

# Life cycle assessment of a self-cleaning coating based on nanoTiO<sub>2</sub>-polyurea resin applied on an aluminium panel

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# Overview



[www.aracne.emr.it](http://www.aracne.emr.it)

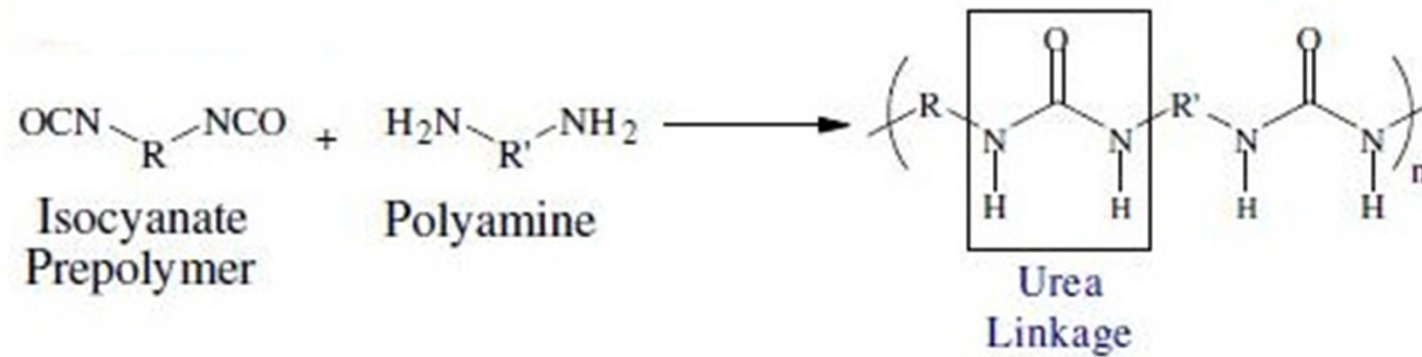
- ARACNE regional Italian project
  - 3 companies of Emilia-Romagna region
    - suppliers of building industries,
  - University of Modena and Reggio Emilia,
  - University of Bologna.
- Aim: study new and eco-friendly building materials with higher technological properties obtained by the addition of specific nanomaterials.

# LCA study

- Application of polyurea resin, functionalized with  $\text{TiO}_2$  nanoparticles, on an aluminum panel with a spraying system.
- Aim: define the most critical aspects of the process and minimize the environmental burdens and define the potential damage of titanium dioxide nanoparticles.



# What is Polyurea?



**R, R' = radicals of isocyanate and polyamine**

*Dudley J. Primeaux II, 2004, Polyurea elastomer technology History, Chemistry & Basic Formulating Techniques*

# Polyurea applications

- **Waterproofing applications**

The parking, traffic area, roofing, flooring and recovery actions.

- **Corrosion protection**

Industry applications: piping, petrochemical, food, energy and mining.

Building applications: residential buildings, showrooms and offices.

The polyurea can be applied directly on the floor or on the metal panels which will be installed to create the walls.

- **Mechanical resistance**

Industrial plants often use resin coatings to provide mechanical properties and to extend the durability when they are subjected to extreme environmental conditions.

