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**Matters related to the implementation of the
Convention: implementation plans**

**Preliminary draft guidance on alternatives to
decabromodiphenyl ether**

Note by the Secretariat

As is mentioned in the note by the Secretariat on the implementation plans (UNEP/POPS/COP.9/11), the annex to the present note sets out preliminary draft guidance on alternatives to decabromodiphenyl ether (decaBDE). The present note, including its annex, has not been formally edited.

* UNEP/POPS/COP.9/1.

Annex

**Preliminary draft guidance on
alternatives to decabromodiphenyl
ether (decaBDE)**

February 2019

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List of acronyms and abbreviations

ATH	Aluminum trihydroxide
ATO	Antimony oxide
BDP/BAPP	Bisphenol A bis(diphenyl phosphate)
BFR	Brominated flame retardant
BSEF	Bromine Science and Environmental Forum
C-decaBDE	Commercial decabromodipheyl ether
DBDPE	Decabromodiphenyl ethane
DecaBDE	Decabromodiphenyl ether
DEFRA	Department for Environment, Food and Rural Affairs
DME	Danish Ministry of the Environment
EBTBP	Ethylene bis(tetrabromophthalimide)
ECHA	European Chemicals Agency
EEE	Electronic and electrical equipment
EPA	Environmental Protection Agency
EU	European Union
EVA	Ethylene-vinyl acetate
IEC	International Electrotechnical Commission
LCSP	Lowell Center for Sustainable Production
MDH	Magnesium hydroxide
NTP	National Toxicology Program
PA	Polyamide/nylon
PAEK	Polyaryletherketone
PES	Polyethersulphone
ppm	Parts per million
PVC	Polyvinyl chloride
PBTE	Poly(butylene terephthalate)
RDP	Resorcinol bis(diphenylphosphate)
RPA	Risk and Policy Analysts
TBBPA	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate
TPP	Triphenyl phosphate
UL	Underwriters' Laboratories Inc.
UNEP	United Nations Environment Programme

1. Introduction

1.1 Listing of decabromodiphenyl ether in Annex A

In 2017, by decision SC-8/10, the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants (POPs) amended Annex A to the Convention to list decabromodiphenyl ether (BDE-209) present in commercial decabromodiphenyl ether (c-decaBDE) with specific exemptions (Table 1), i.e. time limited exemption.

Like all POPs, this chemical possesses toxic properties, resist degradation, and bioaccumulate. It is transported through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems. Information risks of decaBDE can be found in the risk profile of decaBDE (UNEP/POPS/POPRC.10/10/Add.2 and UNEP/POPS/POPRC.11/INF/5).¹

All uses for decaBDE other than those listed as specific exemptions are prohibited because alternatives are readily available. Information on alternatives to decaBDE for the uses not allowed as specific exemptions can be found in the risk management evaluation of decaBDE (UNEP/POPS/POPRC.11/10/Add.1 and UNEP/POPS/POPRC.11/INF/6).²

C-decaBDE is a general-purpose additive flame retardant compatible with a wide variety of materials. Applications include plastics/polymers/composites, textiles, adhesives, sealants, coatings and inks. End uses in plastics/polymers include housings of computers and TV sets, wires and cables, pipes and carpets. BDE-209 is also found in products made from recycled plastics, including food contact materials. In the textile sector, c-decaBDE is used to treat a wide range of synthetic, blended and natural fibres. Main end uses include upholstery, window blinds, curtains, mattress textiles, tentage (e.g. military tents and textiles, commercial marquees, tents, canvasses) and transportation (e.g. interior fabrics in cars, rail passenger rolling stock and aircraft).

Globally up to 90% of c-decaBDE ends up in plastics, primarily in electronics, while the remaining ends up in coated textiles, upholstered furniture and mattresses.

