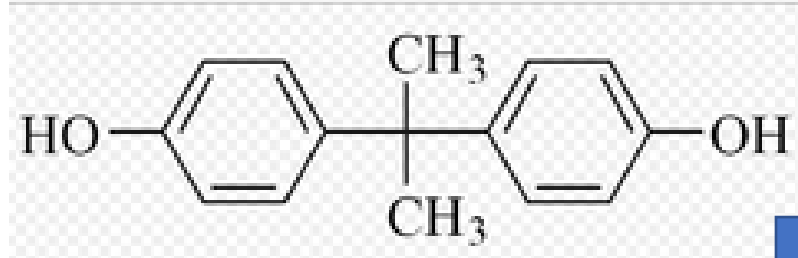


Bisfenol A



Hay dudas sobre la peligrosidad de este producto. Unos dicen que es nocivo por encima de 0.0005 %. Otros dicen que sólo por encima de 0.0010 %

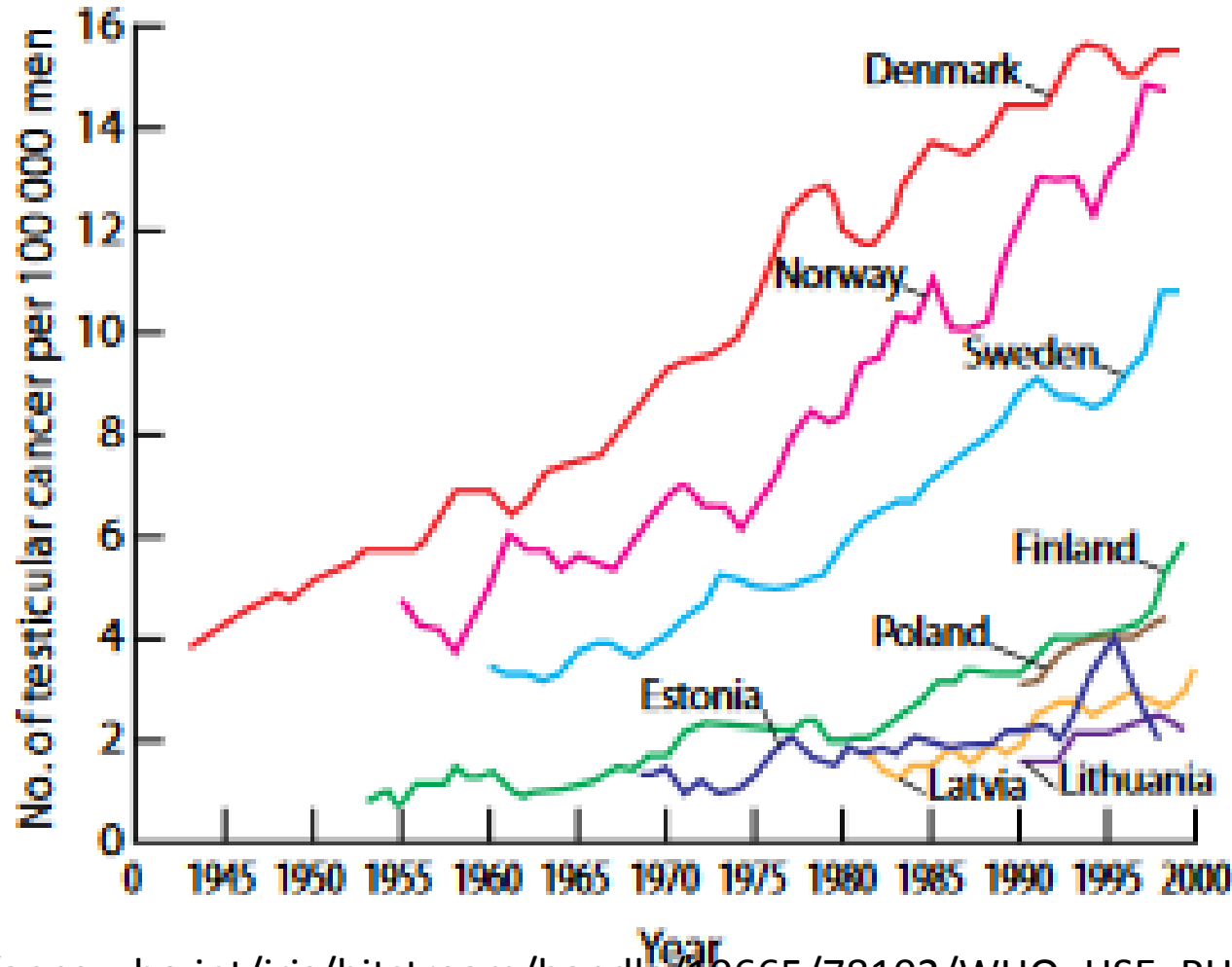


Conceptos fundamentales:

- Es inevitable ingerir una parte del envase. Se estima que hay unas 10 000 sustancias que pueden migrar desde los envases, incluyendo las llamadas añadidas de forma no intencionada (NIASs), por degradación del material o de sustancias que contiene)
- La mayoría de los requisitos sobre migración se refieren exclusivamente a los materiales poliméricos (plásticos)
- La cuestión no es si los componentes del envase van a migrar al alimento. Las preguntas que hay que hacerse son:
 - ¿Cuáles son y cuáles son sus características toxicológicas?
 - ¿En qué cantidades van a migrar?