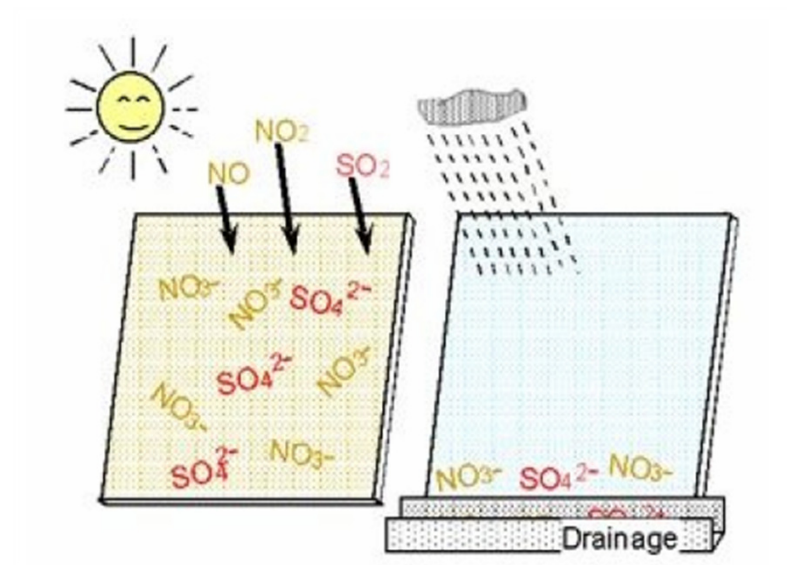
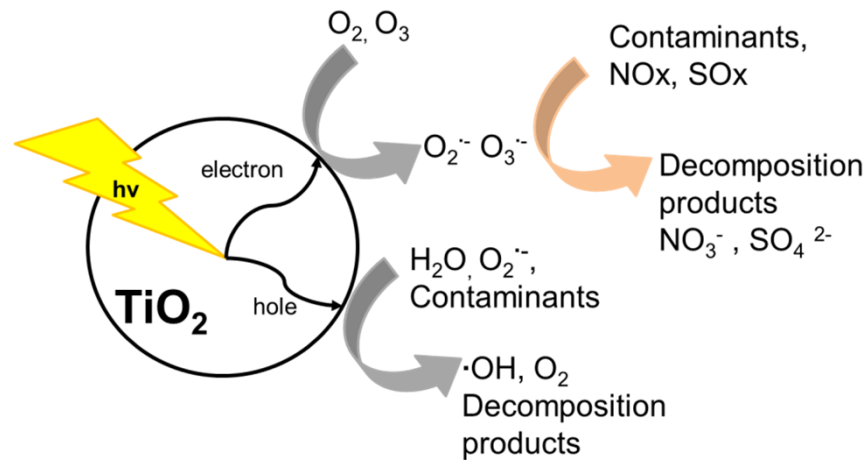
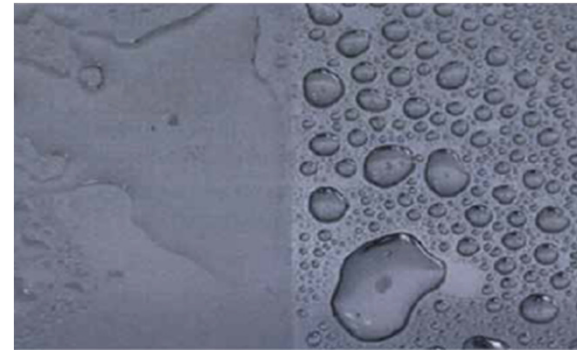
# nanoTiO<sub>2</sub> polyurea resin

Polyurea resin + TiO<sub>2</sub> nanoparticles



Higher technological properties:

- ✓ self-cleaning
- ✓ self-sterilizing
- ✓ anti-fogging



# NanoTiO<sub>2</sub> suspension

Nanotitania suspension obtained by a liquid-phase process has been used to functionalize the polyurea resin.

Composition of nanoTiO <sub>2</sub> suspension		Physical and Chemical properties	+/-	
Titanium isopropoxide	23.22%	TiO <sub>2</sub> concentration (%w/w)	0.5	6
Water	73.40%	Density (g/ml)	0.05	1.15
Nitric Acid 63%	2.38%	Viscosity 20°C (mPas/sec)	0.1	2
Polyethylene glycol	1%	Nanoparticle size (nm)	-	30
		Polydispersity index (pdl)	0.05	0.25
		pH	0.5	5.5