Table 1: Specific exemptions for decabromodiphenyl ether (BDE-209) present in commercial decabromodiphenyl ether

Chemical	Activity	Specific exemption
Decabromodiphenyl ether (BDE-209) present in commercial decabromodiphenyl ether (CAS No: 1163-19-5)	Production	As allowed for the Parties listed in the Register
	Use	<p>In accordance with Part IX of Annex A:</p> <ul style="list-style-type: none"> • Parts for use in vehicles specified in paragraph 2 of Part IX of Annex A • Aircraft for which type approval has been applied for before December 2018 and has been received before December 2022 and spare parts for those aircraft • Textile products that require anti-flammable characteristics, excluding clothing and toys • Additives in plastic housings and parts used for heating home appliances, irons, fans, immersion heaters that contain or are in direct contact with electrical parts or are required to comply with fire retardancy standards, at concentrations lower than 10 per cent by weight of the part • Polyurethane foam for building insulation

¹ <http://chm.pops.int/tabid/5985/Default.aspx>; <http://chm.pops.int/tabid/3778/Default.aspx>.

² <http://chm.pops.int/tabid/5985/Default.aspx>; <http://chm.pops.int/tabid/4558/Default.aspx>.

Specific exemptions for parts for use in vehicles may be available for the production and use of decaBDE limited as presented in Table 2 below.

The specific exemptions for spare parts for aircraft for which type approval has been applied for before December 2018 and has been received before December 2022 shall expire at the end of the service life of those aircraft.

Table 2: Specific exemptions for parts for use in vehicles

Specific exemption	Application	Expire date
(a) Parts for use in legacy vehicles, defined as vehicles that have ceased mass production, and with such parts falling into one or more of the following categories:	<ul style="list-style-type: none"> (i) Powertrain and under-hood applications such as battery mass wires, battery interconnection wires, mobile air-conditioning (MAC) pipes, powertrains, exhaust manifold bushings, under-hood insulation, wiring and harness under hood (engine wiring, etc.), speed sensors, hoses, fan modules and knock sensors; (ii) Fuel system applications such as fuel hoses, fuel tanks and fuel tanks under body; (iii) Pyrotechnical devices and applications affected by pyrotechnical devices such as air bag ignition cables, seat covers/fabrics (only if airbag relevant) and airbags (front and side); (iv) Suspension and interior applications such as trim components, acoustic material and seat belts. 	At the end of the service life of legacy vehicles or in 2036, whichever comes earlier
(b) Parts in vehicles specified in paragraphs (a) (i)–(iv) above and those falling into one or more of the following categories:	<ul style="list-style-type: none"> (i) Reinforced plastics (instrument panels and interior trim); (ii) Under the hood or dash (terminal/fuse blocks, higher-amperage wires and cable jacketing (spark plug wires); (iii) Electric and electronic equipment (battery cases and battery trays, engine control electrical connectors, components of radio disks, navigation satellite systems, global positioning systems and computer systems); (iv) Fabric such as rear decks, upholstery, headliners, automobile seats, head rests, sun visors, trim panels, carpets. 	At the end of the service life of vehicles or in 2036, whichever comes earlier

1.2 Objective of the guidance

This guidance document compiles chemical alternatives and non-chemical alternatives to decaBDE, mainly for the uses listed as specific exemptions in Annex A to the Convention (Table 1). Parties may wish to consider the information available in this guidance when phasing-out the use of decaBDE.

The guidance was prepared based on the information contained in the documents adopted by the POPs Review Committee (UNEP/POPS/POPRC.11/10/Add.1 and UNEP/POPS/POPRC.11/INF/6). Other reports and information on alternatives to c-decaBDE have also been taken into account.

2. Alternatives to decaBDE

There are several assessments of alternatives to c-decaBDE/BDE-209 focusing on various chemicals with flame retardant properties. The first step of such assessment could be to determine whether flame retardancy is needed, and if so, how it can be achieved without adverse environmental and human health consequences, before considering chemical substitutes (UNEP/POPS/POPRC.11/10/Add.1). Alternative techniques such as using inherently fire-resistant materials, adding fire-resistant barriers, or completely redesigning the product can greatly improve fire safety (ECHA, 2015; USEPA, 2014). Alternatives that eliminate the need for chemical flame retardants through material substitution or design while meeting relevant fire safety standards and performance requirements are preferable, especially when they include chemicals of low toxicity and contain recyclable or compostable materials (UNEP/POPS/POPRC.11/INF/6).