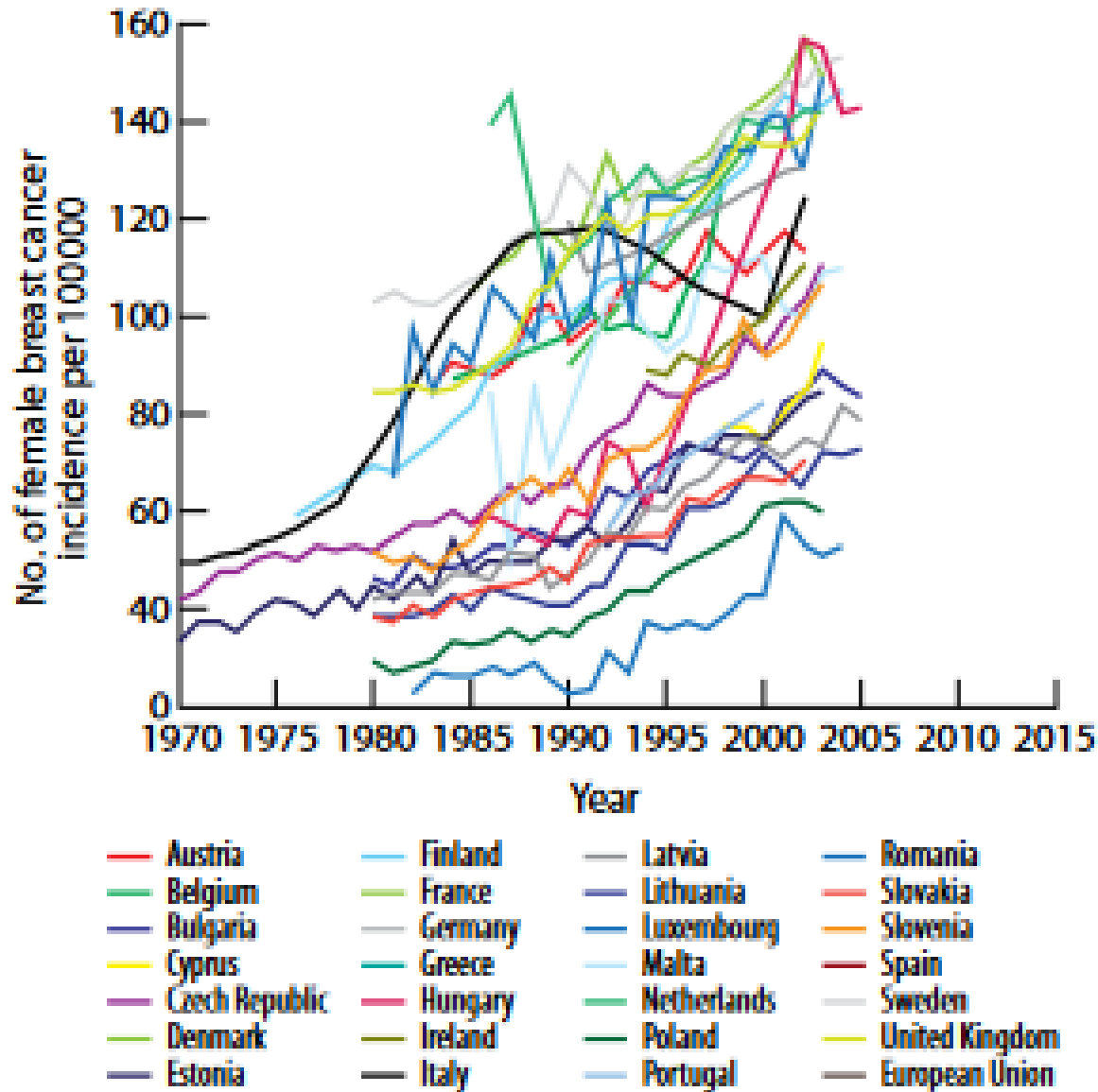
Evolución del número de casos de cáncer de testículos: Norte de Europa



http://apps.who.int/iris/bitstream/handle/10665/78102/WHO_HSE_PHE_IHE_2013.1_eng.pdf;jsessionid=F91A21A966D62CF2292FD36FE61A1C95?sequence=1



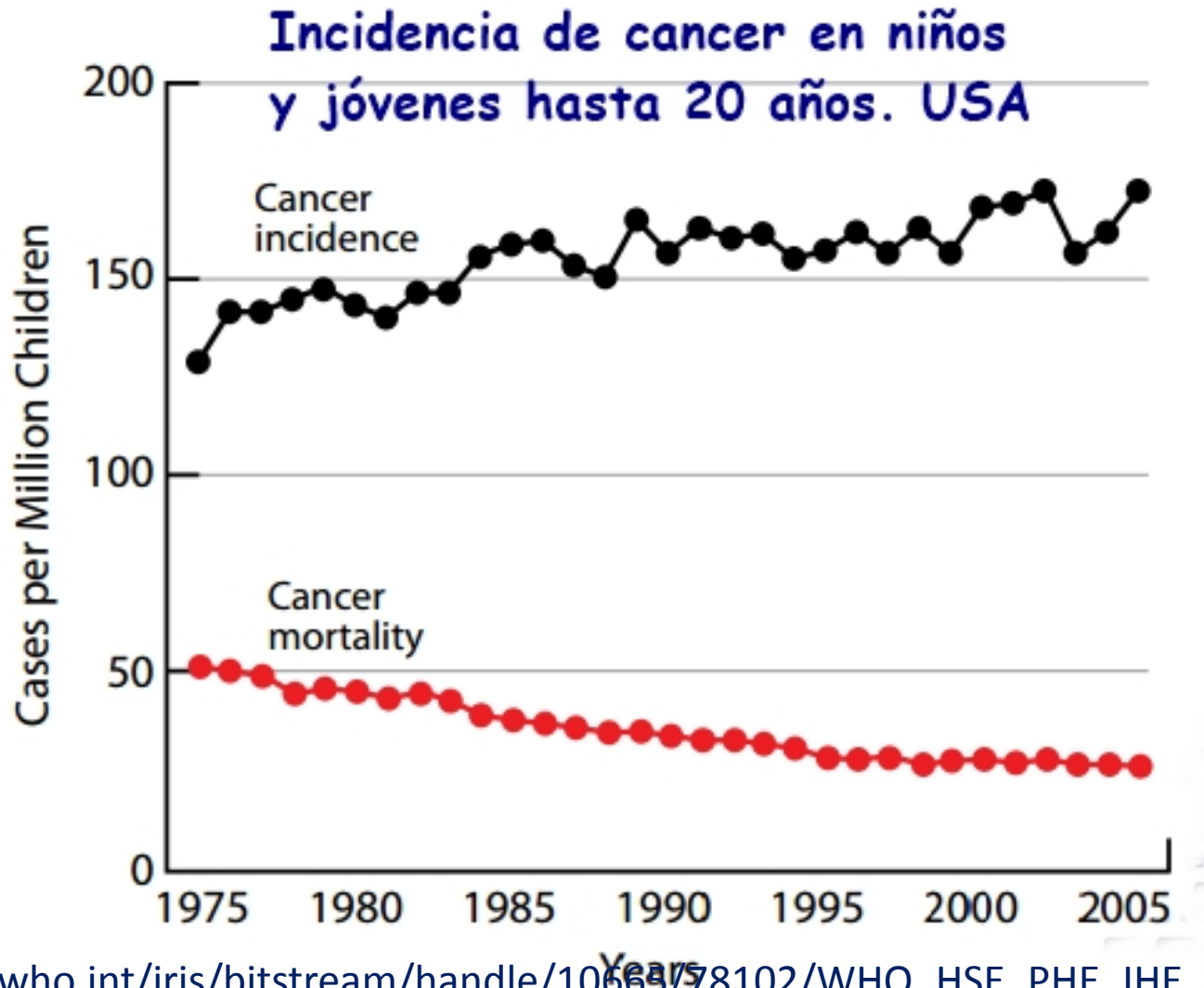
Evolución del número de casos de cáncer de mama: Europa



http://apps.who.int/iris/bitstream/handle/10665/78102/WHO_HSE_PHE_IHE_2013.1_eng.pdf;jsessionid=F91A21A966D62CF2292FD36FE61A1C95?sequence=1