# LCA of nanoTiO<sub>2</sub> suspension

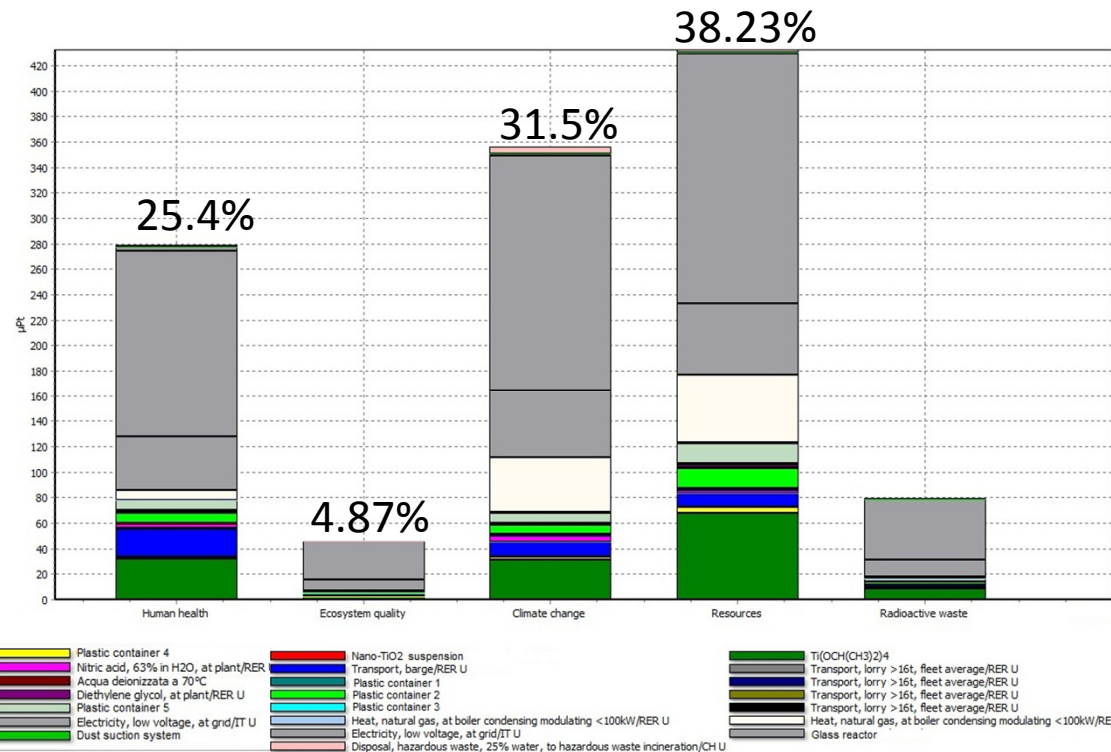
LCA study of 1 kg of nanotitania suspension.

LCIA (Life Cycle Impact Assessment) → IMPACT 2002+ method.

The environmental impact is mainly caused to:

■ 65% electric energy

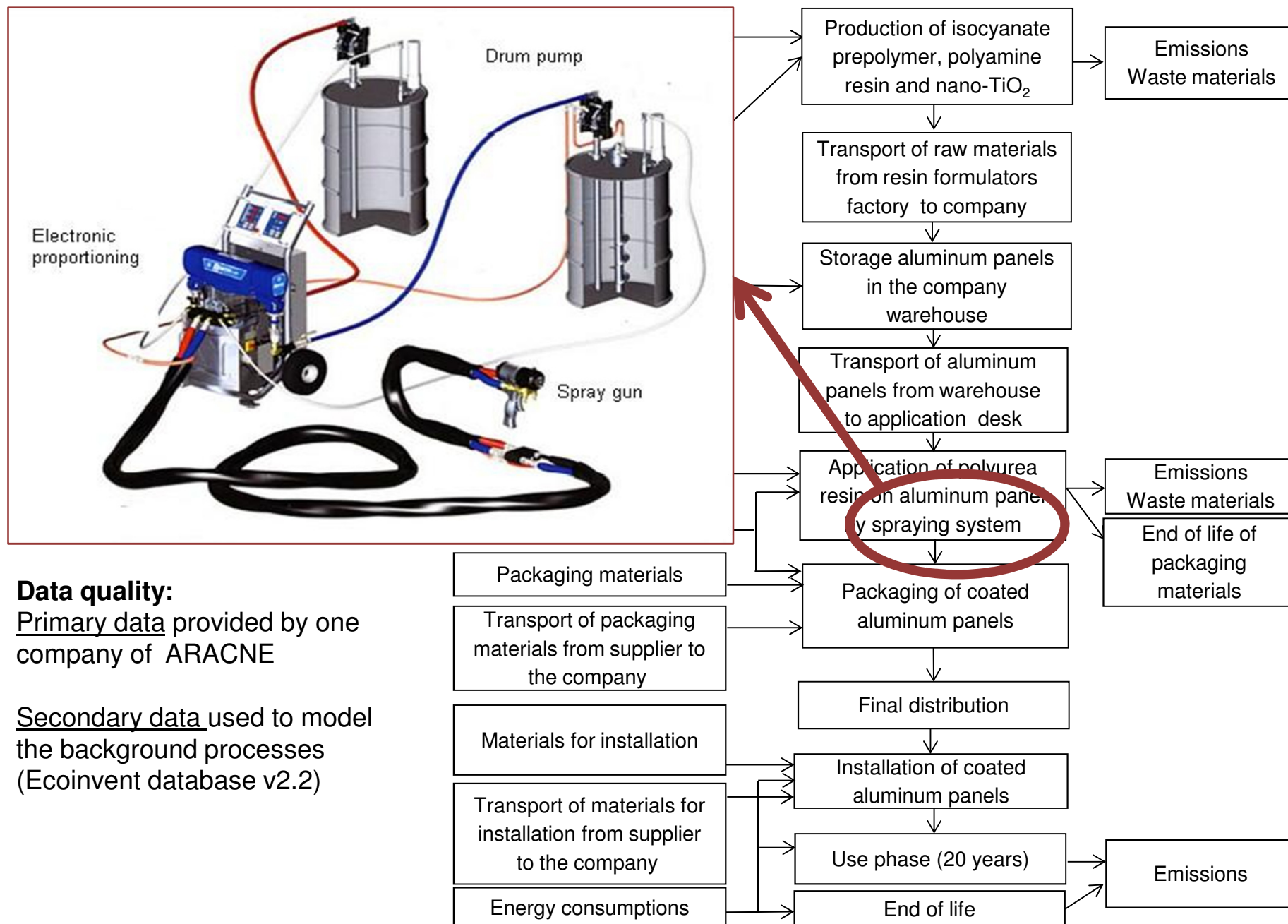
■ 11% titanium isopropoxide precursor



Damage category	Unit	Amount
Human Health	DALY	1,98E-6
Ecosystem Quality	PDF*m <sup>2</sup> *yr	0,63419
Climate change	kg CO <sub>2</sub> eq	3,53
Resources	MJ primary	65,71
Radioactive waste	DALY	7,93E-5



# LCA of nanoTiO<sub>2</sub>-polyurea resin applied on an aluminum panel



## Data quality:

Primary data provided by one company of ARACNE

Secondary data used to model the background processes (Ecoinvent database v2.2)

# Life Cycle Inventory

of 3 m<sup>2</sup> of aluminum panel coated with nanoTiO<sub>2</sub>-polyurea

Category	Components	Quantity	Unit	Source
Energy input	Electricity consumption	1355.23	kWh	Straight from the company.
Materials I/O	Polyamine resin	2.5456	kg	
	Isocyanate prepolymer	2.8001	kg	
	nanoTiO <sub>2</sub>	0.1283	kg	
	Harder	1.0691	kg	
	Aluminum panel	16.2	kg	
	Cardboard	3.6	kg	
	EUR-pallet	0.0417	kg	
	Plastic protective films	0.2052	kg	
Emissions to air	Particulates < 2.5 µm	0.104579	kg	Emissions were derived from literature.
	Particulates, > 2.5 µm, and <10 µm	0.007	kg	
	Particulates < 100 nm (outdoor)	2.603E-6	kg	
	Particulates < 100 nm (indoor)	2.355E-7	kg	
	NO <sub>2</sub>	1.79E-5	kg	
	CO <sub>2</sub>	0.0022111	kg	
	Water	0.065804	kg	
	NMVOG	0.32167	kg	
	Ammonia	0.024866	kg	
	Ethyne	3.31E-5	kg	
	Aluminum	0.046231	kg	
Transports	Road	4115.15	kgkm	Straight from the company. Transport processes I/O data derived from Ecoinvent database.
	Freight	8481.69	kgkm	
Waste of materials	Waste of polyurea resin with nanoTiO <sub>2</sub> retained by air filter	0.51098	kg	Disposal scenario was given from the company. Waste treatment were derived from Ecoinvent process.
	Waste of polyamine resin remained into drums	6E-4	kg	

# Benefits of nanoTiO<sub>2</sub>

- Reduction of *NO<sub>2</sub> emissions* in air

It has been considered an *Italian environmental protection agency* study (ARPA Lombardia, 2004).

Results: reduction of 37% NO<sub>2</sub> indoor emissions in two buildings coated with nanotitania based paints.

- Evaluating of the survival ratio of *Escherichia Coli* exposed to a TiO<sub>2</sub> loading

It has been assessed in agreement with the results of Caballero et al., 2009. The survival ratio of E. Coli is 16.83%.

- No maintenance operations (*cleaning*)

Fujishima et al., 2008 estimated that a building treated with self-cleaning coatings remain clean 20 years without any maintenance.

