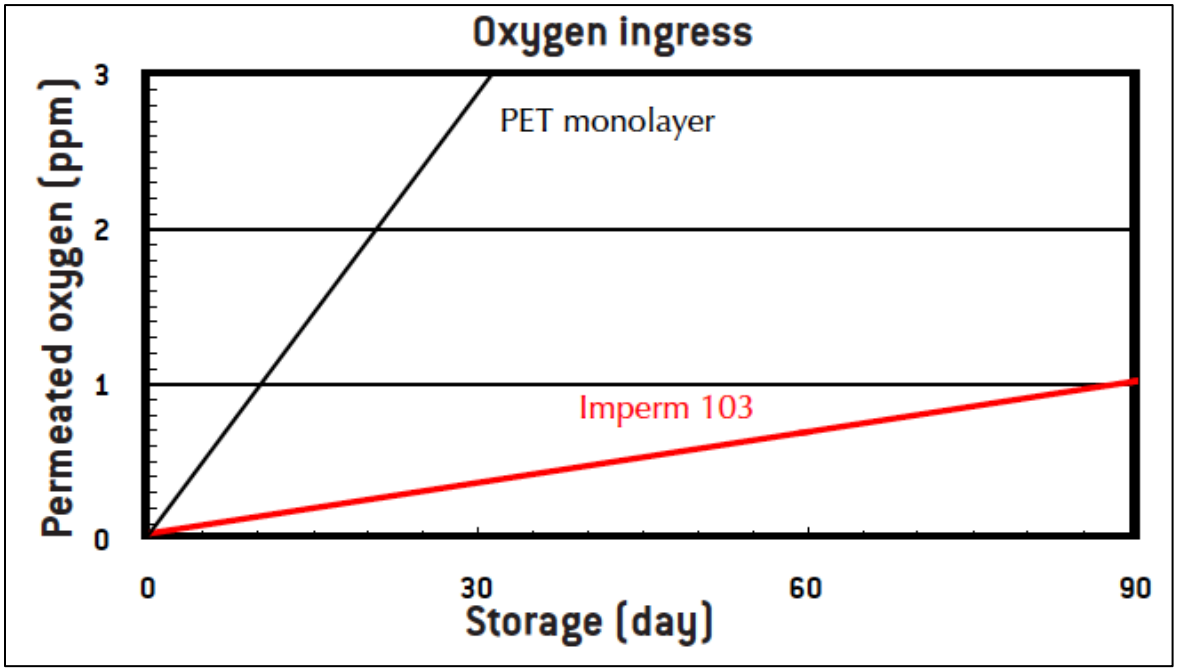
IMPERM®



# Case history 3

## Food Packaging

IMPERM®




(Nanocor technical bulletin, 2015)