Furthermore, some fire safety requirements leading to the use of flame retardants may need to be re-evaluated. For instance, the state of California, whose Technical Bulletin 117 had led to added flame retardants in furniture for decades, passed Assembly Bill 2998 in September 2018 (California, 2018). The Assembly Bill 2998 states that “The State of California has found that flame retardant chemicals are not needed to provide fire safety,” in a range of applications and bans the sale or distribution in commerce in California on or after 1 January 2020, of any “not previously owned juvenile products, mattresses, or upholstered furniture” containing flame retardants that are “halogenated, organophosphorus, organonitrogen, or nanoscale” chemicals at levels above 1,000 ppm.

In some cases, however, a chemical substitute for decaBDE is needed. The USEPA and ECHA have published comprehensive assessments of 29 and 13, respectively, chemical alternatives to c-decaBDE (USEPA, 2014; ECHA, 2015). Other brominated flame retardants (BFRs) could act as drop-in replacements for many of the known c-decaBDE applications (ECHA, 2015; USEPA, 2014). Viable non-halogenated flame retardants and polymer combinations have also been identified as alternatives for most c-decaBDE uses, and some may even have better performance than c-decaBDE (ENFIRO, 2013; Table 8, UNEP/POPS/POPRC.11/INF/6). However, while chemical alternatives are readily available for all uses of c-decaBDE, some of them also have problematic hazard profiles (ECHA, 2015; USEPA, 2014).

2.1 Plastics (parts for use in vehicles and in aircraft, additives in plastic housings and parts used for heating home appliances, irons, fans, immersion heaters)

2.1.1 Background

Plastics and electronics account for approximately 90% of the use of c-decaBDE. Some plastics must comply with flammability tests such as those established by the International Electrotechnical Commission (IEC) or the Underwriters’ Laboratories Inc. (Keml, 2005). However, although these fire safety regulations are mandatory, none of them require the use of specific flame retardants. It is up to the manufacturers to decide how to achieve compliance.

In the transportation sector, c-decaBDE was used in plastics for electronic and electrical equipment (EEE), reinforced plastics, under the hood, and in inner parts, as well as in the interiors of cars. Most of the fire-retarded plastics used in vehicles are found in the engine compartment and are often polyamides (PA). The firewall between the engine and the cabin is also fire-retarded.

The aviation industry has been using c-decaBDE in electrical wiring and cables, interior components, and EEE components in older airplanes and spacecrafts.

The automotive and aviation industry are phasing out c-decaBDE. However, for service and some legacy spare parts for use in articles already in use, as well as for aircrafts currently in production under existing type certificates require continuous production and use for a certain period (UNEP/POPS/POPRC.11/10/Add.1).

An assessment by the EU (ECHA, 2015) identified various alternative techniques that could replace c-decaBDE in plastics, including chemical alternatives, inherently fire-resistant materials, intumescent systems, nanocomposites, expandable graphite, smoke suppressants, polymer blends, and product redesign. These alternatives techniques are described in detail in Table 14 of document UNEP/POPS/POPRC.11/INF/6.

2.1.2 Alternative materials

Metal or inherently fire-resistant plastics can be used as alternative materials in certain electronic products. New inherently fire-resistant materials are increasingly being mentioned in the literature or on commercial websites,

often promoted as replacements for c-decaBDE (ECHA, 2012; DEFRA, 2010; PR Newswire, 2010; UNEP/POPS/POPRC.11/10/Add.1).

The following plastics are inherently fire-resistant and could replace polymers typically treated with c-decaBDE such as poly(butylene terephthalate) (PBTE) and polyamide/nylon (PA) (DME, 2006):

- (a) Halogen-free polyketone;
- (b) High performance thermoplastics such as polysulphone, polyaryletherketone (PAEK), or polyethersulphone (PES).

Polymers that char, such as polyimides, polyaramides, liquid crystal polyesters, polyphenylene sulphide, polyarylenes, and many thermosets, also tend to have greater fire resistance.

Halogenated polymers such as PVC also have flame retardant properties because they release halogen radicals during combustion. The effect is often enhanced by the addition of synergists such as ATO to halogenated polymer blends. However, like brominated flame retardants, PVC can form dioxins and acids upon combustion, and is therefore not a preferred alternative material (Blomqvist et al., 2007).