# IMPACT 2002+ Modified

## NO<sub>2</sub> reduction

New impact category: **Respiratory inorganics indoor** (Unit: kg)

*Characterization factor:* 1kg/kg

New damage category: **Respiratory inorganics indoor** (Unit: DALY)

Duration of respiratory disease: 7 days. Disability class: 0.01

Probability to get the respiratory disease: 10%

*Damage assessment factor:*  $7\text{days}/365\text{days/year} \times 0.01 \times 0.1 \text{DALY}/60\mu\text{g of NO}_2 =$   
**0.319635 DALY/kg of NO<sub>2</sub>**

## Escherichia coli reduction

New impact category: **Non carcinogens indoor** (Unit: p)

*Characterization factor:* 1 CFU/person/p [Colony Forming Unit=CFU]

New damage category: **Non carcinogens indoor** (Unit: DALY)

Duration of urinary tract infection: 7 days. Disability class: 0.1

Probability to intake E. Coli: 10%

Probability to get the urinary tract infection: 10%

*Damage assessment factor:*  $7\text{ days}/365\text{days/year} \times 0.1 \times 0.1 \times 0.1 \text{DALY}/1\text{CFU/person} =$   
**1.918E-5 DALY/CFU/person**

# NO<sub>2</sub> reduction

*Use phase: indoor environment → e.g. clean room volume = 27 m<sup>3</sup>*

Annual limit values for the protection of human health: 40 µg/m<sup>3</sup>

Assumption: NO<sub>2</sub> concentration **that causes respiratory** disease = 60 µg/m<sup>3</sup>

NO<sub>2</sub> emitted: 60 µg/m<sup>3</sup> \* 27 m<sup>3</sup>

NO<sub>2</sub> reduction: -0.37 \* 60 µg/m<sup>3</sup> \* 27 m<sup>3</sup>

# Escherichia coli reduction

*Use phase: indoor environment → e.g. clean room volume = 27 m<sup>3</sup>*

Assumption: E. Coli concentration that causes urinary tract infection = 1CFU

*Caballero L, Whitehead KA, Allen NS, Verran J, Inactivation of Escherichia coli on immobilized TiO<sub>2</sub> using fluorescent light , Journal of Photochemistry and Photobiology A: Chemistry 202 (2009) 92–98*

Survival ratio for a TiO<sub>2</sub> loading of 15592 mg/m<sup>2</sup> = 30%

Survival ratio for a TiO<sub>2</sub> loading of 520 mg/m<sup>2</sup> = 15%

TiO<sub>2</sub> loading in polyurea resin: 2353.3 mg/m<sup>2</sup>

Linear trend of survival ratio (SR), SR = 16.825%

E. Coli concentrations per day: 1 CFU of *Escherichia coli*

E. Coli concentrations over 20 years (panel lifetime): 1 CFU\*365days/yr\*20yrs.

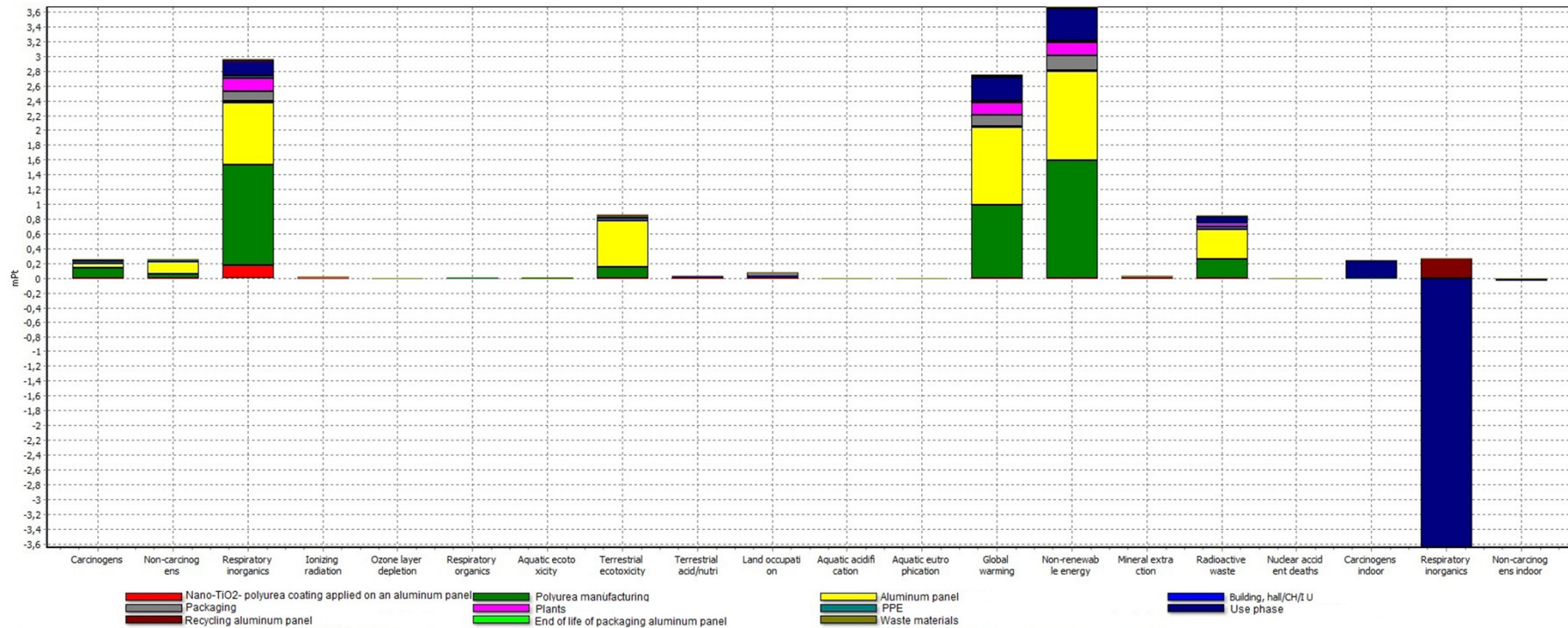
The room does not host the same person every day.