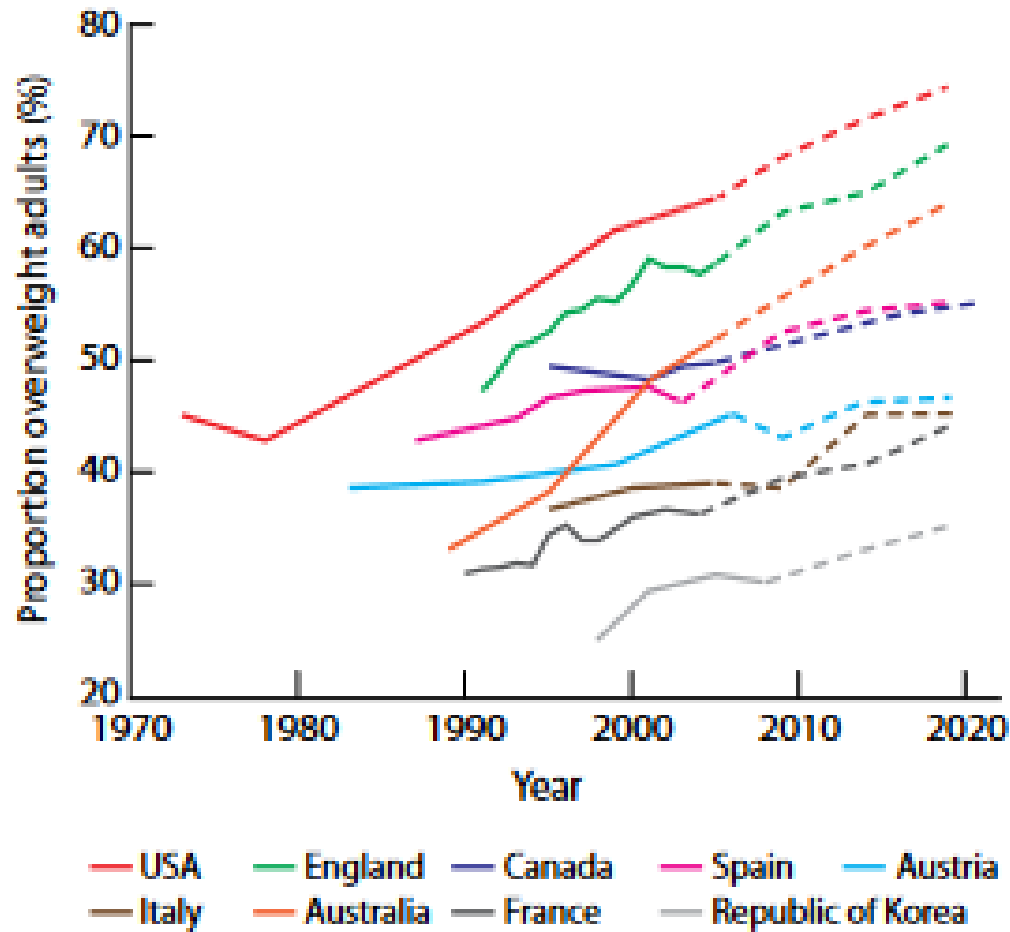
Incidencia de cáncer en niños y jóvenes en USA



http://apps.who.int/iris/bitstream/handle/10665/78102/WHO_HSE_PHE_IHE_2013.1_eng.pdf;jsessionid=F91A21A966D62CF2292FD36FE61A1C95?sequence=1



Evolución del número de casos de sobrepeso



http://apps.who.int/iris/bitstream/handle/10665/78102/WHO_HSE_PHE_IHE_2013.1_eng.pdf;jsessionid=F91A21A966D62CF2292FD36FE61A1C95?sequence=1



¿Qué es el Bisfenol A?

Bisphenol A (BPA) is a crystalline, prilled or flake material with a slightly phenolic odour.

TECHNOLOGY

BPA is produced by the condensation of phenol and acetone in the presence of an acid catalyst (hydrogen chloride) and usually a promoter such as methyl mercaptan. Cationic ion exchange resins can replace the acid catalyst in newer plants. After the reaction and recovery of acid and phenol, the BPA is washed with water, neutralised with milk of lime and distilled under vacuum. Newer processes employ distillation and extractive crystallisation under pressure to purify the BPA. Two grades are produced: one for epoxy resin production and a higher purity grade for PC manufacture.



Para qué

A- production of polycarbonate (PC), which accounts for about 65% of consumption: Manufacture of modern optical media, such as DVDs and CDs, sports equipment, medical and dental devices, building and construction materials, automotive parts and domestic appliances, as well as food containers, such as reusable beverage bottles and some manufacturing equipment .

B- epoxy resins, responsible for roughly 30% of consumption.

C- Other uses include:

- flame retardants (mainly tetrabromobisphenol A)
- unsaturated polyester resins and polyacrylate,
- thermal papers, (exposure of cashiers in frequent contact with thermal paper in receipts)
- polyetherimide and polysulphone resins.

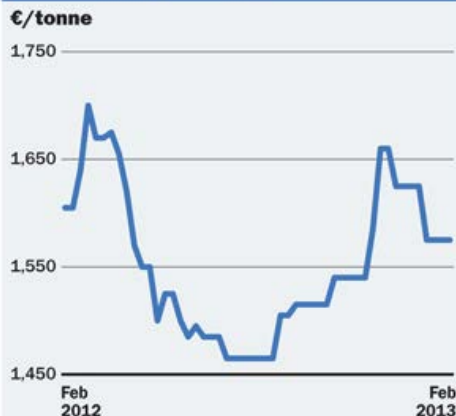


¿Quién? (1)

SABIC Innovative Plastics	Bergen op Zoom, the Netherlands	180
Momentive Specialty Chemicals	Pernis, the Netherlands	160
Kumho P&B Chemicals (KPB)	Yosu, South Korea	150
PTT Phenol	Map Ta Phut, Thailand	150
Momentive Specialty Chemicals	Deer Park, US	140
Nan Ya Plastics	Mailiao, Taiwan	130
Vinmar International	Haverhill, US	110
Dow Chemical	Stade, Germany	100
SABIC Innovative Plastics	Burkville, US	75

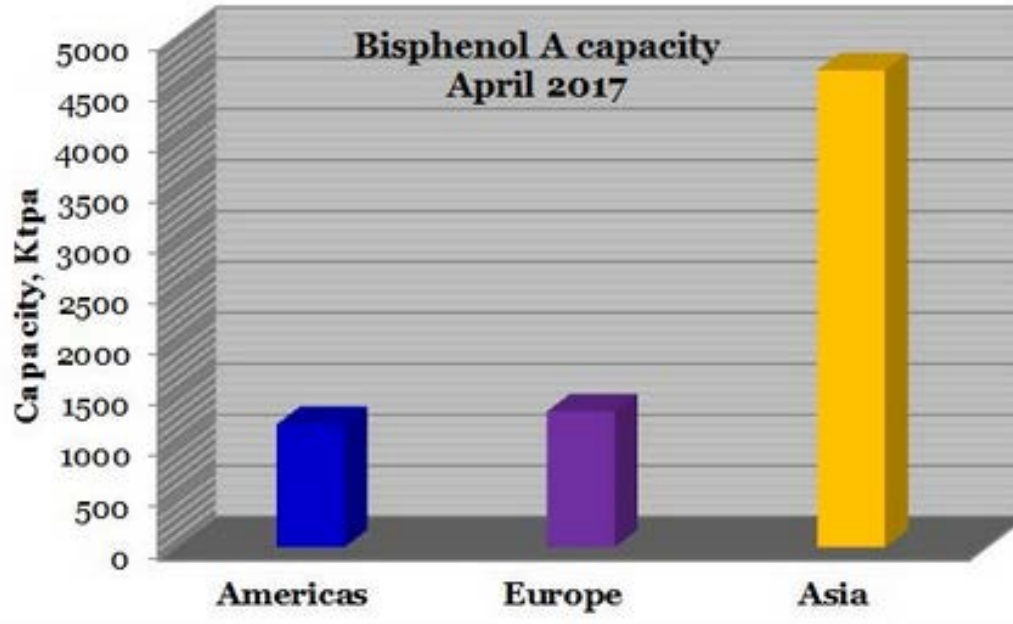
GLOBAL BPA CAPACITY '000 TONNES/YEAR		
Company	Location	Capacity
SABIC Innovative Plastics	Cartagena, Spain	340
LG Chem	Yosu, South Korea	300
Bayer	Krefeld, Germany	270
Chang Chun Petrochemical	Kaohsiung, Taiwan	270
Saudi Kayan Petrochemical	Al-Jubail, Saudi Arabia	270
SABIC Innovative Plastics	Mount Vernon, US	265
Mitsui Chemicals Asia Pacific	Sakra, Singapore	230
Bayer	Baytown, US	190
Dow Chemical	Freeport, US	190
Bayer Polymers	Map Ta Phut, Thailand	190