# Case history 3

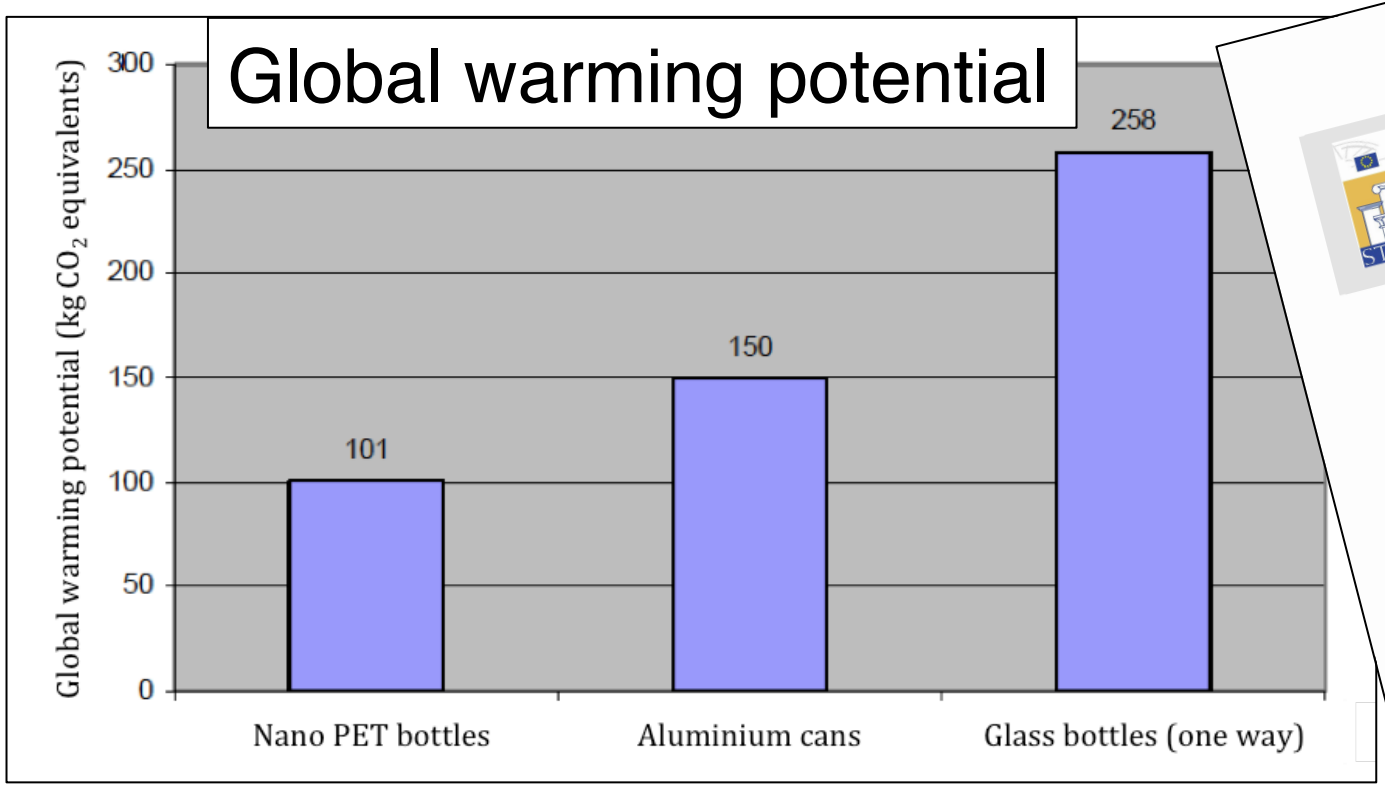

*"Our new plastic bottle ensures **product integrity** and **drinkability**.*
*This plastic bottle achieves the same **4-month shelf-life** and keeps the beer as fresh as glass or aluminum.*
*We're proud that Miller is the first U.S. brewer to solve the plastics puzzle."*

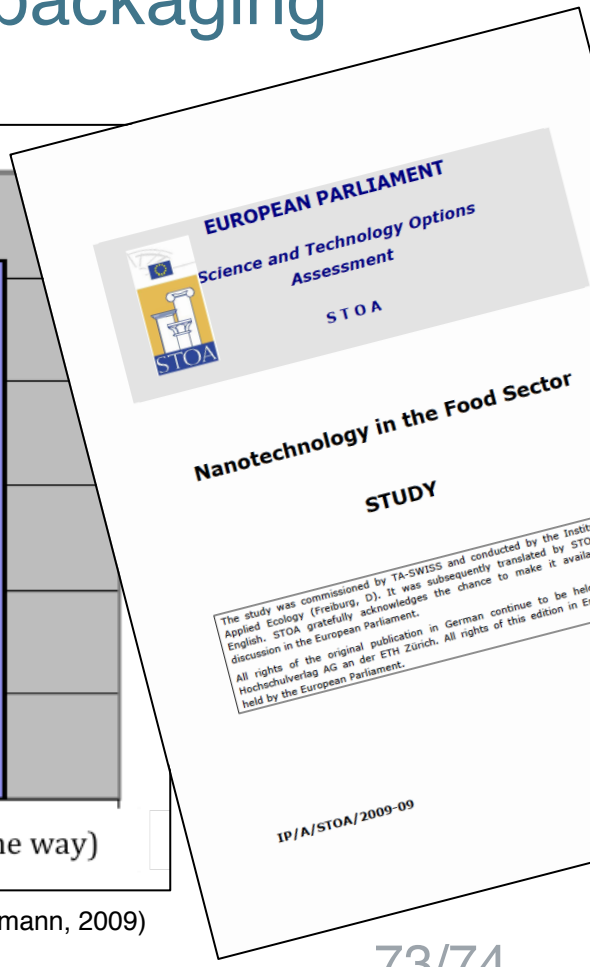
*Miller's executive vice president*
*Virgis Colbert*

(PRNewsWire, 2006)

# Case history 3

## “Ecological relevance analysis of packaging”




(Möller, Eberle, Hermann, Moch, & Stratmann, 2009)

# Conclusions

- Evolving scenario

- Regulation is likely to be upgraded

- Limited awareness (for the moment)

- Acceptance nano outside >>> inside

- Trust in industries can play a key role

# Conclusions

*THUS…*

- Keep an eye on **regulation updates** (i.e. 257/10)

- Be prepared to **stakeholders' questions** and request of **Certifications** and Policies

- Monitor raw materials **suppliers** and internal activities which may represent a risk

- Follow the development of viable applications (i.e. **packaging**)

# Thank you for your attention!

SOREMARTEC

food science, technology and human nutrition
MASTER UNIVERSITARIO DI SECONDO LIVELLO - MICHELE FERRERO
scienza e tecnologia dell'alimentazione e nutrizione umana