2.1.3 Fire barriers

Using fire-resistant metal barriers to separate or isolate the most flammable parts from the rest of the product can eliminate the need for flame retardants such as c-decaBDE (LCSP, 2005).

2.1.4 Intumescent systems

In plastics, like in textiles, fire safety may be achieved via the use of intumescent systems (Klif, 2011; USEPA, 2014). Intumescence is the formation of a foamed char, which acts as heat insulation. An intumescent system is generally a combination of a source of carbon to build up char, an acid-generating compound, and a decomposing compound that generates blowing gases to produce foamed char (Weil and Levchik, 2009). This foam attains a thickness of 10 to 100 times that of the originally applied coating and insulates the substrate material through its low thermal conductivity. This makes intumescent systems efficient at reducing both flammability and exposure to toxic gases and fumes (Keml, 2006). Intumescent systems include use of expandable graphite impregnated foams, surface treatments, and some barrier technologies (Klif, 2011).

2.1.5 Product redesign

Electronic and electrical equipment can be redesigned to eliminate or reduce the need for chemical flame retardants. Possible redesign strategies include:

- (a) Separating the high-voltage components that need greater ignition protection from the low-voltage components;
- (b) Reducing the operating voltage requirements, therefore reducing the need for fire-resistant enclosure materials;
- (c) Separating the power supply from the product, which reduces the fire-retardancy requirements of the electronic enclosure;
- (d) Shielding power supplies with metal to eliminate the need for additive flame retardants.

2.1.6 Chemical alternatives

Flame retardants ideal for plastics must:

- (a) Not alter the mechanical properties of the plastic;
- (b) Not change the colour of the plastic;
- (c) Not cause corrosion;
- (d) Have good light stability;
- (e) Resist aging and hydrolysis;
- (f) Begin their thermal behaviour before the thermal decomposition of the plastic;
- (g) Not have harmful physiological effects;

- (h) Not emit toxic gases, or at least emit them at low levels;
- (i) Be as inexpensive as possible – although function is more important than price for engineering polymers, and typically not the most important factor for alternatives selection (Keml, 2005).

According to the EU restriction proposal, eight chemical flame retardants appear to be possible substitutes for c-decaBDE in plastic polymers (ECHA, 2015):

- (a) Decabromodiphenyl ethane (DBDPE);
- (b) Bisphenol A bis(diphenyl phosphate) (BDP/BAPP);
- (c) Resorcinol bis(diphenylphosphate) (RDP);
- (d) Ethylene bis(tetrabromophthalimide) (EBTBP);
- (e) Magnesium hydroxide (MDH);
- (f) Triphenyl phosphate (TPP);
- (g) Aluminium trihydroxide (ATH);
- (h) Red phosphorous.

2.2 Textile products that require anti-flammable characteristics

2.2.1 Background

C-decaBDE has traditionally been applied to textiles as a back-coating in combination with antimony oxide (ATO) as a synergist (LCSP, 2005). C-decaBDE is first mixed with ATO to form an aqueous dispersion, which is then mixed with a polymer emulsion containing for instance natural or synthetic rubber, ethylene-vinyl acetate (EVA), styrene-butadiene copolymer, or polyvinyl chloride (PVC) (ECHA, 2012). The c-decaBDE-ATO mixture can account for 18 to 27% of the total product weight (LCSP, 2005). Lighter fabrics usually require higher flame retardant loadings. Fire-resistant back-coatings are used on a wide range of fabrics, including polyamide/nylon, polypropylene, acrylics, and blends such as nylon–polyester.

In the US, c-decaBDE is used in textile applications for transportation (e.g., public transit buses, trains, aviation, ships); draperies for public occupational spaces; furniture for high-risk occupational areas (e.g., nursing homes, hospitals, prisons, hotels); military tarps, tents, and protective clothing – but is not used in consumer clothing (LCSP, 2005; BSEF, 2018; USEPA, 2014). However, the use of c-decaBDE in residential upholstery and mattresses is no longer allowed in several states in the US (LCSP, 2015), and the sale of “not previously owned juvenile products, mattresses, or upholstered furniture” containing flame retardants that are “halogenated, organophosphorus, organonitrogen, or nanoscale” chemicals at levels above 1,000 ppm is banned in California as of January 1, 2020 (California, 2018).