EUROPE BPA, SPOT PRICES



¿Quién? (2)

Bisphenol A is among the highest volume of chemicals produced world-wide

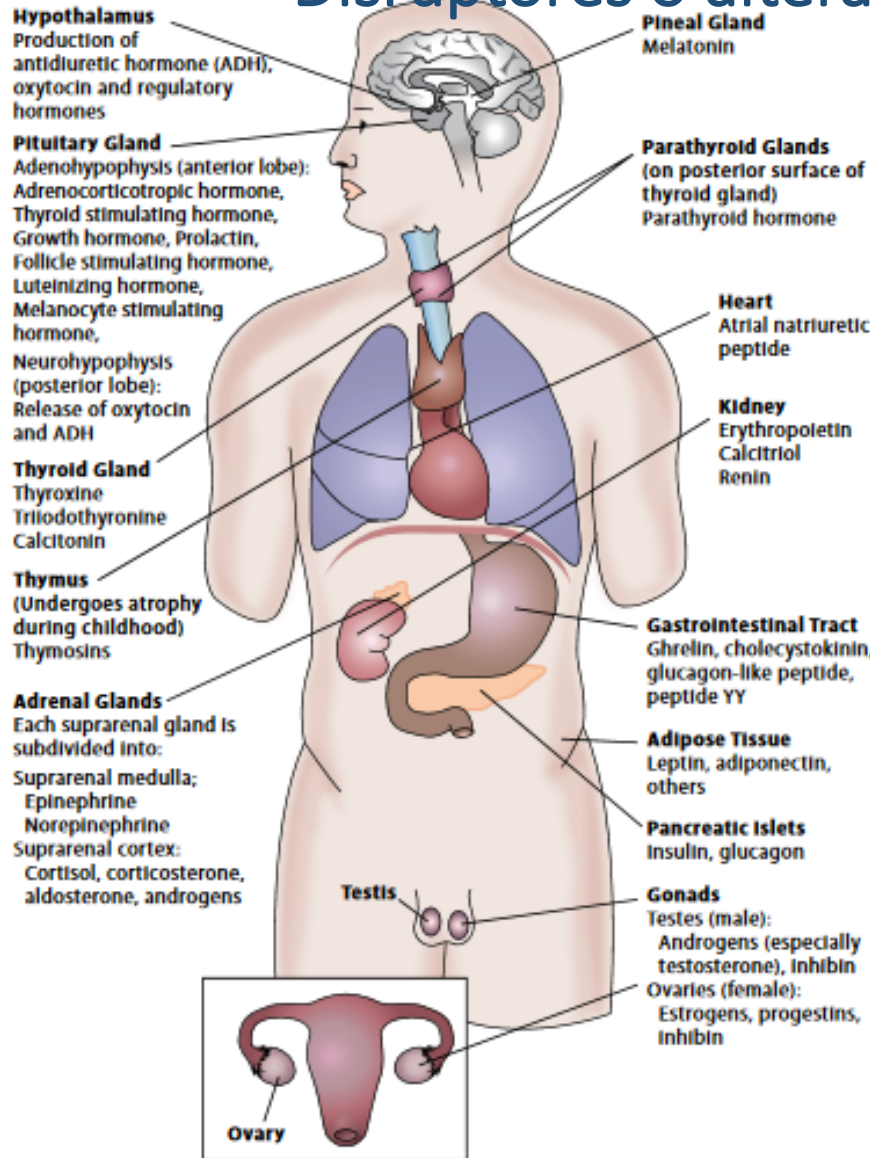


Capacidad global: 8 millones de Tm/año

Precios: Entre 900 y 2000 US\$/Tm

Mercado Mundial: Unos 12 billones de US\$/año

Disruptores o alteradores endocrinos



Las hormonas son sustancias producidas por los tejidos endocrinos, como los ovarios, los testículos, las suprarrenales, la pituitaria o el páncreas, que se liberan en la sangre para actuar como mensajeros químicos, dirigiendo la comunicación y la coordinación entre otros tejidos del organismo.

Las hormonas actúan sobre receptores de las células de destino. Estos receptores son específicos para cada hormona

Esquema del Sistema endocrino: Glándulas endocrinas y algunos ejemplos de las hormonas que producen



Un **disruptor o alterador endocrino** es una sustancia exógena o mezcla que altera funciones del sistema endocrino y en consecuencia causa trastornos de la salud en un organismo intacto, en su progenie o en sub-poblaciones del mismo

Un **disruptor endocrino potencial** es una sustancia exógena o mezcla que tiene propiedades que cabe esperar que lleven a una disrupción endocrina en un organismo intacto, en su progenie o en sub-poblaciones

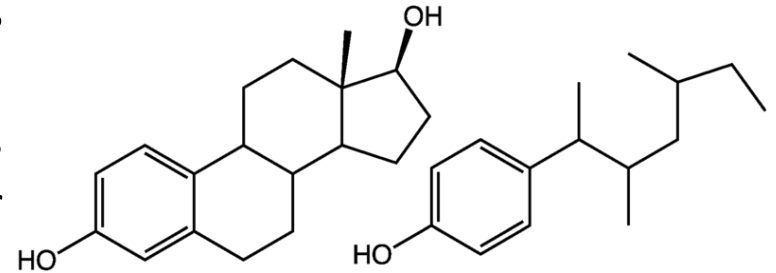
Disruptores endocrinos: Base estructural

Pueden ser compuestos que se dan en la naturaleza o sustancias artificiales. Imitan o interfieren con las funciones de las hormonas en el organismo.

Pueden activar, desactivar o modificar las señales transmitidas por las hormonas y alterar así las funciones normales de tejidos y órganos.

Se los ha relacionado con problemas del desarrollo, la reproducción, inmunológicos, neuronales, inmunológicos y otros. En animales salvajes y en el laboratorio.

