

# NEW POPS IN STOCKHOLM CONVENTION

## (SHORT CHAIN CHLORINATED PARAFFINS, DECABROMODIPHENYL ETHER AND HEXACHLOROBUTADIENE)



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### SHORT CHAIN CHLORINATED PARAFFINS (SCCPs)

#### INTRODUCTION

Chlorinated paraffins (CPs) are chlorinated derivatives of n-alkanes and include complex mixtures of homologues and isomers. These are classified depending upon the carbon chain<sup>[1]</sup>. Short Chain Chlorinated Paraffins (SCCPs) containing 10-13 carbon atoms (C10-C13), Medium Chain Chlorinated Paraffins (MCCPs) containing 14-17 carbon atoms (C14-C17) while Long Chain Hydrocarbons (LCCPs) having carbon atoms greater than 17 in their chains. SCCPs have been classified as carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer (IARC)<sup>[1]</sup>.

#### APPLICATIONS OF SCCPs

- Plasticizers (flame retardant properties) in plastics (PVC), rubbers, paint & sealants<sup>[2]</sup>
- Flame retardants in textiles
- Lubricants in metal cutting fluids<sup>[2]</sup>
- Leather production<sup>[2]</sup>
- PVC production<sup>[1]</sup>

#### EXPOSURE DUE TO SCCPs

The potential routes of exposure include inhalation, dermal contact and ingestion primarily through contamination of food. CPs used as adhesives in food packaging is a potential exposure route through

ingestion of contaminated food products wrapped in these materials<sup>[3]</sup>. SCCPs have also been detected in food products contaminated through environmental exposure. Releases can occur during production, storage, transportation, use and disposal of SCCPs and SCCPs containing products.

#### SCCPs AS POPS: STOCKHOLM CONVENTION

At Persistent Organic Pollutants Review Committee (POPRC) 11, the committee recommended listing of SCCPs in Annex A for global elimination. Importantly, decision also deals with controlling contamination of SCCPs in mixtures of MCCPs and LCCPs. China was successful in getting the exemption request at COP by saying that alternatives were not available in the developing countries.

#### REGULATION

POP Regulation (Regulation (EC) 850/2004) in EU prohibited production, market, selling and use of SCCPs since 2012. Exemption for substances and mixtures (but not for articles) with a concentration below 1% SCCPs. Regulation includes 2 exemptions: Use as fire retardants in dam sealants and in rubber used in conveyor belts in the mining industry

SCCPs have been added to Annex A in Stockholm Convention in COP-8 held in Geneva in May 2017

#### CHARACTERISTICS OF CHLORINATED PARAFFINS

- Can persist for more than 50 years in sub-surface anaerobic sediments
- Half-life in sediments is longer than 1 year
- Low volatility and non-flammable
- Insoluble in water but may be emulsified with water
- Lipophilic in nature and persistent in environment
- Tend to volatile at high temperatures & deposit or settle down when the temperature is lowered
- When heated to decomposition, they emit toxic fumes of hydrochloric acid and other chlorinated compounds
- Bio accumulate in human beings
- Highly toxic to aquatic invertebrates
- Along with chlorinated aromatic compounds, PCBs are also formed during degradation

#### GLOBAL SCENARIO

- Global chlorinated paraffins market is expected to grow at Compound Annual Growth Rate (CAGR) of 4.44% during period 2016-2020
- Key players in Global CPs Market are Ajinomoto Fine-Techno Co. Inc., Caffaro Industrie SpA, Dover Chemical Corp., INOVYN ChlorVinyls Ltd and JSC Kaustik
- Other manufacturers are International Industrial Chemical Park (IICP), LeunaTenside and Quimica del Cinca
- China is the largest producer and consumer of SCCPs in the world

#### ALTERNATIVES

- Non-chlorinated paraffin like alkylphosphates and sulphonated fatty acids esters, natural animal and vegetable oils as substitutes in leather production
- Polyacrylic esters, diisobutyrate and phosphates may be used in paints and coating applications
- Aluminium hydroxides and phosphate containing compounds can be used as flame-retardant alternatives

### Deca-BDE USES IN ELECTRIC AND ELECTRONIC COMPONENTS:

- Housing and TV internal components
- Mobile phone sets and fax machine parts
- Audio/Video components
- Communication cables
- Components for scanner, printing and photocopy machines
- Circuit breakers
- Light sockets and decorative lights

### Deca-BDE USES IN TEXTILE SECTORS:

- Furnishings and upholstery like sofas, office chairs
- Manufacturing curtains
- Tents
- Protective clothing

with specific exemptions for mining and forest industries, leather production and lubricant additives and plasticizer of PVC except toys and children products.

