



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

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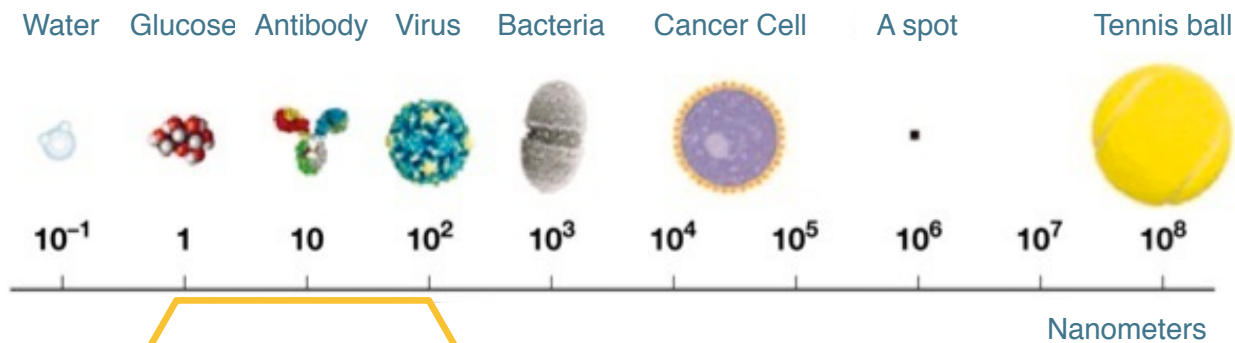
Aim of the work

Give an overview of nanotechnologies within the food sector concerning:

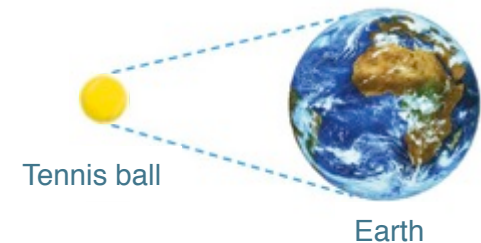
- Definition & Legislation
- Applications
- Risk Assessment
- Awareness and Attitudes

In order to support the company in an appropriate orientation.

Definition & Legislation



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

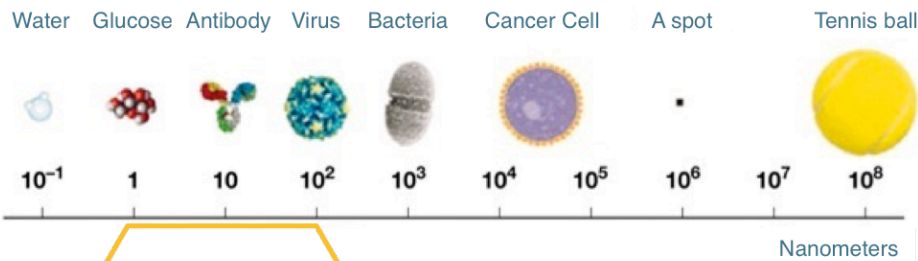


Nanodevices:



Liposome Nanoparticles Nanoshell

Definition & Legislation



Nanodevices:



Possible change of....

- Chemical reactivity
- Morphology
- Biopersistence
- Solubility
- Bioactivity



Definition & Legislation

European Commission Recommendation 696/2011:

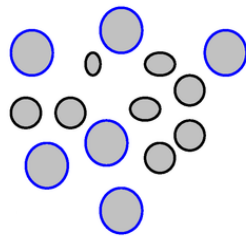
*“Nanomaterial means a **natural, incidental** or **manufactured** material containing particles,*

*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**.”*

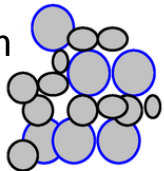
Definition & Legislation

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

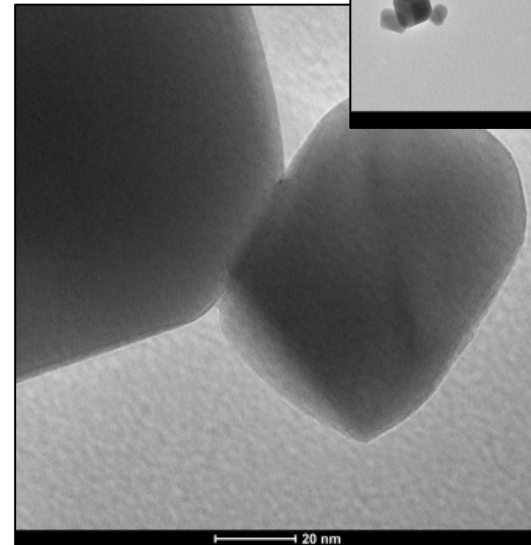
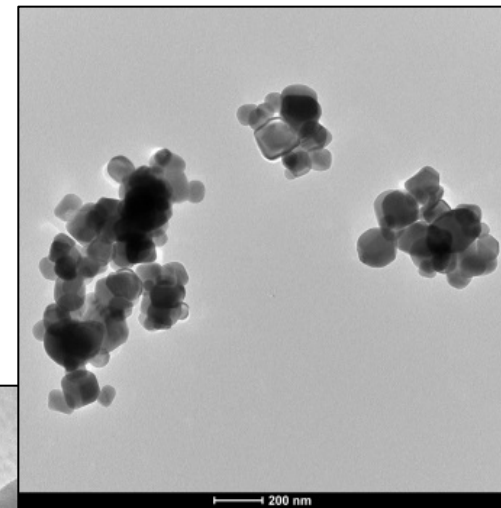
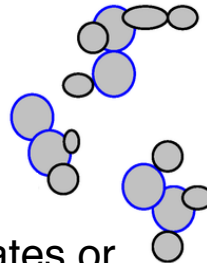


Primary
nanoparticles
5-20 nm

Aggregate
(chemically
bound)
30-200 nm

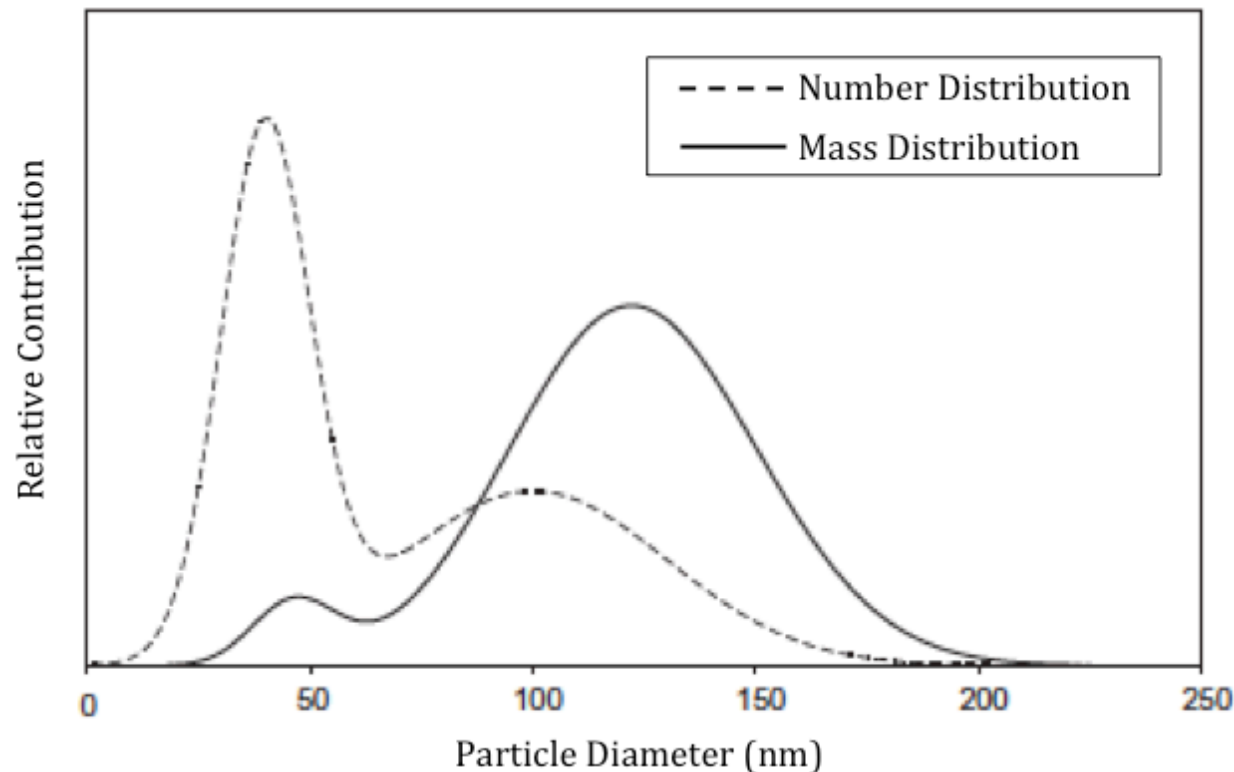


Weak Agglomerates or
Floculates 1-100 μm



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:

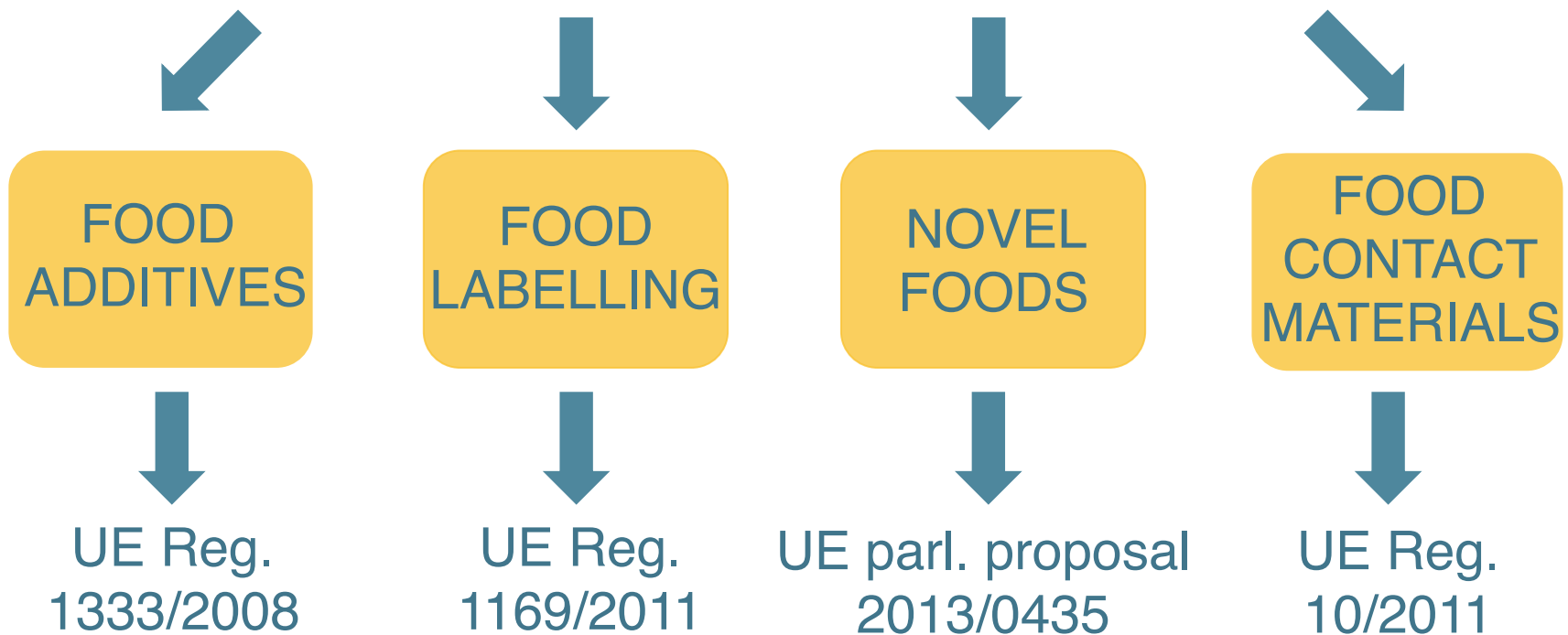
“the surface area divided by the mass of the relevant phase, when the area of the interface between two phases is proportional to the mass of one of the phases” (IUPAC, 1972)

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



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".				



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 Commission itself released the 346/89 corrigendum which **nullled and voided** the publication.

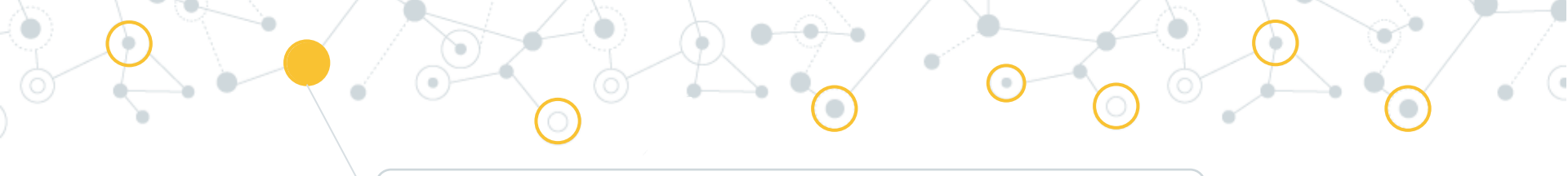


Definition & Legislation

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)

TiO₂, Ag, Au, Fe oxides within 31/12/2015

SiO₂ 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 Journal 2012;10(3):2641

SCIENTIFIC OPINION

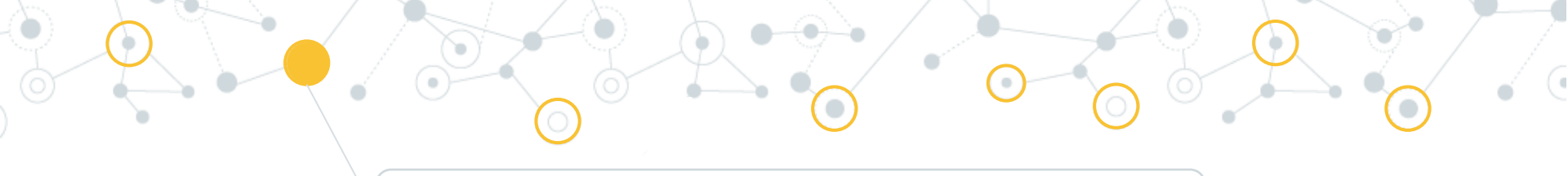
Scientific Opinion on the safety evaluation of the substance, titanium nitride, nanoparticles, for use in food contact materials¹

**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

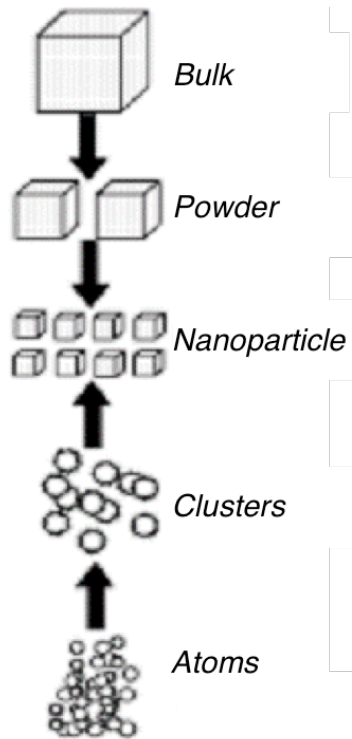
**Intentional
Production**

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

Nanoencapsulates

SiO₂

TiO₂

Top Down

Bottom up



Production & Applications

FOOD INGREDIENTS:

Nanoemulsions

Top Down

Bottom up

Nanoencapsulates



Production & Applications

FOOD INGREDIENTS:

Nanoemulsions

Nanoencapsulates

Top Down

Bottom up



Production & Applications

FOOD INGREDIENTS:

Nanoemulsions

Nanoencapsulates

Top Down

Bottom up

SiO_2

TiO_2



Production & Applications

FOOD CONTACT MATERIALS:



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 materials¹

EFSA Panel on food contact materials, enzymes,
flavourings and processing aids (CEF)^{2,3}