Algunas investigaciones sugieren que estas sustancias afectan de formas similares a la salud humana con resultados como fertilidad reducida y aumento de las frecuencias de algunas enfermedades como obesidad, diabetes, endometriosis y algunos cánceres (por ejemplo, de mama y de próstata)

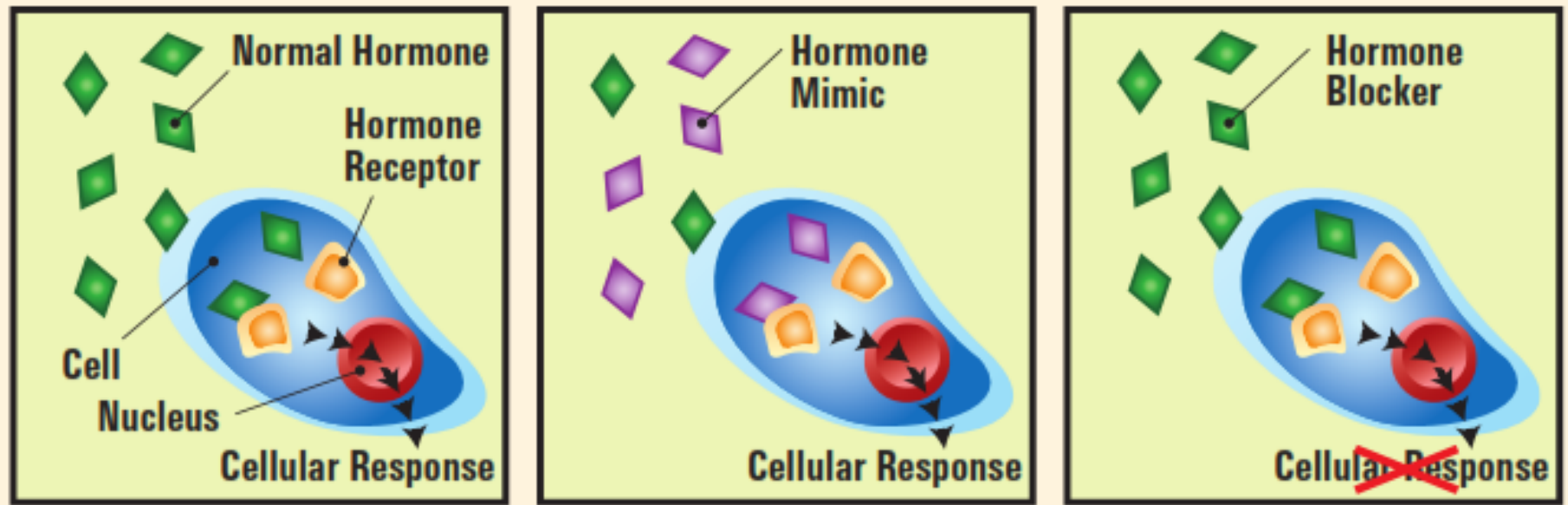


A comparison of the structures of the natural hormone [estradiol](#) (left) and one of the [nonyl-phenols](#) (right), an endocrine disruptor

http://en.wikipedia.org/wiki/Endocrine_disruptor



Mecanismos de acción de los disruptores endocrinos



Una vez absorbido por el organismo, el disruptor endocrino puede reducir o aumentar el nivel normal de hormonas (izquierda), imitar la producción de hormona natural (centro) o alterar la producción normal de hormonas (derecha)

Enfermedades relacionadas con la exposición a los alteradores endocrinos

• Reproductive/endocrine

- Breast/prostate cancer
- Endometriosis
- Infertility
- Diabetes/metabolic syndrome
- Early puberty
- Obesity

• Immune/autoimmune

- Susceptibility to infections
- Autoimmune disease

• Cardiopulmonary

- Asthma
- Heart disease/hypertension
- Stroke

• Brain/nervous system

- Alzheimer disease
- Parkinson disease
- ADHD/learning disabilities

Algunos alteradores endocrinos preocupantes

Alterador	Principales vías de exposición
Bisfenol A (BPA)	Artículos en contacto con alimentos. Papel térmico
Dioxinas	Alimentos en general. Más en los de origen animal
Atrazina	Herbicida. Básicamente es un riesgo ocupacional.
Ftalatos	Envases y artículos en contacto con alimentos
Perclorato	Agua de consumo humano. Compite con el yodo
Retardantes de llama	(Bifenilos polibromados) Tejidos, alfombras
Plomo	Pigmentos en pinturas viejas de edificios
Arsénico	Agua de consumo humano
Mercurio	Alimentos. Sobre todo, pescado
Compuestos perfluorados	Superfs. antiadherentes (Utensilios, tejidos, muebles)
Pesticidas organofosforados	Pesticidas en agricultura
Éteres de glicoles	Productos de limpieza



Contaminantes químicos preocupantes

The first list of HBM4EU priority substances includes:

- **Aniline family**
- **Bisphenols**
- **Cadmium and chromium VI**
- **Chemical mixtures**
- **Emerging substances**
- **Flame retardants**
- **PAHs**
- **Per-/poly-fluorinated compounds**
- **Phthalates and Hexamoll® DINCH**

<https://www.hbm4eu.eu/the-substances/>



Peligros asociados con el Bisfenol A

Bisphenol A could be associated with increased risk for:

- **Fetal development: miscarriages, decreased birth weight at term,**
- **Reproductive and sexual dysfunctions,**
- **Breast and prostate cancer or at least significant breast tissue remodelling.**

Studies have indicated that those effects were associated with gestational and neonatal exposure

- **Altered immune system activity,**
- **Obesity and metabolic dysfunctions and diabetes in adults,**
- **Cardiovascular disease in adults**
- **Cognitive and behavioural development in young children.**

Despite the wealth of studies, there are still controversies concerning the toxic effects of BPA. Those are related to some lack of reproducibility of the experimental studies possibly due to different designs.



Bisfenol A clasificado como disruptor endocrino

Helsinki, 16 June 2017 - The Member State Committee unanimously agreed on the identification as substances of very high concern (SVHCs) of:

- **4,4'-isopropylidenediphenol (bisphenol A, BPA)** (EC 201-245-8, CAS 80-05-7), proposed by France, due to its endocrine disrupting properties for human health;
- **Perfluorohexane-1-sulphonic acid and its salts (PFHxS)**, proposed by Sweden, due to their very persistent and very bioaccumulative (vPvB) properties.

Bisphenol A is already listed in the Candidate List due to its toxic for reproduction properties.

[Regulation \(EC\) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals \(REACH\).](#)

<https://echa.europa.eu/-/msc-unanimously-agrees-that-bisphenol-a-is-an-endocrine-disruptor>



Vías de exposición

There is evidence that contamination can occur through different routes, including food, water, air and skin (particularly in occupational exposure of cashiers).