One person per year gets the bacteria: 1 pers\*365days/yr\*20yrs.

E. Coli reduction:  $-(1-0.16825)*1\text{CFU}*365\text{days/yr}*20\text{yrs}/(1\text{pers}*365\text{days/yr}*20\text{yr})=$   
 $-(1-0.16825)\text{CFU/pers}.$

# Life Cycle Impact Assessment

of 1 m<sup>2</sup> of aluminum panel coated with nanoTiO<sub>2</sub>-polyurea



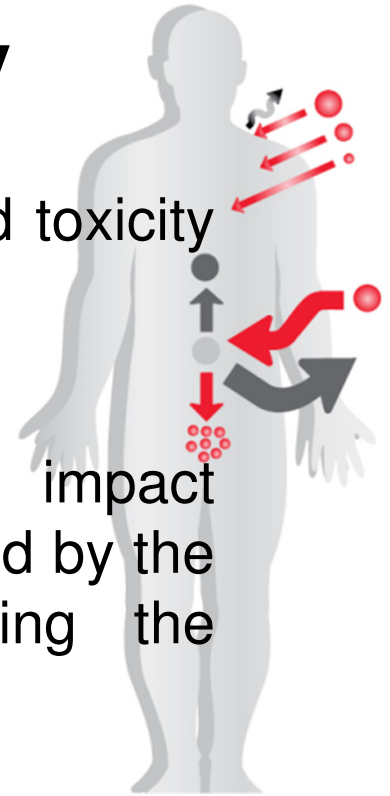
Damage category	Unit	Total	Nano-TiO <sub>2</sub> -polyurea coating applied on an aluminum panel	Polyurea manufacturing	Aluminum panel	Building, hall/CH/I U	Packaging	Plants	Personal protective equipment (PPE)	Use phase	Recycling aluminum panel	End of life of packaging of aluminum panel	Waste materials
Total	Pt	0,008596	0,000176	0,004596	0,004407	3,89E-05	0,000641	0,000611	9,04E-05	-0,00233	0,000305	4,51E-05	1,49E-05
Human health	DALY	2,48E-05	1,25E-06	1,11E-05	7,68E-06	1,32E-07	1,14E-06	1,35E-06	2,63E-07	1,7E-06	7,14E-08	1,16E-07	3,92E-08
Ecosystem quality	PDF*m2*yr	13,48496	0	2,40955	9,010849	0,042438	1,187209	0,426891	0,031262	0,315812	0,023419	0,026917	0,010611
Climate change	kg CO <sub>2</sub> eq	27,20272	0	9,816133	10,44	0,076903	1,53682	1,661315	0,231445	3,169551	0,099496	0,115935	0,055122
Resources	MJ primary	562,8361	0	245,9995	183,4781	1,111294	30,04023	27,19374	3,506947	67,75128	1,421908	1,979038	0,354129
Radioactive waste	kg	0,000846	0	0,000252	0,000404	2,13E-06	4,03E-05	4,31E-05	4,64E-06	9,05E-05	5,88E-06	2,06E-06	7E-07
Carcinogens indoor	DALY	1,73E-06	1,87E-09	0	0	0	0	0	0	1,73E-06	5,52E-11	0	0
Respiratory inorganics indoor	DALY	-2,4E-05	0	0	0	0	0	0	0	-2,6E-05	1,9E-06	0	0
Non-carcinogens indoor	DALY	-3E-07	0	0	0	0	0	0	0	-3E-07	0	0	0

# Attempt of nanotoxicity

- Uncertainties and knowledge gaps on behavior and toxicity of nanoparticles.