TiN

Nanoclays

TiO₂

Ag

Top Down

Bottom up



Production & Applications

FOOD CONTACT MATERIALS:

TiN

Top Down

Nanoclays



Bottom up

TiO₂

Ag

Production & Applications

FOOD CONTACT MATERIALS:

TiN

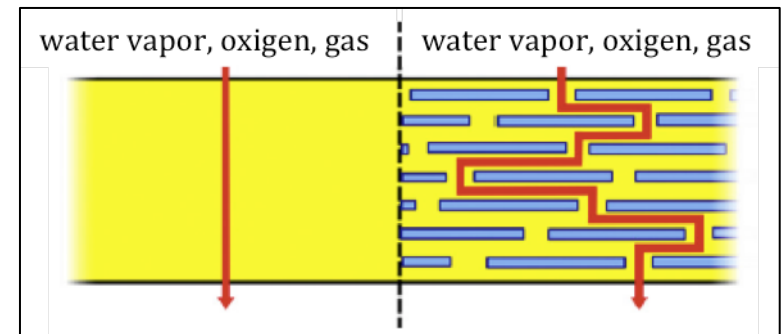
Top Down

Nanoclays

Bottom up

TiO₂

Ag



Production & Applications

FOOD CONTACT MATERIALS:

TiN

Top Down

Nanoclays

Bottom up

TiO_2

Ag



Production & Applications

FOOD CONTACT MATERIALS:

TiN

Top Down

Nanoclays

Bottom up

TiO₂

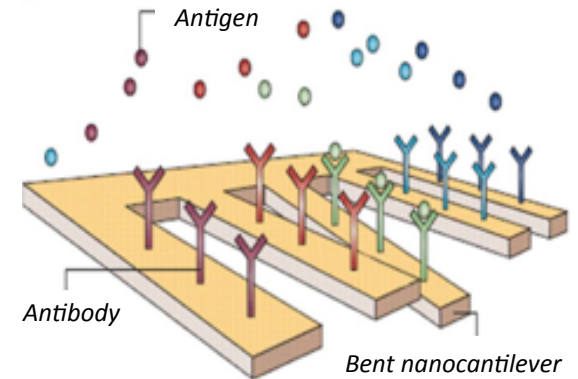
Ag



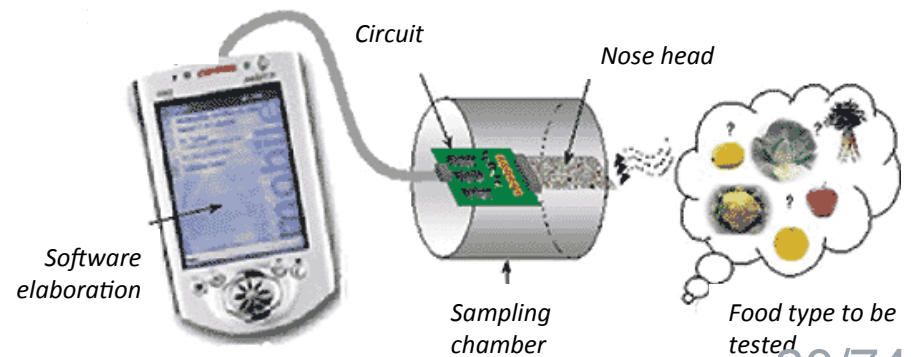
Production & Applications

FOOD PROCESSING:

Nanocantilevers



Electronic nose/tongue

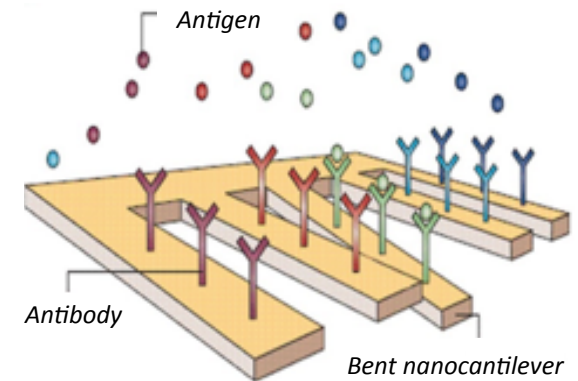


Production & Applications

FOOD PROCESSING:

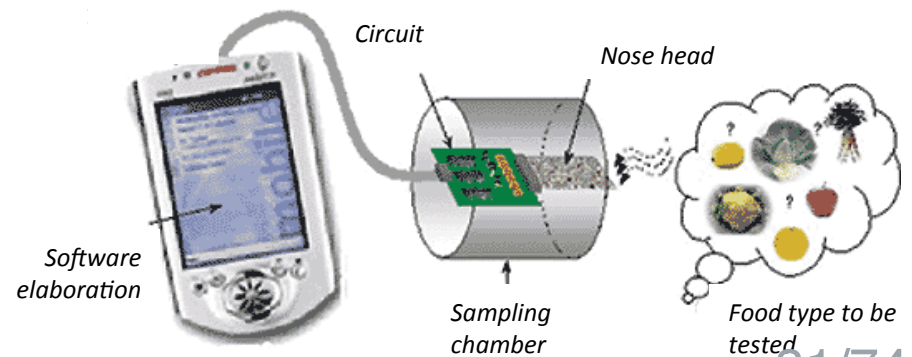
Top Down

Nanocantilevers

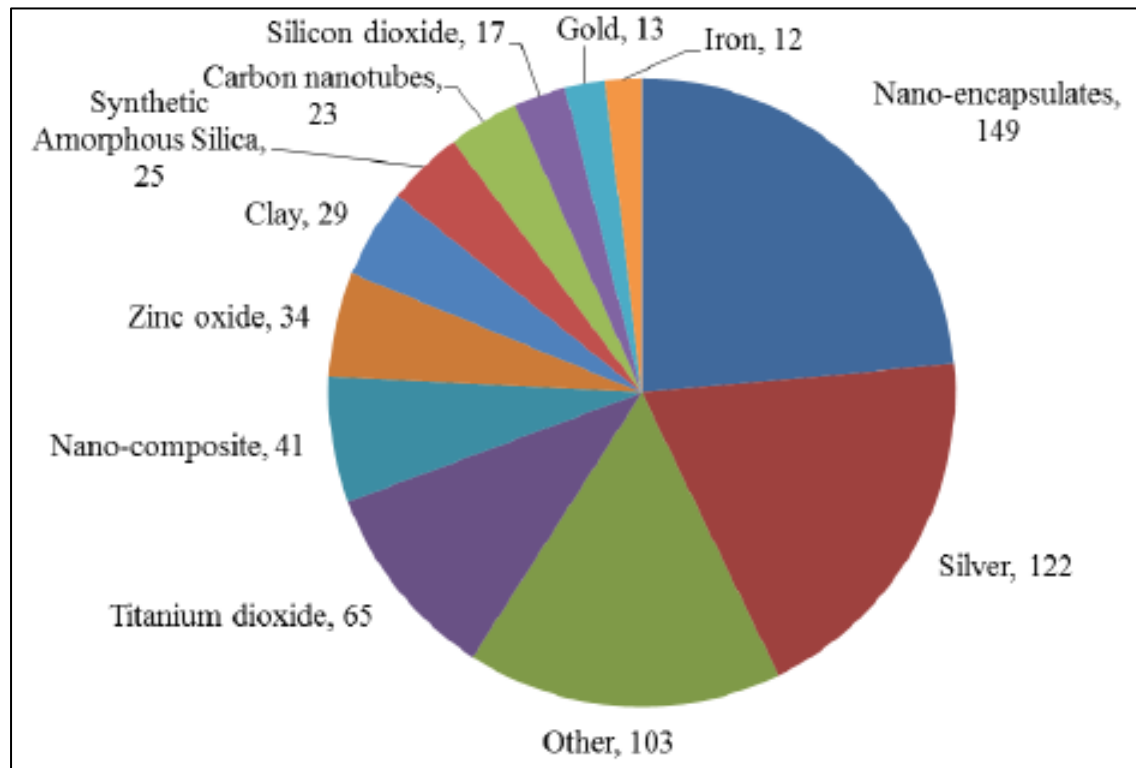


Bottom up

Electronic nose/tongue



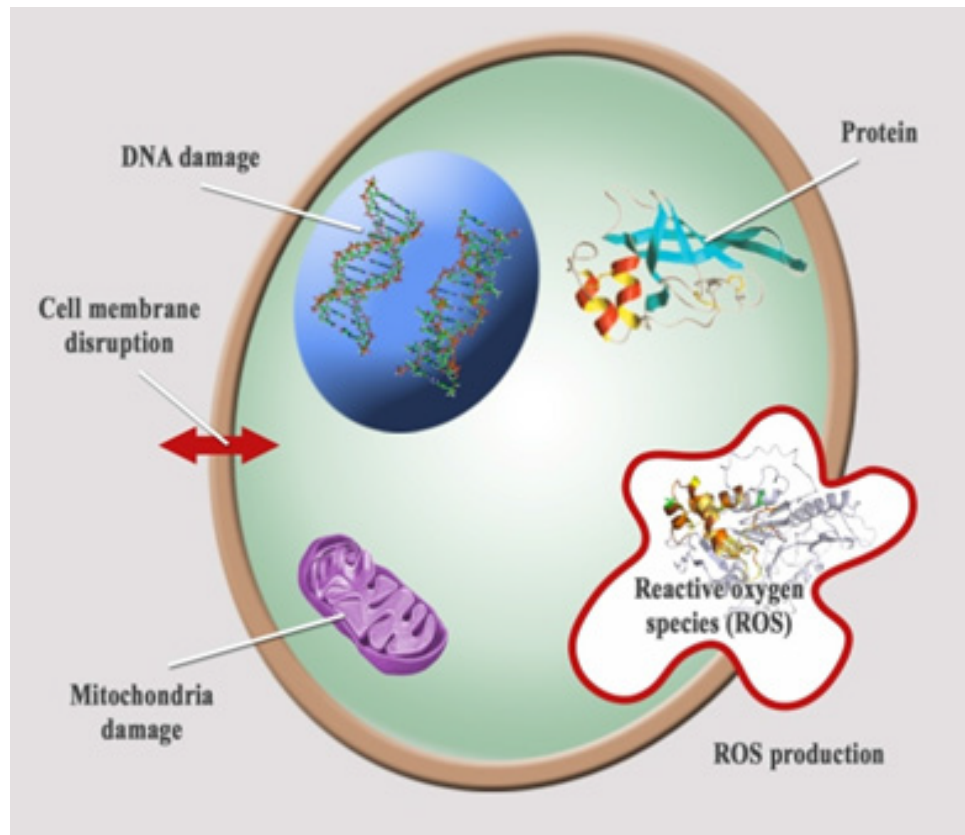
Production & Applications



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

Risk Assessment

Mechanism of toxicity of nanomaterials





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 activity ^b	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. 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 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 methods ^b - e.g. TEM, SEM, STEM, AFM, STXM. Separation methods: Flow separation, chromatography methods – e.g. FFF, HDC, SEC, RP/NP-HPLC; DMA/IMS (ultra)Centrifugation methods. Spectroscopy methods – e.g. XRD (for crystal size, crystallite size) Light (laser) scattering methods ^c – 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 methods ^c (for dispersions). Particle concentration (in pure dry powders) may also be calculated from particle size, mass concentration and density of the material. 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



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 Chromatography; IMS: Ion Mobility Spectroscopy; LDE: Laser Doppler Electrophoresis; MALS: Microwave Absorption Line-Spectra; NTA: Nanosecond Transient Absorption; OES: Optical Emission Spectroscopy; PCCS: Photo Cross Correlation Spectroscopy; SAXS: Small-Angle X-ray Scattering; SEC: Size Exclusion Chromatography; 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	+	+	++	—	++
<i>In-situ</i> measure	—	—	+	++	++
Ease of use	—	—	+	++	+
Cost	—	—	++	+++	+

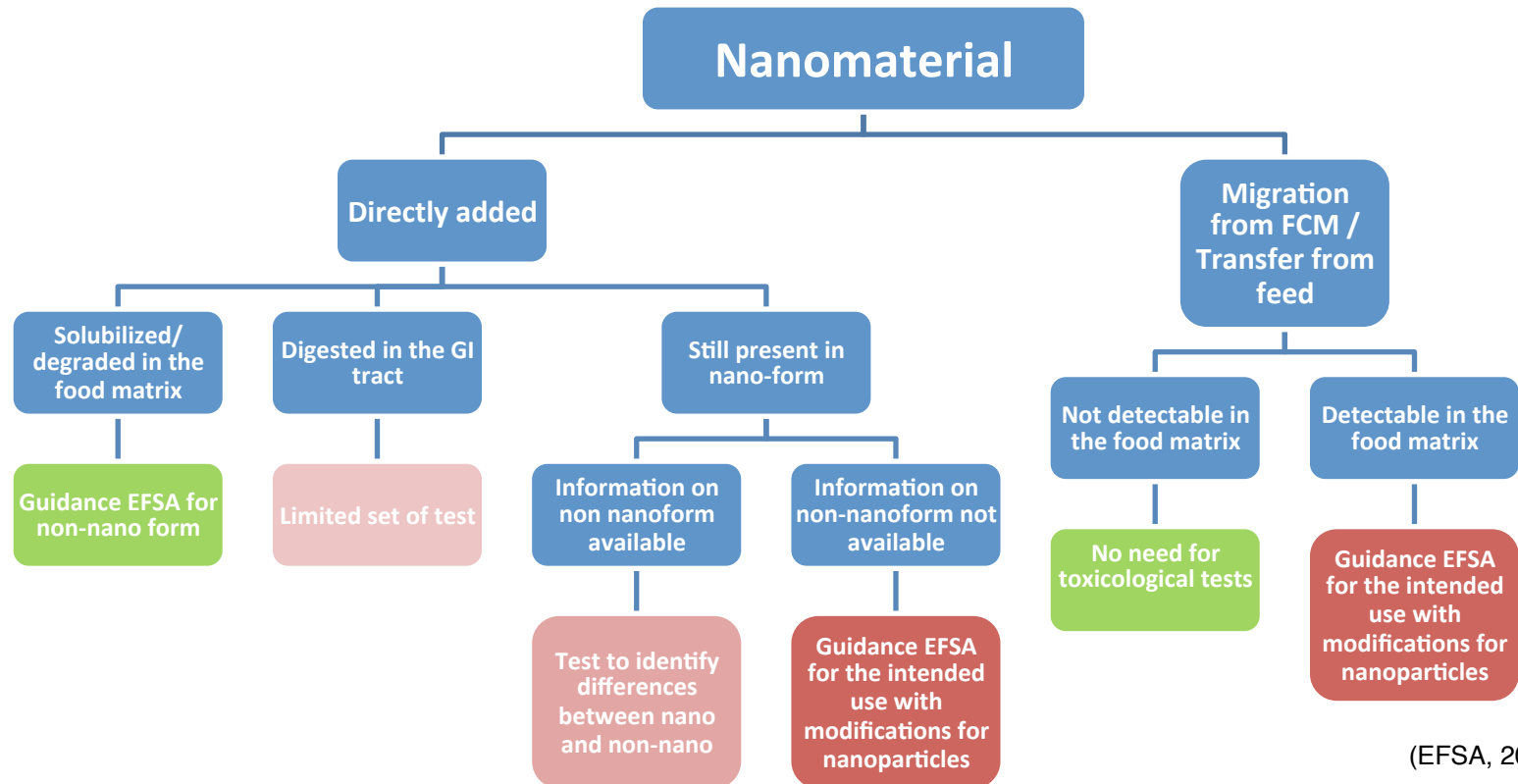
(Calzolari, Gilliland, & Rossi, 2012).