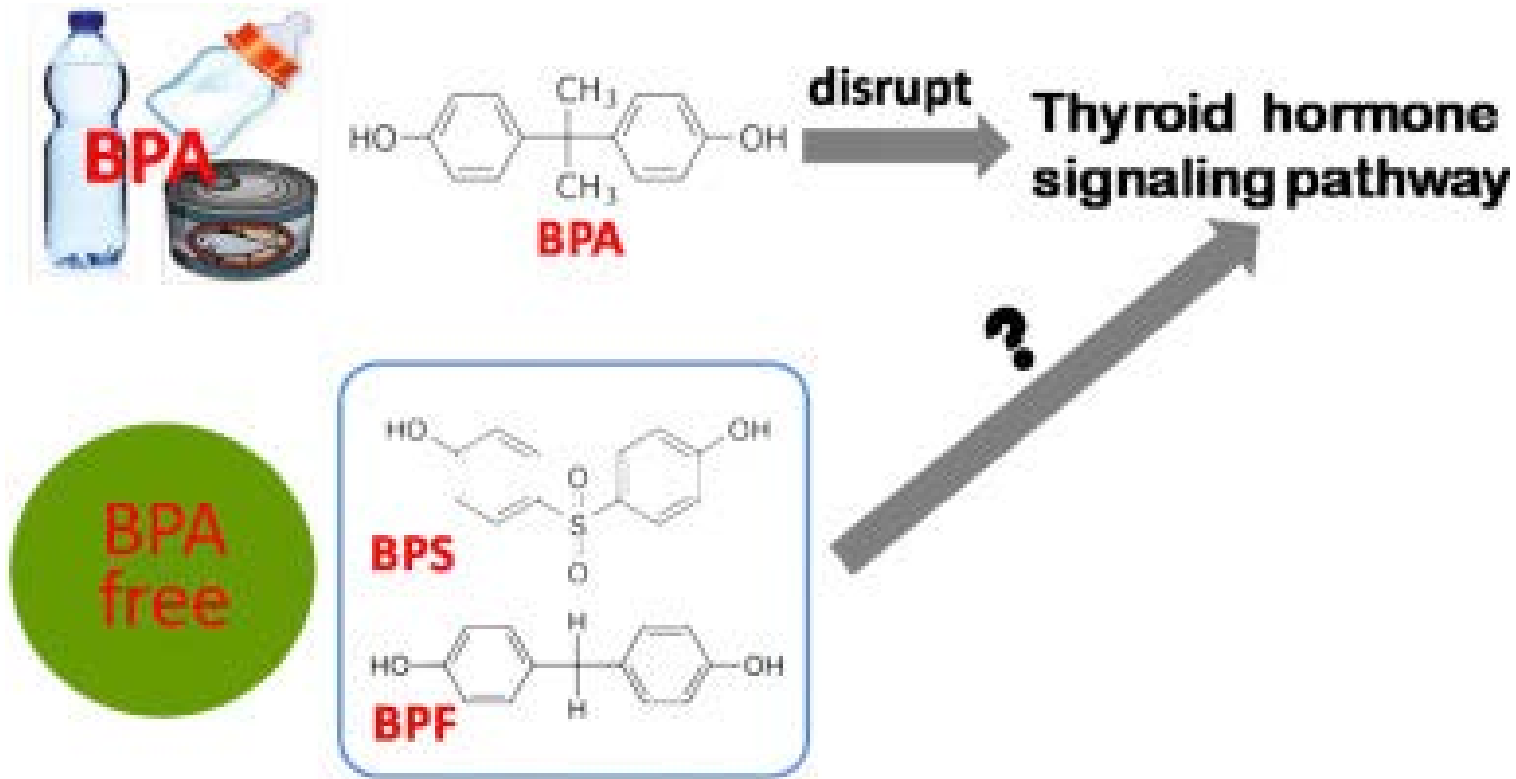
Alternativas para substituir al bisfenol A (BPA):

- Substituir directamente el BPA por otra substancia
- Substituir el plástico del que el BPA es un componente, por otro plástico con propiedades funcionales parecidas (Por ej. Copoliester);
- Substituir por otro tipo de material (Vidrio, metal, etc) o por otro tipo de envase (Por. Ej tetrabrick);
- Substituir por un proceso diferente (Ej: Pagos sin contacto, con el recibo pasado directamente al teléfono)

<https://www.anses.fr/en/content/potential-alternatives-bisphenol>



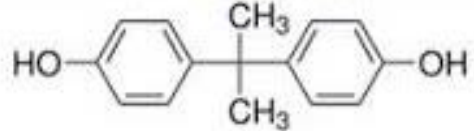
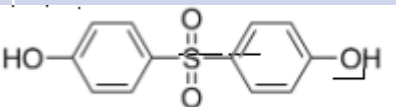
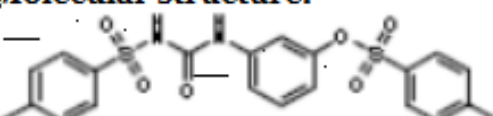
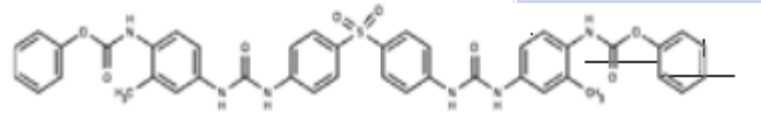
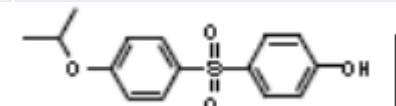
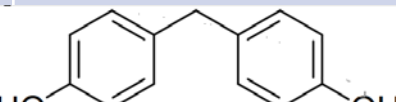
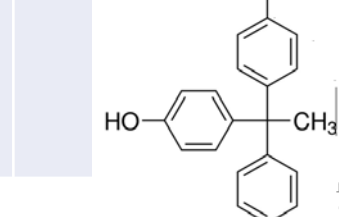
Posibles alternativas para el Bisfenol A



“These results for the first time demonstrate that BPS and BPF, like BPA, have potential to interfere with TH signaling pathway”

Yin-FengZhang et al. (2018) "Bisphenol A alternatives bisphenol S and bisphenol F interfere with thyroid hormone signaling pathway in vitro and in vivo", Environmental Pollution, Volume 237, June 2018, Pages 1072-1079

Algunos miembros de la familia de los bisfenoles

Bisfenol A		4,4'-(propane-2,2-diyl)diphenol
Bisfenol S		4,4'-Sulfonyldiphenol
Pergafast 201		N-(p-Toluenesulfonyl) -N'-(3- p-toluenesulfonyloxyphenyl)urea
Urea urethane compound (UU)		
D-8		
Bisfenol F		Bis(4- hydroxyphenyl) methane
Bisphenol AP, BPAP		4,4''-(1- Phenylethylidene) bisphenol

Sustitutivos de Bisfenol A en papel térmico: Precios

Category of alternative paper	Source 1 (manufacturer)	Source 2 (manufacturer)	Source 3 (distributor)	Source 4 (manufacturer)
BPA free (lowest price)	bisphenol S 5-10% more	BPA free 5% more	BPA free 20-30% more	bisphenol S 10-12% more
Bisphenol free (medium price)	D-8 and D-90 a bit more expensive than bisphenol S but cheaper than Pergafast	Bisphenol free 15-20% more	Bisphenol free 30-40% more	
Phenol free (highest price)	Pergafast >10% more	Phenol free 20-25% more		


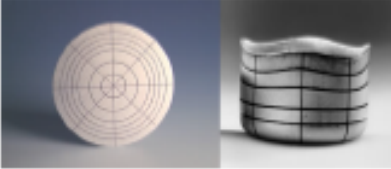
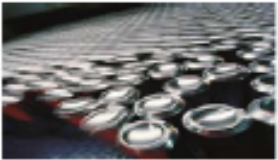