***We cannot remain silent!!***

- Preliminary attempt to introduce in life cycle impact assessment the damage on human health generated by the emissions in air of titania nanoparticles during the application, use and end of life phases.



## References

NIOSH <i>National Institute for Occupational Safety and Health</i>	Occupational exposure limits for ultrafine TiO <sub>2</sub> (primary particles diameter < 100 nm)	0.3 mg/m <sup>3</sup>
	Reducing the risk of developing lung cancer with concentration level of 0.3 mg/m <sup>3</sup>	< 1/1000
IARC <i>International Agency for Research on Cancer</i>	TiO <sub>2</sub> review → sufficient evidence of carcinogenicity in experimental animals and inadequate evidence of carcinogenicity in humans	Group 2B “possibly carcinogenic to humans”



# Calculation of nanoTiO<sub>2</sub> hourly production limit

## Assumptions:

- Concentration limit outdoor and indoor= 0.3mg/m<sup>3</sup>
- probability that an average individual will develop cancer when exposed to nanoTiO<sub>2</sub> with a concentration  $\geq 0.3\text{mg/m}^3$  is 1/1000
- Emissions release during the production: 1%
- 99% of emissions are captured by the air cleaner with 99.97% of efficiency and other 1% of emissions are release directly into the production room.

Hourly production limit [**P**]:

$$C = (\text{P} \cdot p) / V \cdot 0.03\% \cdot 99\%$$

$C = 0.3 \text{ mg/m}^3$  (concentration limit)

$p = 1\%$  (emissions which occur during the production)

$V = 2700 \text{ m}^3/\text{h}$  (flow rate of air cleaner)

$$\text{P} = 272.725 \text{ kg/h}$$

# Determination of damage to human health caused by outdoor nanoTiO<sub>2</sub> emissions

Assumption: nanoTiO<sub>2</sub> fate factor= PM 2.5  $\mu$ m fate factor

- Characterization factor= 0.10904 kg C<sub>2</sub>H<sub>3</sub>Cl/kg of TiO<sub>2</sub> nanoparticles
- Modification of IMPACT 2002+ method
- New substance in *Carcinogens* impact category:  
*Particulates, <100 nm*, with the calculated characterization factor
- Data input: amount of emissions which are captured by the air cleaner plus the amount of emissions which are not inhaled by workers

# The calculation of the damage caused by carcinogenic substance by Eco-indicator 99 method:

## Fate analysis: from emission to concentration

**Fate factor (F)** of P.M 2.5  $\mu\text{m}$ : **1.70E-5 m<sup>2</sup>a/m<sup>3</sup>**

## Effect analysis: from concentration to cancer per kg emission

**Unit risk factor (UR)**: (1/1000) cases / 0.3E3 mg/m<sup>3</sup>= **0.333E-6 cases/mg/m<sup>3</sup>** per year.

European population density (PD)= 9.44E-5 persons/m<sup>2</sup>

**Effect (E)**: **UR\*PD**= 0.333E-6 cases/mg/m<sup>3</sup>/ 70 years (average life)\* 9.44E-5 persons/m<sup>2</sup>  
**= 4.49E-13 cases/mg/m<sup>3</sup>/a\*persons/m<sup>2</sup>**

**Incidence factor (I)**: **E\*F**= 4.49E-13 cases/mg/m<sup>3</sup>/a\*persons/m<sup>2</sup>\*1.7E-5m<sup>2</sup>a\*m<sup>3</sup>=  
7.633E-18 cases/mg = **7.633 E-9 cases/kg of TiO<sub>2</sub> nanoparticles**

## Damage analysis: from cancer per kg to DALYs per kg emission

DALY= 40 years\*7.633E-9 cases/kg = **3.0532E-7 DALY/kg** of TiO<sub>2</sub> nanoparticles.