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

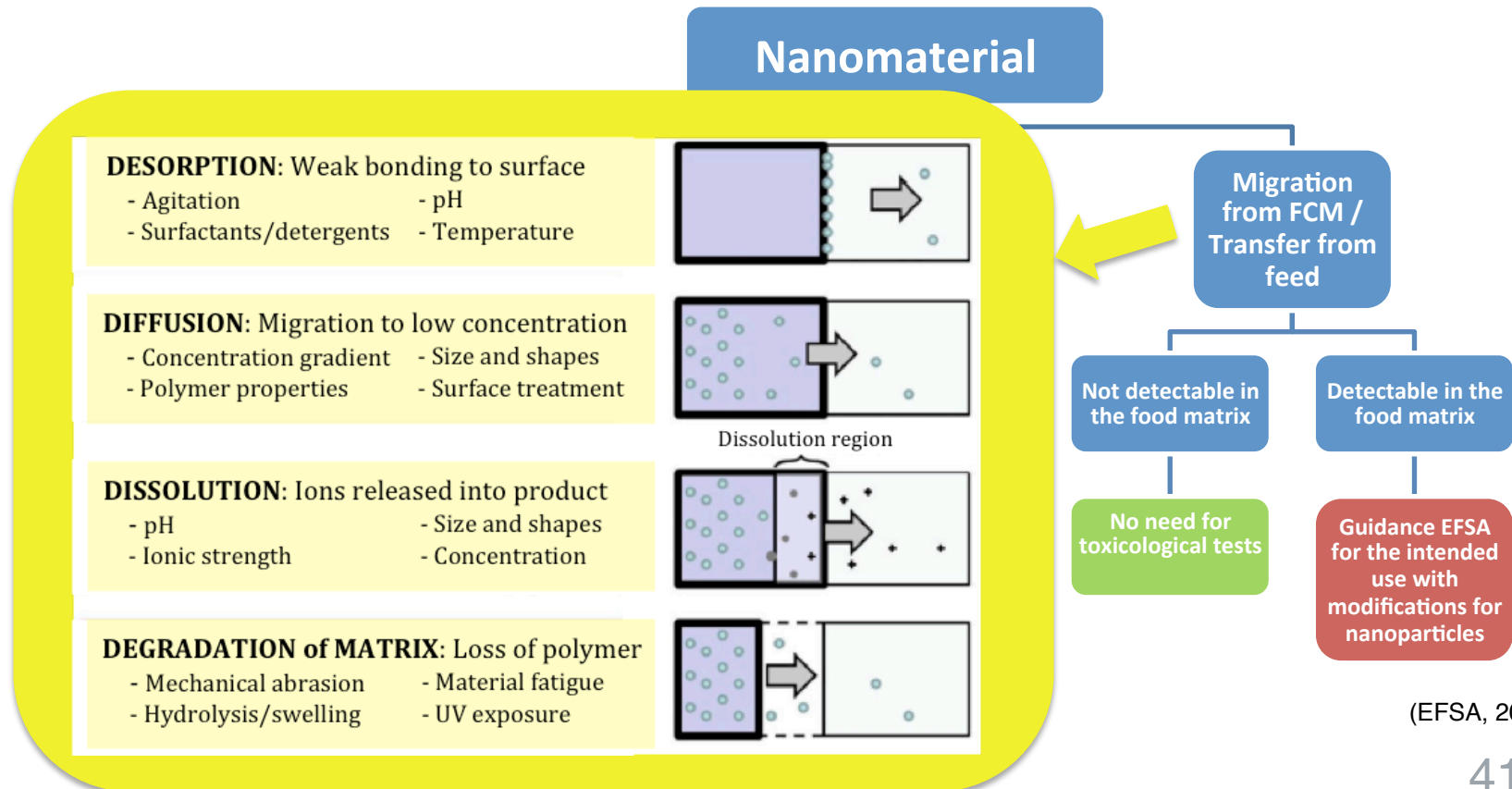
EFSA Guidance on the risk assessment of the application of nanotechnologies in the food and feed chain (2011)



(EFSA, 2011)

Risk Assessment

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





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
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)
Targeted or controlled release
Persistence/stability (e.g., in water, fat, and body fluids, lack of solubility/degradation)
Bioaccumulation

Indicators of potential toxicity

High level of reactivity (e.g., catalytic, chemical, biological)
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)
Interactions with biomolecules such as enzymes, DNA, receptors, 'Trojan horse' effect
Complex transformations (e.g., aging, changes of surface properties, porosity) or metabolites (e.g., changes to or loss of coating, 'dynamic corona')
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)
Increased rate of degradability (e.g., biological or photocatalytic) to non-nanoform degradation products
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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 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 <i>et al.</i> , 2013

(Rossi *et al.*, 2014)

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



Awareness & Attitudes

STAKEHOLDERS



CONSUMERS

RAW
MATERIALS
PRODUCERS

LEADING FOOD
COMPANIES

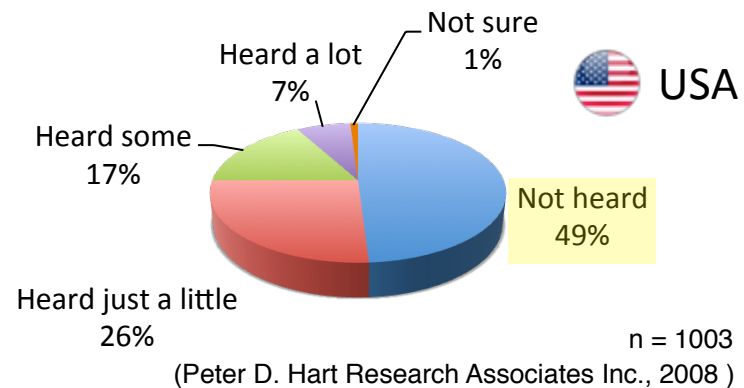
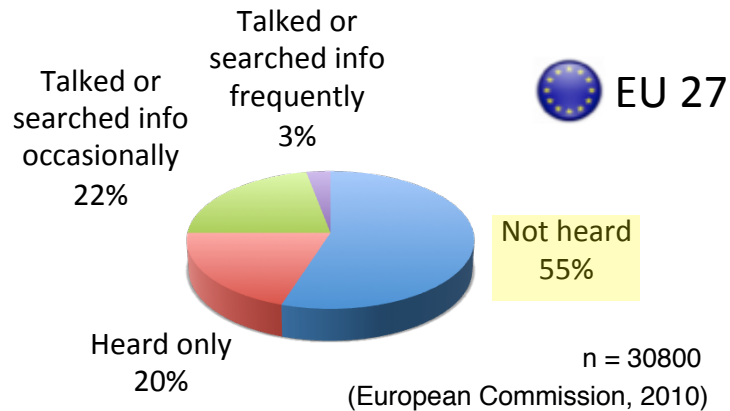