Enfoque de los fabricantes de papel térmico

EU paper manufacturers have started to substitute BPA with BPS, The amount of BPS used as developer in thermal paper on the EU market almost doubled between 2016 and 2017. Reflecting the overall increase in the use of thermal paper in the EU in 2017, BPA use also increased in the same time period. (ECHA's Risk Assessment Committee in its opinion on BPA indicated that BPS *"is suspected to have many of the same adverse health effects as BPA"*)







Barnices: Características funcionales

Feature	Description	Implication
Chemical Resistance 	Coatings must withstand a wide variety of food types from very acidic peppers to mild products such as beans	Coatings can keep food safe for several years. A failure could lead to corrosion and ultimately food spoilage
Flexibility 	Coatings must be able to withstand the forming of the can or end after application	Flexible - allows for unique can designs that enable metal reduction. Corrosion could result if the coating is not flexible enough
Application 	Coatings must be applied at high speed levels	Higher application speeds result in increased productivity for the customer
Process-ability 	Coatings must be able to withstand heat and pressure for cooking or retort	Retorting sterilizes the packed food ensuring food safety

<https://www.google.ch/url?sa=t&rct=j&q=&esrc=s&source=web&cd=7&cad=rja&uact=8&ved=0ahUKEwiltubd6KTNAhUFPhQKHcmID6sQFgg-MAY&url=http%3A%2F%2Fphx.corporate-ir.net%2FExternal.File%3Fitem%3DUGFyZW50SUQ9NTA5MzE5fENoaWxkSUQ9NTUxNzQ1fFR5cGU9MQ%3D%3D%26t%3D1&usg=AFQjCNGXJt0IfWHlqwECmla7SwKRCMmjuA>



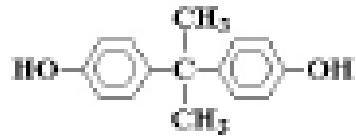
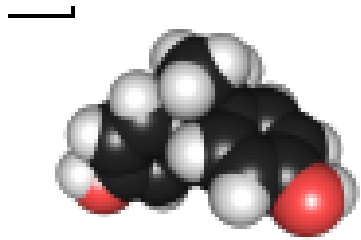
Barnices: Formas de aplicación

	3 Piece Food 	2 Piece Food 	2 Piece Beverage 	Monobloc 
Metal Thickness	200 microns 0.008 inches	175 microns 0.007 inches	150 microns 0.006 inches	350 microns 0.014 inches
Substrate Used	100% Steel	90% Steel 10% Aluminum	75% Aluminum 25% Steel (NA 100% Al)	100% Aluminum
Coatings Application Method	Rollcoat – Flat sheet	Interior – Spray	Interior – Spray Exterior - Rollcoat	Interior – Spray Exterior - Rollcoat
Reason Utilized	Aggressive food products	Lowest cost - best for low/medium aggressive foods	Lowest cost (materials & efficiency)	Beverage design aerosol – higher end packages/designs

<https://www.google.ch/url?sa=t&rct=j&q=&esrc=s&source=web&cd=7&cad=rja&uact=8&ved=0ahUKEwiltubd6KTNAhUFPhQKHcmID6sQFgg-MAY&url=http%3A%2F%2Fphx.corporate-ir.net%2FExternal.File%3Fitem%3DUGFyZW50SUQ9NTA5MzE5fENoaWxkSUQ9NTUxNzQ1fFR5cGU9MQ%3D%3D%26t%3D1&usg=AFQjCNGXJt0IfWHlqwECmla7SwKRCMmjuA>

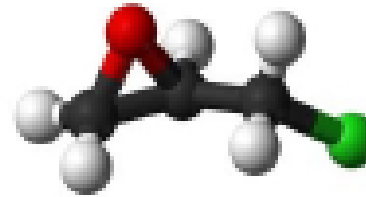


Resinas epoxi: Obtención

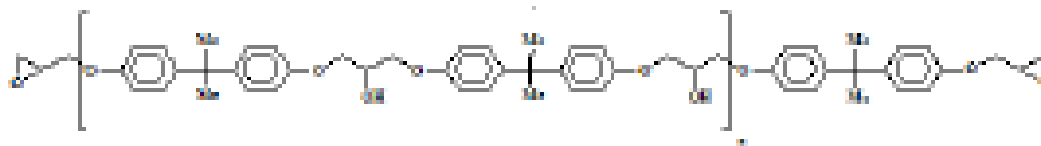


Bisphenol A

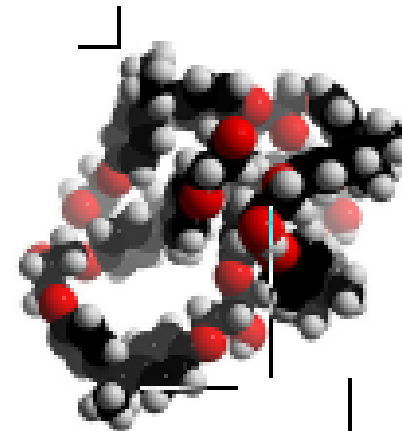
+



Epichlorohydrin



Epoxy



Epoxy coatings

In the 1950s, epoxy resins were introduced as coatings for aluminum and steel cans. Their stability, protective function, and technical properties made them the most commonly used coating material. Most epoxy coatings are synthesized from bisphenol A (BPA, CAS 80-05-7) and epichlorohydrin forming bisphenol A-diglycidyl ether epoxy resins. Many different blends of epoxy coatings were developed with epoxy-phenolic coatings being the most important subgroup. Other blended resins are e.g. epoxy amines, acrylates, and anhydrides.

Oleoresins

First can coatings were made of oleoresins, which are mixtures of oil and resin extracted from plants. Oleoresins are rather flexible and easily applied, but do not adhere well to metal surfaces, have a limited corrosion resistance, and need long curing times. Furthermore, they may change the organoleptic properties of food.

<https://www.foodpackagingforum.org/food-packaging-health/can-coatings>



Phenolic

Phenolic resins are composed of phenols and aldehydes. They are highly corrosion resistant and protect cans from sulfide staining. Phenolics have low flexibility, do not adhere well to metal, and may change the odor and flavor of foods. They are applied as coatings for drums and pails, but unblended phenolic resins are not used in food and beverage cans. However, phenolics are common crosslinkers (e.g. in epoxide resins) and increase their resistance.

Acrylic

Acrylic resins are most commonly synthesized from ethylacrylate. They have a clean appearance and display corrosion and sulfide stain resistance, but they are brittle and may change the taste and odor of foods.

Polyester

Isophthalic acid (IPA) and terephthalic acid (TPA) are the main carboxylic acids used in polyester coatings. Polyester resins are easy to handle during the production process and adhere well to the metal surface, but they are usually not stable under acidic conditions and have a poor corrosion resistance. Alternatively, polyethylene terephthalate (PET) coatings are used to laminate beverage cans, but adhesives are needed to bind the PET onto the metal.



Vinyl

Vinyl coatings are synthesized from vinyl chloride and vinyl acetate. They are highly flexible and stable under acidic and alkaline conditions, but they do not adhere well on metal and do not withstand at high temperatures. Vinyl coatings need plasticizers and stabilizers and are often blended with other resins. Vinyl organosols are prepared from suspensions of resin in organic solvent. Organosols offer comparably higher chemical resistance, thermal stability, and adhesion properties than vinyl coatings.