## DECABROMODIPHENYL ETHER (DECA-BDE)

### INTRODUCTION

Polybromodiphenyl ethers (PBDEs)<sup>[4]</sup> comprise of 209 compounds having similar chemical structures. Deca-BDE does not occur naturally and is commercially produced in industries.

### EXPOSURE DUE TO DECA-BDE

Three primary routes of exposure include inhalation, dermal absorption and ingestion<sup>[5]</sup>. Workers involved in the manufacturing, recycling or disposal of products containing PBDE flame-retardants have higher exposure to chemical in comparison to general population. These workers may carry particles containing chemical to home with them leading to their family being exposed through household dust or direct contact. Consumer exposure to Deca-BDE is due to dust released from common household products. Children are highly susceptible to exposure to Deca-BDE due to their uncontrolled hand to mouth behavior.

Individuals are exposed to different forms of PBDEs than those initially released from the source due to its transformation and differential partitioning in the environment and food animals. For instance, Deca-BDE released from polymers or plastics may degrade to lower-brominated PBDEs, like tetra- or penta-BDE.

## ENVIRONMENT AND HEALTH ISSUES SURROUNDING DECA-BDE

Deca-BDE can degrade into the environment into other forms of PBDEs like nona- and octa-BDE that might have higher toxicity. These BDEs are not readily broken down in the environment and may be present at low levels in soils and sediments for several years.

### REGULATION<sup>[6]</sup>

The following table shows the recent policies adopted by the European Union for Deca-BDE.

Substance	Scope	Requirement	Proposed Effective Date
Deca-BDE	Substance	Prohibited	From early 2018
	• Constituent of substance		
	• Mixture	≤0.1%	18 months after date of entry into force
	• Article or any part thereof		

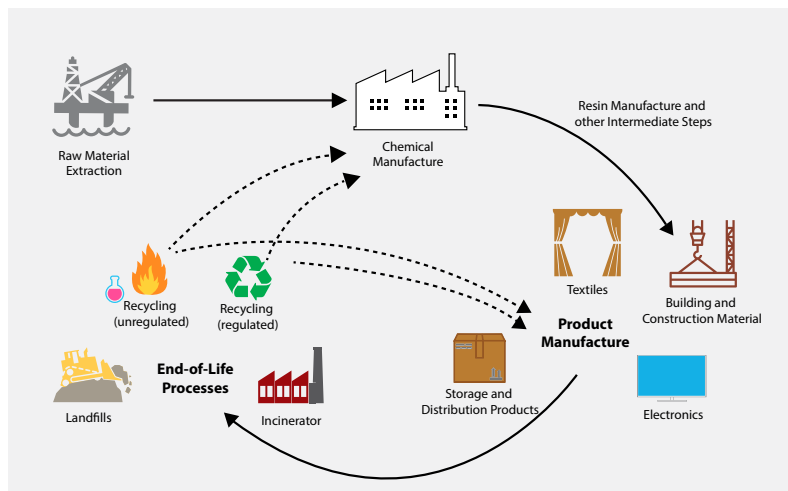
According to E-Waste (Management) Rules, 2016, new electrical and electronic equipment and their components or consumables or parts do not contain Lead, Mercury, Cadmium, Hexavalent Chromium, polybrominated biphenyls and polybrominated diphenyl ethers beyond a maximum concentration value of 0.1% by weight in homogeneous materials (RoHS Regulation).

## DECA-BDE AS POPs: STOCKHOLM CONVENTION

POPRC listed Deca-Bromodiphenyl ether (Deca-BDE) in Annex A of the Stockholm Convention during COP-8 held in Geneva in May 2017 with specific exemptions for critical spare parts for automotive and aerospace sector, polystyrene and polyurethane foam for housing insulation. As per the agreed text of the Convention, Deca-BDE has been allowed to be used in the automobiles until 2036. However, the key obstacles are concerns regarding technical and practical challenges related to its substitution that will include testing and authentic certification scheme.