Consumers

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

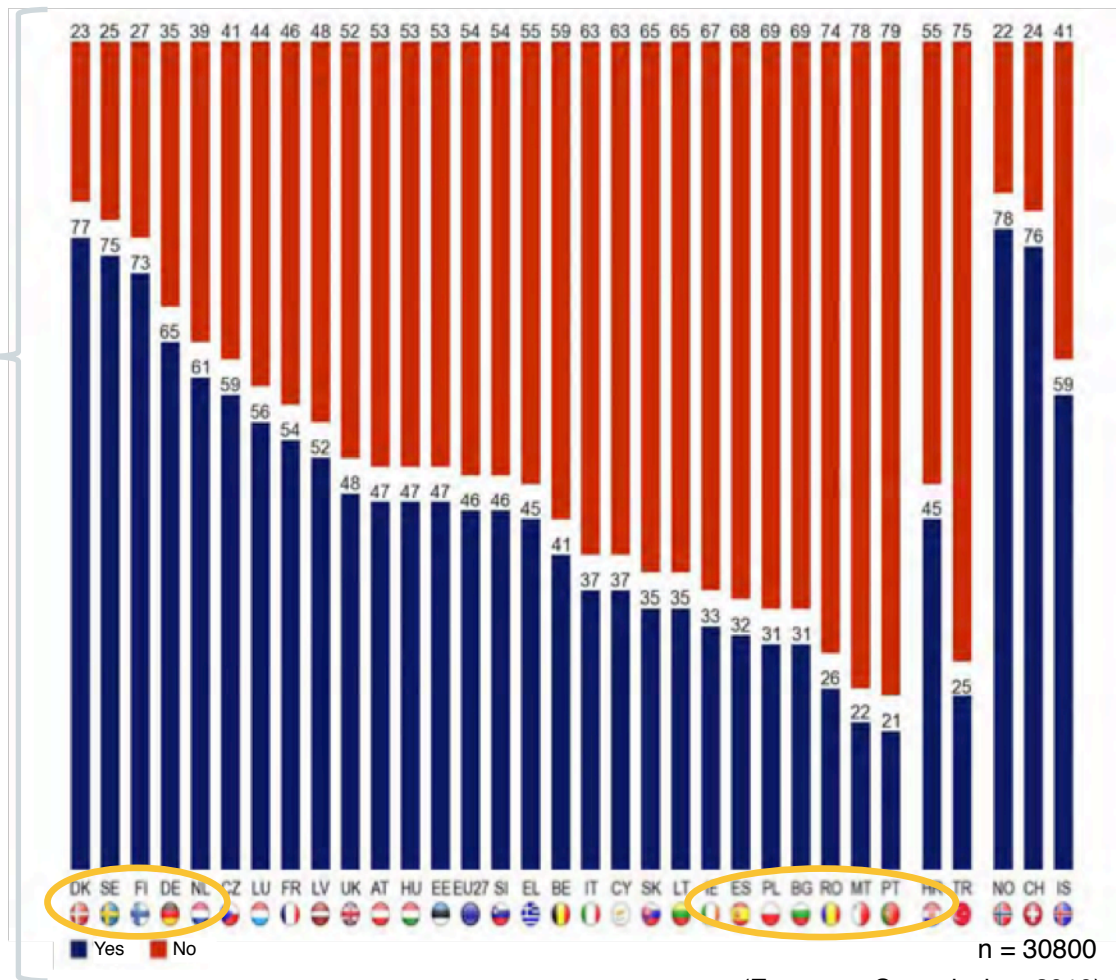
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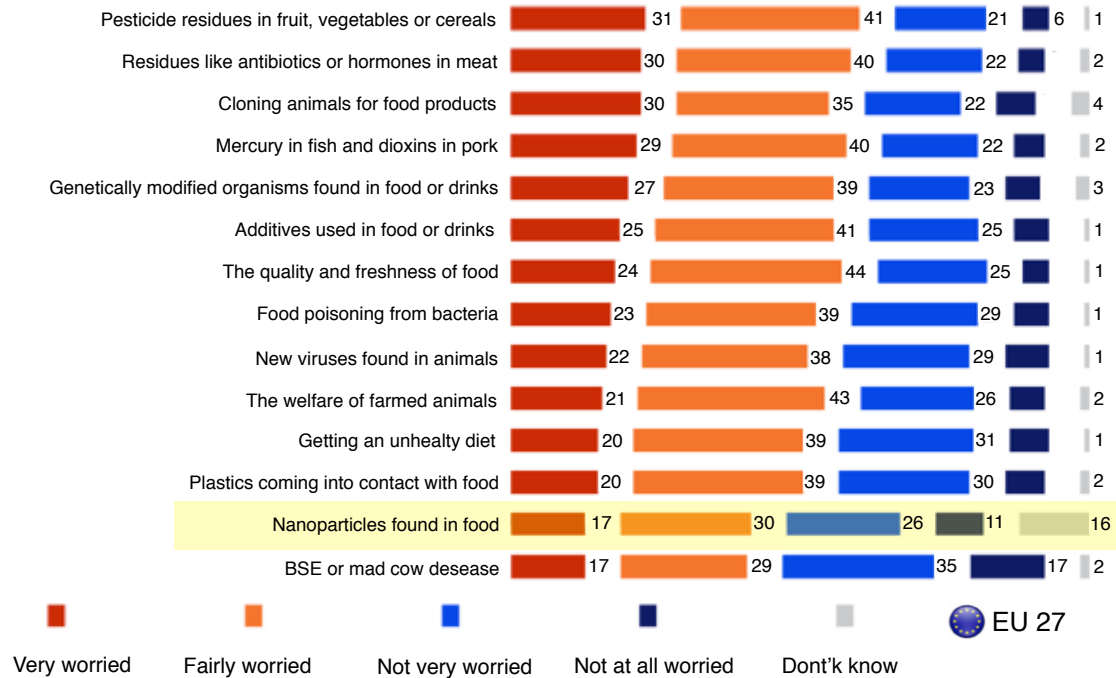
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Consumers

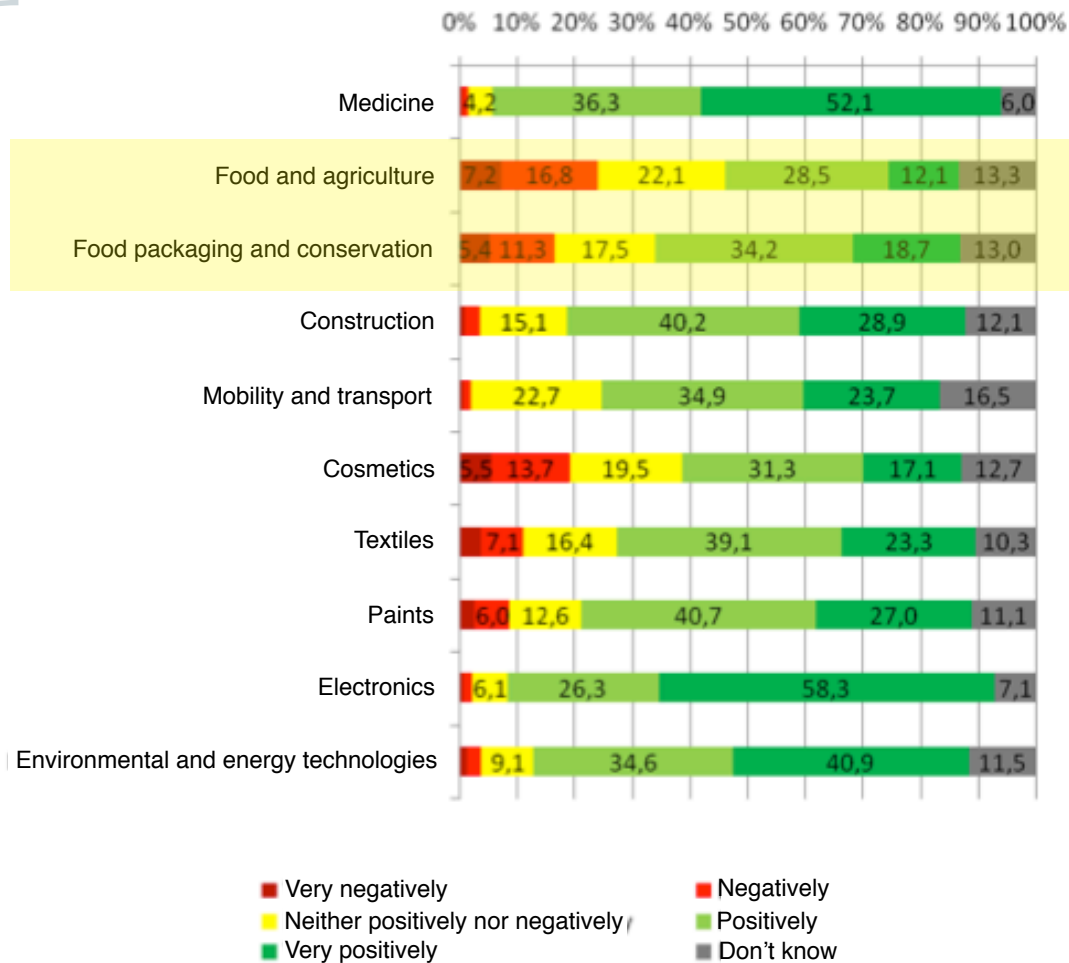
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- Trust in food industries



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 which 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 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



“Currently we’re not using nanotechnology. But we need to understand the potential of this technology...especially regarding packaging materials”



Food Companies



“Currently we’re not using nanotechnology. But we need to understand the potential of this technology...especially regarding packaging materials”

Food Companies



“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”