Phenolic

Phenolic resins are composed of phenols and aldehydes. They are highly corrosion resistant and protect cans from sulfide staining. Phenolics have low flexibility, do not adhere well to metal, and may change the odor and flavor of foods. They are applied as coatings for drums and pails, but unblended phenolic resins are not used in food and beverage cans. However, phenolics are common crosslinkers (e.g. in epoxide resins) and increase their resistance.

Polyolefins

Coatings that are based on dispersions of polyolefins have recently entered the market. According to the manufacturer, the final polyolefin coating exhibits corrosion protection, adhesion, and flexibility without impacting the flavor of the food.



Enfoque de los fabricantes de envases metálicos

At least 90% of today's food cans have replaced linings that previously contained the controversial chemical bisphenol-A (BPA), according to the Can Manufacturers Institute.

“Food can linings now are typically made from acrylic and polyester. And all new materials are extensively tested and are cleared by regulatory agencies before being sold in the market.”

<https://www.packagingdigest.com/food-packaging/most-food-cans-no-longer-use-bpa-in-their-linings-2018-02-20>

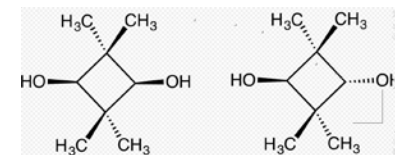


Enfoque de los fabricantes de policarbonato: Copoliésteres

Polyester / Copolyester ⇄	Diacid (s) ⇄	Diol (s) ⇄
PET	Terephthalic acid (TPA)	Ethylene glycol (EG)
PCTG	TPA	<u>Cyclohexanedimethanol (CHDM)</u> +EG
PCTA	TPA + isophthalic acid (IPA)	CHDM
PETG	TPA	CHDM+EG
PCT	TPA	CHDM

**Tritan (Eastman
Chemical Company)**

2,2,4,4-Tetramethyl-1,3-cyclobutanediol (CBDO)



Enfoque de los fabricantes de policarbonato: Marco legal en Europa

Commission Directive [2002/72/EC](#) of 6 August 2002 relating to plastic materials and articles intended to come into contact with foodstuffs [[See amending acts](#)].

SUMMARY

Scope

The Directive applies to plastic materials and articles intended to come into contact with foodstuffs. Such materials and articles, and parts thereof, may be composed either of plastic material only or of several layers of plastic material or of different types of materials.

Approved substances

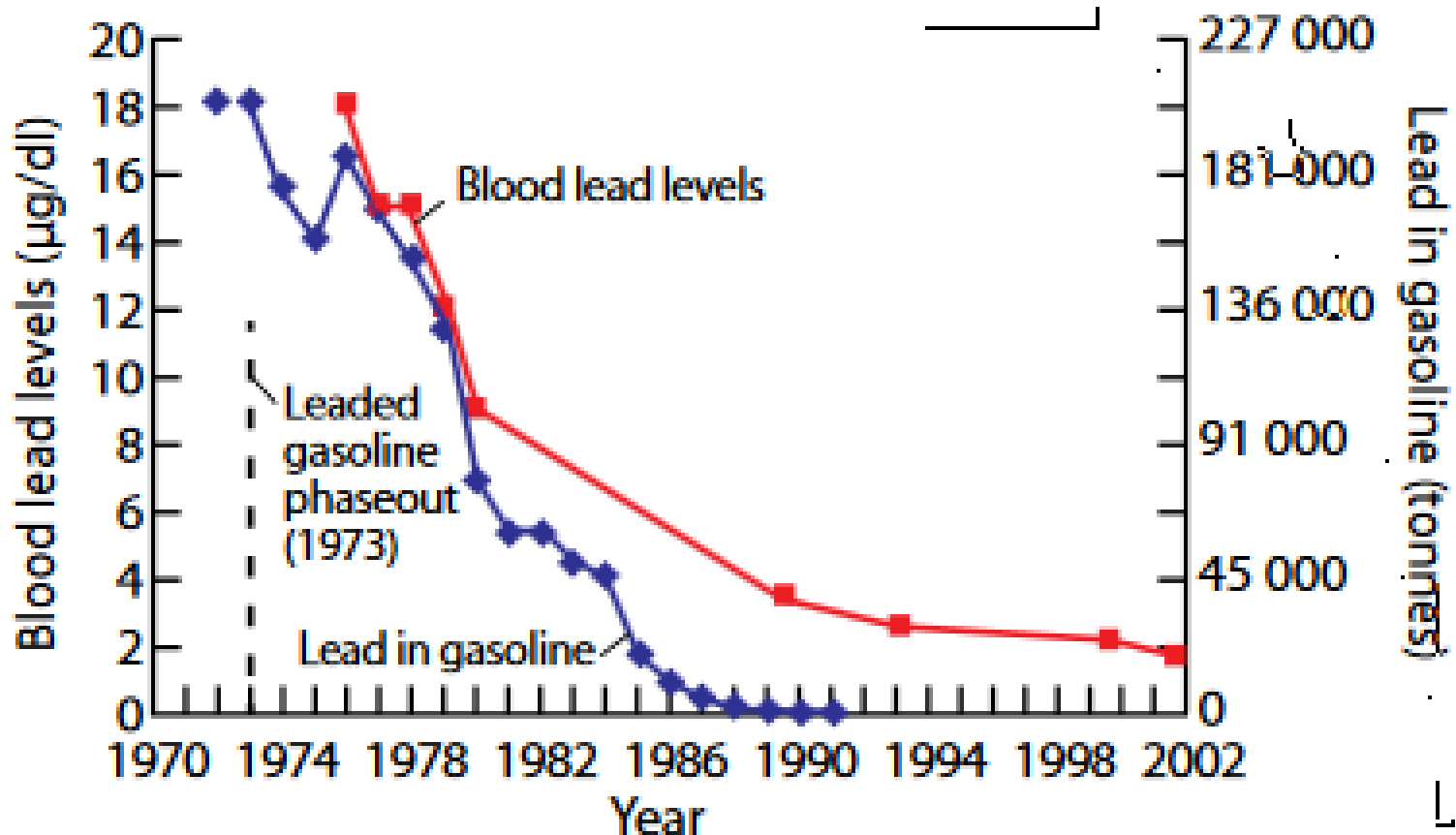
Monomers and other starting substances which may be used in the manufacture of plastic materials and articles (Annex II);

Additives which may be used in the manufacture of plastic materials and articles (Annex III). At the moment a new additive can always be included in the list after evaluation and authorisation by the [European Food Safety Authority](#) (EFSA).



¿Qué hacer? ¿Sería efectivo prohibir el Bisfenol A?

No parece fácil establecer una relación tan clara para el Bisfenol A porque sus efectos forman parte de los del resto de disruptores endocrinos.



http://apps.who.int/iris/bitstream/handle/10665/78102/WHO_HSE_PHE_IHE_2013.1_eng.pdf;jsessionid=F91A21A966D62CF2292FD36FE61A1C95?sequence=1