In the EU, c-decaBDE is used in domestic draperies and furniture (in foams, fillings, and back-coatings), predominantly in countries with certain fire safety standards such as the UK (ECHA, 2015). In Japan, vehicle seats accounts for 60% of the c-decaBDE use, while an additional 15% is reportedly used for other textile applications (Sakai et al., 2006).

Substitution of c-decaBDE in textiles is not straightforward due to the complexity of the end-products and the wide array of possible substitution approaches. These approaches include alternative flame retardants, alternative fibres, and barrier layers.

2.2.2 Alternative fibres

Natural fibres are easier to chemically flame retard than synthetics. Several non-halogenated c-decaBDE chemical substitutes are available for natural cellulose or protein fibres such as cotton, wool, rayon (viscose, modal, and lyocell), and linen, including:

- (a) Ammonium polyphosphates;
- (b) Dimethylphosphono (N-methylol) propionamide;
- (c) Phosphonic acids such as (3-[[hydroxymethyl]amino]-3-oxopropyl)-dimethyl ester;
- (d) Tetrakis (hydroxymethyl) phosphonium urea ammonium salt.

Furthermore, some natural materials like leather and wool have inherently fire-resistant properties and, depending on the thickness of the weave, can meet fire safety requirements without additional chemical treatment (Klif, 2011; Weber et al. 2018).

Nonwoven fabrics are also inherently fire-resistant, as are a number of synthetic fibres including aramids, viscose, novoloid, polyamides, melamine, and polyester. Some of these fire-resistant fibres, such as polyhaloalkenes, contain PVC, vinyl bromide, and other halogens, while others, such as polyaramides and melamine, are halogen-free (LCSP, 2005; UNEP/POPS/POPRC.11/INF/6).

Some fabrics for upholstery, mattresses, and drapery are made from blends of inherently fire-resistant fibres with fibres of lower flame performance. For instance, cotton is usually blended with polyester ('poly-cotton' blend), nylon, or melamine to reduce its flammability (DEFRA, 2010).

2.2.3 Fire barriers

Fire-resistant barrier layers can be used between the surface fabric and the interior foam core in furniture and mattresses. They fully encapsulate the interior materials and must be combined with fire-resistant border seams, tape, and threads (LCSP, 2005). Fire barriers are made from inherently fire-resistant fibres such as wool, para aramids, melamines, modacrylics, or glass fibre, without the need for flame retardant chemicals. Moreover, many of these fibres are made from non-halogen materials. Some barriers can also be made from blends of inexpensive fibres and expensive inherently fire-resistant fibres. In addition to fibre blends, many manufacturers use cotton-batting materials treated with boric acid. Plastic films have also been used as barriers, especially films made of inherently fire-resistant plastics such as neoprene (polychloroprene) (LCSP, 2005).

2.2.4 Intumescent systems

In textiles, like in plastics, fire safety may also be achieved via the use of intumescent systems (Klif, 2011; USEPA, 2014). Intumescence is the formation of a foamed char, which acts as heat insulation. An intumescent system is generally a combination of a source of carbon to build up char, an acid-generating compound, and a decomposing compound that generates blowing gases to produce foamed char (Weil and Levchik, 2009). This foam attains a thickness of 10 to 100 times that of the originally applied coating and insulates the substrate material through its low thermal conductivity. This makes intumescent systems efficient at reducing both flammability and exposure to toxic gases and fumes (Keml, 2006). Intumescent systems include use of expandable graphite impregnated foams, surface treatments, and some barrier technologies (Klif, 2011).

2.2.5 Chemical alternatives

The following seven substances were identified as the most likely chemical alternatives to the use of c-decaBDE in textiles (ECHA, 2015):

- (a) Aluminum trihydroxide (ATH);
- (b) Magnesium hydroxide (MDH);
- (c) Tris(1,3-dichloro-2-propyl) phosphate (TDCPP);
- (d) Ethylene bis(tetrabromophthalimide) (EBTBP);
- (e) 2,2'-oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane] 2,2'-disulphide;
- (f) Tetrabromobisphenol A bis (2,3-dibromopropyl ether) (TBBPA) (only in polymer applications);
- (g) Red phosphorous;
- (h) Decabromodiphenyl ethane (DBDPE).