Food Companies



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





Food Companies



2012: “We monitor all nanotechnologies developments... We make limited use of NMs in packaging”
2014: NO STATEMENT



Food Companies

Mondelēz
International

Coca-Cola



2011: “We are working to understand NMs and their application ...but actually we do not support their use”
2015: NO STATEMENT


Unilever

Kellogg's


Nestle

Case history 1

Titanium Dioxide (E171)



Case history 1

Titanium Dioxide (E171)



ENVIRONMENTAL
Science & Technology

Article

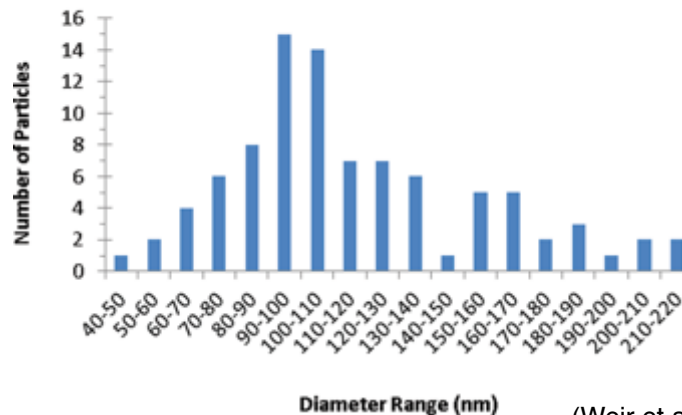
pubs.acs.org/est

Titanium Dioxide Nanoparticles in Food and Personal Care Products

Alex Weir,[†] Paul Westerhoff,^{*,†} Lars Fabricius,^{‡,§} Kiril Hristovski,^{||} and Natalie von Goetz[‡]



Distribution of Primary Particle Size of Food Grade
Titanium Dioxide



(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



Donut Products Tested for TiO₂

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.



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



CNN Money

Business Markets Tech Personal Finance Small Business Luxury

Dunkin' Donuts to remove titanium dioxide from donuts

Food Safety News

Breaking news for everyone's consumption

Dunkin' Donuts Plans to Phase Out Whitening Agent

BY NEWS DESK | MARCH 10, 2015

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

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

...a groundbreaking decision. Dunkin' ...onstrated strong industry leadership in making this potential



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**

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

[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.

FOREIGN PATENT DOCUMENTS

43-71016507 6/1968 Japan .

OTHER PUBLICATIONS

[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;**

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 Bi-material 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.