Damage assessment factor of **Carcinogens** impact category in **Human Health** of IMPACT 2002+ method: 2.8E-6 DALY/kg<sub>C<sub>2</sub>H<sub>3</sub>Cl</sub>

**Characterization factor**: 3.0532E-7 DALY/kg<sub>NP</sub> / **2.8E-6 DALY/kg<sub>C<sub>2</sub>H<sub>3</sub>Cl</sub>**=  
**0.10904 kg<sub>C<sub>2</sub>H<sub>3</sub>Cl</sub>/ kg of TiO<sub>2</sub> nanoparticles**

# Determination of damage to human health caused by indoor nanoTiO<sub>2</sub> emissions

## Assumptions:

- The emissions must be removed by workers with a ventilation of the room air such as to maintain the concentration below the limit concentration
- The workers must wear the PPE (personal protective equipment) as the face mask with 95% of efficiency
- Room production volume: 150 m<sup>3</sup>
- Life expectancy: 80 years
- YLL (years of life lost): 40 years
- Number of workers in the production room: 5
- Amount of indoor emissions [IE]:  $IE = 1\% \cdot 1\% \cdot 275.275 \text{ kg/h} = 0.0275275 \text{ kg/h}$
- Concentration limit of indoor emissions:  $0.0275275 \text{ kg/h} / 150 \text{ m}^3 = 181.517 \text{ mg/m}^3/\text{h}$
- Characterization factor =  $5 \text{ workers} \cdot 40 \text{ YLL} / 1000 \text{ workers} / 0.0275275 \text{ kg/h} = 7.35 \text{ DALY/kg/h}$
- Modification of IMPACT 2002+ method
- New substance: *Particulates, <100 nm indoor*
- New impact category: *Carcinogens indoor*, with characterization factor =  $1 \text{ kg}_{\text{C}_2\text{H}_3\text{Cl}}/\text{kg}$
- New damage category: *Carcinogens indoor*, with the calculated characterization factor =  $7.35 \text{ DALY/kg/h}$
- Data input: amount of emissions which are not captured by face mask and inhaled by workers

# Nanotoxicology and No Nanotoxiloggy impacts

Involved steps:

1. polyurea spray application
2. use phase
3. recycling aluminum panel phase

Data input:

*Particulates, <100 nm indoor* = 0.23556 mg

*Particulates, <100 nm* = 2.6 mg

		Nanotoxicity				No Nanotoxicity				Δ%			
	Unit	Total	Nano-TiO <sub>2</sub> -polyurea coating applied on an aluminum panel	Use phase	Recycling aluminum panel	Total	Nano-TiO <sub>2</sub> -polyurea coating applied on an aluminum panel	Use phase	Recycling aluminum panel	Total	Nano-TiO <sub>2</sub> -polyurea coating applied on an aluminum panel	Use phase	Recycling aluminum panel
Impact category													
Carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	0,6409472	2,287E-07	0,0741373	0,00093	0,6409469	0	0,07414	0,0009299	4,43E-05	100	0	0,0059277
Carcinogens indoor	kg	2,355E-07	2,547E-10	2,353E-07	7,515E-12	0	0	0	0	100	100	100	100
Damage category													
Human health	DALY	2,48E-05	1,25E-06	1,7E-06	7,14E-08	2,48E-05	1,25E-06	1,7E-06	7,14E-08	3,205E-06	5,14E-05	0	0,000216
Carcinogens indoor	DALY	1,73E-06	1,87E-09	1,73E-06	5,52E-11	0	0	0	0	100	100	100	100
Total damage	Pt	0,008596	0,000176	-0,00233	0,000305	0,008352	0,000176	-0,0026	0,000305	0,149926	10,45948	0,00256	0,008596

HEPA air filter: efficiency of 99,97%

PPE (*Personal protective equipment*): efficiency of 95%

Low nanoparticles emissions in air

# Conclusions and remarks

- Validation of Life Cycle Impact Assessment with nanotoxicological aspects.

Parametric analysis → varying:  $\text{TiO}_2$  concentration, filter efficiency, nanoparticles emitted in air.

- LCA of glass panel functionalized with nano $\text{TiO}_2$ .
- Assessment of the actual environmental performance of functionalized building materials once embedded in entire building.



*Thank you for your attention*

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# Disability Class – Eco-indicator99

Disability Class	Severity weights	Indicator conditions
1	0.00-0.02	Vitiligo on face, weight-for-height less than 2 SDs
2	0.02-0.12	Watery diarrhoea, severe sore throat, severe anemia
3	0.12-0.24	Radius fracture in a stiff cast, infertility, erectile dysfunction, rheumatoid arthritis, angina.
4	0.24-0.36	Below-the-knee amputation, deafness
5	0.36-0.50	Rectovaginal fistula, mild mental retardation, Down syndrome
6	0.50-0.70	Unipolar major depression, blindness, paraplegia
7	0.70-1.00	Active psychosis, dementia, severe migraine, quadriplegia