Co-polymerization, i.e., including an additive in the fibre melt spinning process, makes the flame-retardant chemical a physical part of the fibre matrix. The most common flame retardant for polyester is polyethylene terephthalate with built-in phosphorus on the polyester backbone. This modified polyester is used in the majority of textile applications, is wash resistant, and is thought to be a good substitute for c-decaBDE-ATO. Polyester accounts for 30% of the world fibre production, with applications including clothing and draperies.

2.3 Polyurethane foam for building insulation

2.3.1 Background

Rigid polyurethane foam has good insulating properties that make it suitable for insulation of walls and roofs in new buildings and when buildings are renovated.

Sprayed polyurethane foam provides weatherproof sealants, forms a seamless layer of insulation, fills gaps and seams during application, and covers irregular, hard-to-insulate shapes (American Chemical Council 2018). Spray polyurethane foam (SPF) insulation can be categorized into two different types: light-density open-cell spray foam insulation and medium-density closed-cell spray foam insulation. Both types of SPF are thermoset cellular plastics. Closed cell spray polyurethane foam insulation forms an air barrier and moisture barrier.

2.3.2 Resin/Material substitution

A variety of insulation materials are used in buildings, each having some advantages for specific applications determining its use, and many with general application (Secretariat of the Stockholm Convention 2017). In terms of market volumes major insulation alternatives are EPS/XPS, mineral wool, and fibre glass wool, but a number of other insulation materials are used to some extent.

Expanded and extruded polystyrene (EPS/XPS)

Expanded and extruded polystyrene (EPS/XPS) are major insulation used in a variety of installations for the entire building envelope.

Expanded polystyrene (EPS) foam is a closed-cell insulation that's manufactured by "expanding" a polystyrene polymer. Extruded polystyrene (XPS) foam is a rigid insulation that's also formed with polystyrene polymer but manufactured using an extrusion process.

Stone wool

Stone wool is made from volcanic rock, typically basalt or dolomite, an increasing proportion of which is recycled material in the form of briquettes. Slag wool is made from blast furnace slag (waste). The stone wool is a subgroup of the mineral wool together with glass wool. Over the last decade, glass wool, rock (stone) wool and slag wool have together met just over half of the world demand for insulation.

The structure and density of the product can be adapted to its precise final usage. Inorganic rock or slag is the main components (typically 98%) of stone wool. The remaining 2% organic content is generally a thermosetting resin binder (an adhesive), usually phenol formaldehyde and a little mineral oil (Secretariat of the Stockholm Convention 2017).

Glass wool (fibre glass insulation)

For glass wool the raw materials are sand, limestone and soda ash, as well as recycled off cuts from the production process. The glass wool is a subgroup of the mineral wool.

Small quantities of binding agents are added to the fibres. Glass wool products usually contain 95% to 96% inorganic material (Eurima 2018).

Phenolic foams

Phenolic foam insulation is made by combining phenol-formaldehyde resin with a foaming agent. In the process phenol is polymerized by substituting formaldehyde on the phenol's aromatic ring via a condensation reaction and a rigid thermoset material is formed (Secretariat of the Stockholm Convention 2017).

Natural fibre-based insulation materials

Various modern insulation materials are based on natural fibres, primarily plant fibres but also sheep wool. Some of these have been known for centuries but have got a renaissance over the last decades with the growing interest for environment friendly building techniques. They are available as loose insulation fill, as insulation batts or/and as rolls. A number of the other natural fibre-based insulation materials have been considered as alternatives (Secretariat of the Stockholm Convention 2017).

2.3.3 Chemical Alternatives

The EU restriction proposal for c-decaBDE identified the following six alternative flame-retardant chemicals for applications such as in polyurethane foam for building insulation:

- (a) Magnesium hydroxide (MDH);
- (b) Aluminum trihydroxide (ATH);
- (c) Ethylene bis(tetrabromophthalimide) (EBTBP);
- (d) Substituted amine phosphate mixture (P/N intumescent systems);
- (e) Red phosphorous;
- (f) Decabromodiphenyl ethane (DBDPE).

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