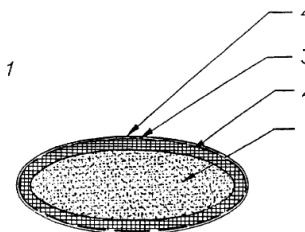
U.S. Patent

Apr. 21, 1998

Sheet 1 of 3

5,741,505

Fig. 1



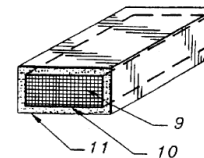
U.S. Patent

Apr. 21, 1998

Sheet 2 of 3

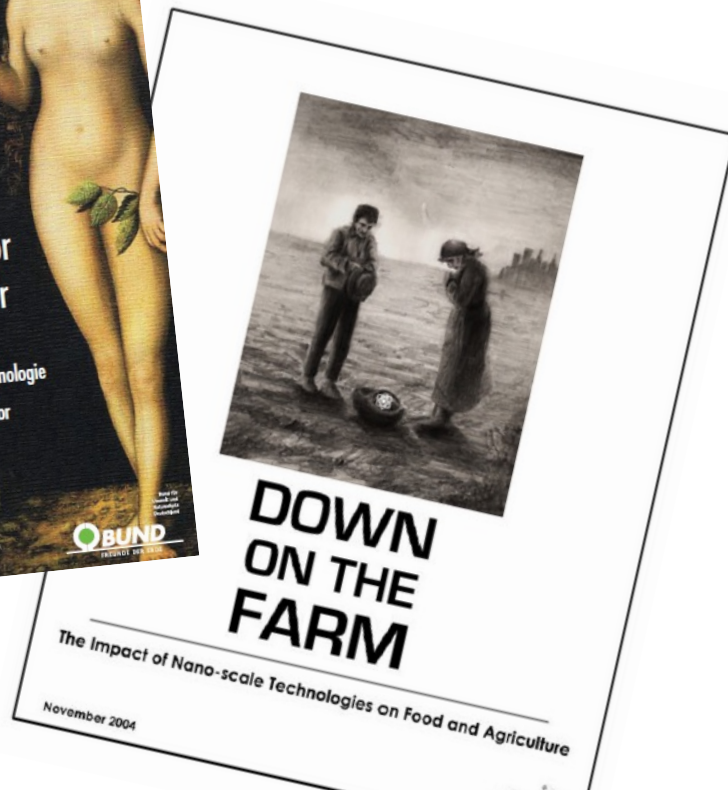
5,741,505

Fig. 3



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

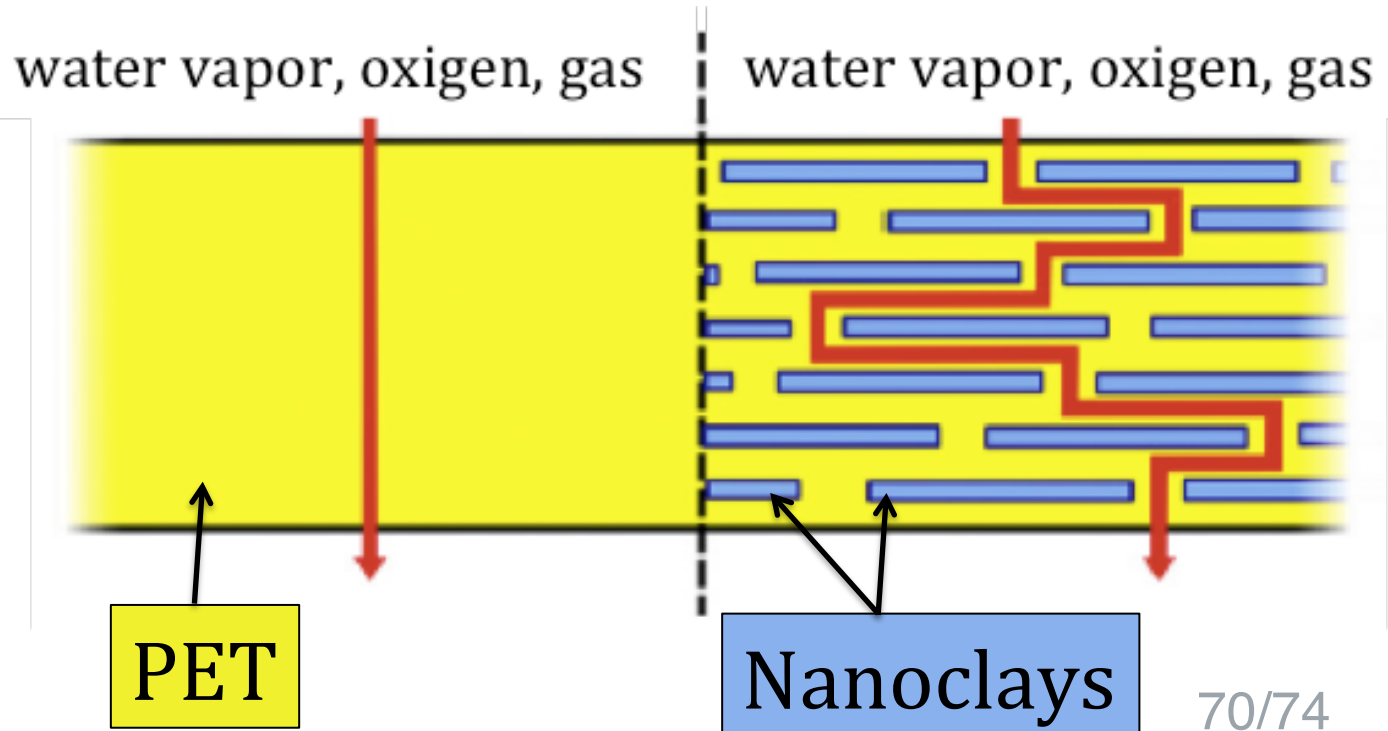
PLASTIC MATERIALS



Case history 3

Food Packaging

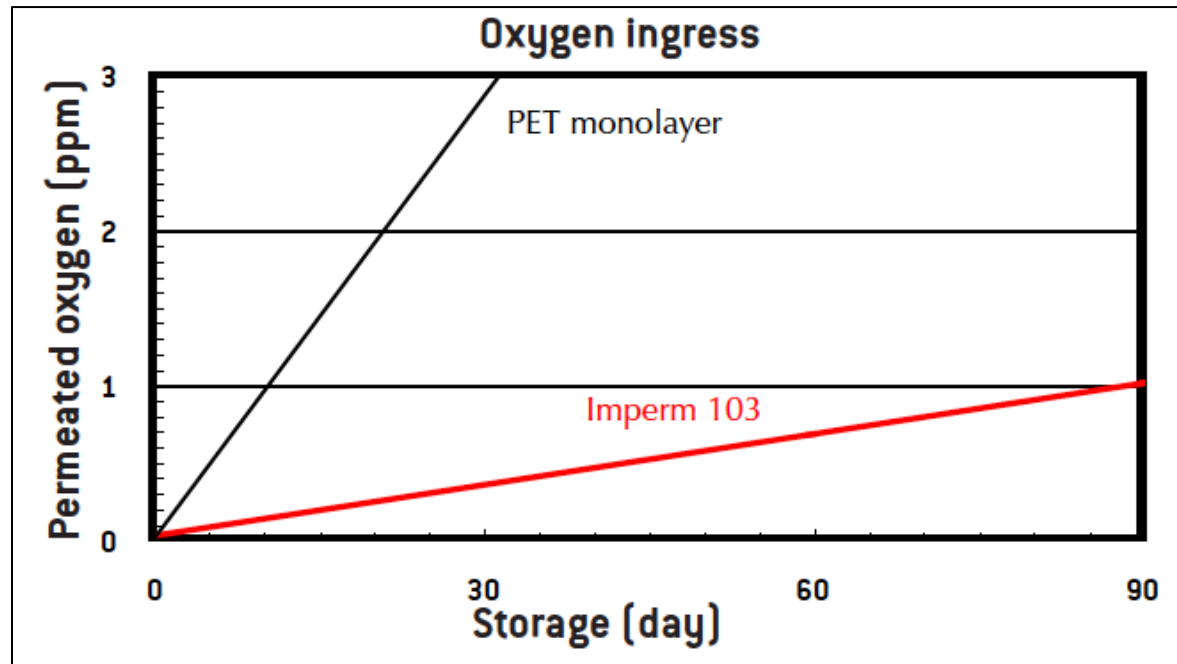
IMPERM[®]



Case history 3

Food Packaging

IMPERM[®]



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.*

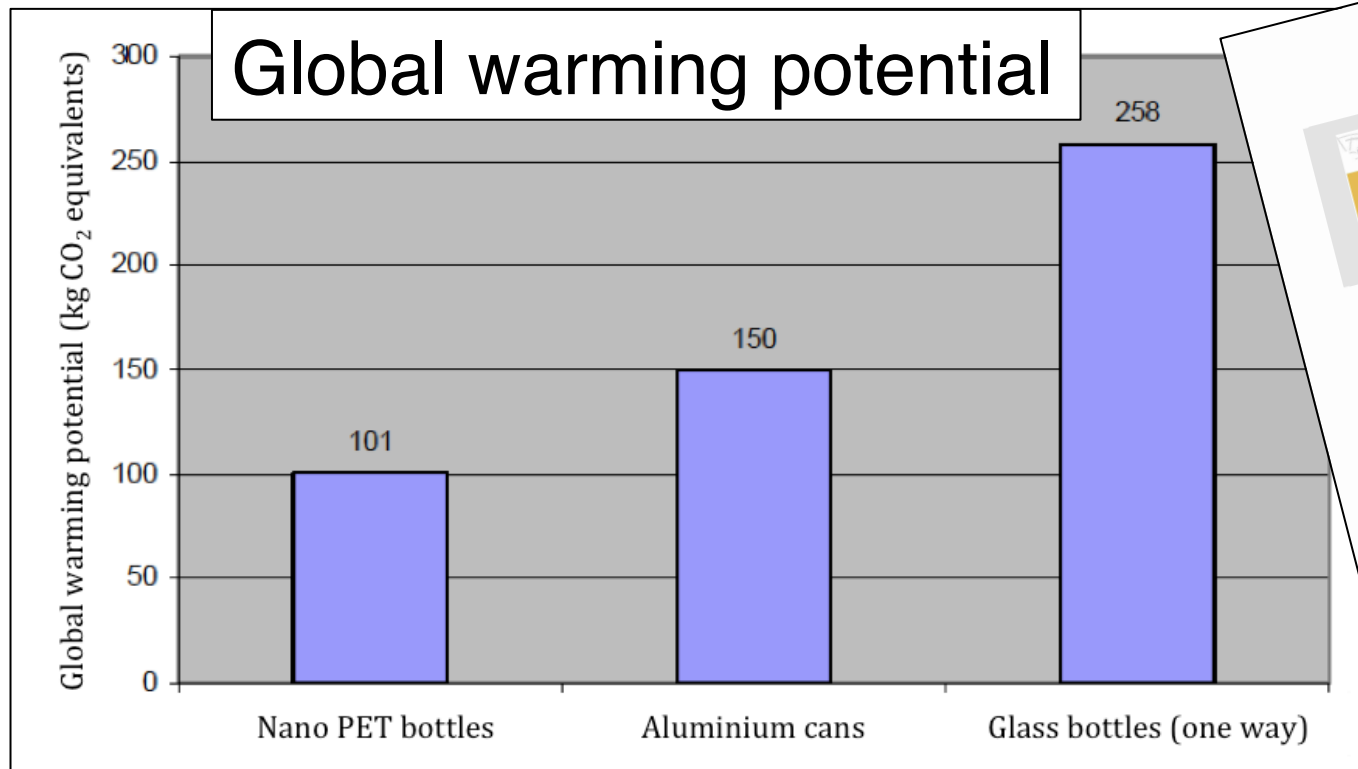
We're proud that Miller is the first U.S. brewer to solve the plastics puzzle.”

*Miller's executive vice president
Virgis Colbert*

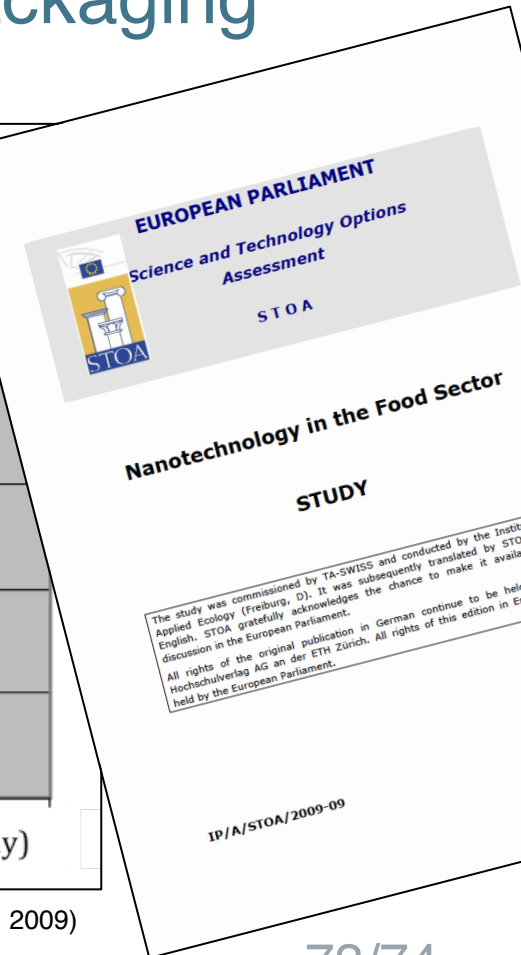
(PRNewsWire, 2006)

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