The Indian auto industry is one of the largest in the world and accounts for 7.1% of the country's Gross

### LIFE CYCLE STAGES FOR FLAME RETARDANT CHEMICALS<sup>[5]</sup>



Domestic Product (GDP). India is a prominent auto exporter and has strong growth expectations in the coming future; but with the listing of Deca-BDE in Annex A, India may have to look for suitable and safer alternatives to continuously grow in the long run. Further going by the present phenomenon, Deca-BDE has been phased out globally by many countries from the automobile sectors, so Indian automobile industries should prepare themselves to brace this change instead of waiting until 2036. India should also come out with a plan to phase out Deca-BDE from the textile industry, both small and medium scale.

## HEXACHLOROBUTADIENE (HCBD)

### INTRODUCTION

HCBD is a chlorinated aliphatic diene. The chemical formula of the compound is  $\text{Cl}_2\text{C}=\text{C}(\text{Cl})\text{C}(\text{Cl})=\text{CCl}_2$ . It is used as a solvent for other chlorine containing compounds. There are no natural sources of HCBD in the environment. It is also detected in groundwater and drinking water at certain sites.

### PRODUCTION

HCBD is produced in chlorinolysis in plant as a by-product in the production of carbon tetrachloride and tetrachloroethane. Chlorinolysis is a process of radical chain reaction in which hydrocarbons are exposed to chlorine gas under pyrolytic conditions. HCBD can also be synthesized directly by chlorination of either butane or butadiene.

The manufacturers of Carbon tetrachloride in India are Gujarat Alkalies & Chemicals Limited (Dahej)<sup>[7]</sup>, Adarsh Chemicals (Chennai)<sup>[8]</sup> and Nutan Chemicals (Pune)<sup>[9]</sup>. Global Chloromethane is expected to witness a significant growth of 2171.6 million by 2022 with Compound Annual Growth Rate (CAGR)<sup>[10]</sup> of 4.63% for a period from 2016 to 2022. China consumes largest market share of more than 45% owing to growing demand from industries like pharmaceuticals, automobile and silicone polymer manufacturers. India, Indonesia and Brazil expect their growing demand owing to relaxed regulations by government in setting up industries and producing large amounts of products to meet growing population demand.

### EXPOSURE DUE TO HCBD

Mostly workers will be exposed to HCBD released while production processes. Other local sources of HCBD are landfills, combustion and production sites

of other chlorinated chemicals. The most common exposure route is breathing. The other routes include oral, inhalation, and dermal absorption. Effects may include fatty liver degeneration, epithelial necrotizing nephritis, central nervous system depression and cyanosis. The USEPA has classified hexachlorobutadiene as a Group C possible human carcinogen.

### HCBD AS POPs: STOCKHOLM CONVENTION

At seventh meeting of Stockholm Convention, POPRC adopted a decision on HCBD to be listed in Annex A, B and/or C. It can undergo atmospheric long-range transport due to its high persistence in air and its occurrence in abiotic and biotic matrices in remote locations. At COP-8, HCBD has been listed in Annex C for unintentional release. India needs to put in efforts in minimizing its emission by upgrading the technology that can be a costly process.

India was apprehensive about listing of HCBD in the Convention, however finally supported listing of the chemical in SC. There are production processes in India that releases HCBD and efforts are needed to minimize the release by upgrading our technology since this chemical has carcinogenic properties.



### CHARACTERISTICS OF HCBD

- Lipophilic compound, high vapour pressure, low water solubility, turpentine like odour
- Predicted atmospheric half lives is one year
- Half life in water 3 days to 12 months
- Half life in soil 4 to 26 weeks
- Does not hydrolyse due to lack of hydrolysable functional groups
- Toxic after repeated & chronic exposure at low levels 0.2 mg/kg
- Persistent, bioaccumulative and very toxic to aquatic organisms and toxic to birds
- HCBD TDI value (WHO): 0.2 µg/kg of body weight
- Drinking water limit (WHO guidelines): 0.6 µg/l

### APPLICATIONS

#### HCBD (CURRENT AND HISTORICAL)

- Solvent for rubber & other polymers
- Transformer liquid in heat transfer fluids
- Manufacturing processes of aluminium and graphite rods
- Seed dressing and fungicide

#### CARBON TETRACHLORIDE

- Fluorocarbon refrigerants & propellants
- Grain fumigants and bleaching
- Solvent in chlorinated rubber manufacturing & petroleum refining industry
- Grease removing agent for machinery & tool
- Dry cleaning fluid
- Fire extinguisher and floatation fluid
- Synthesis of Nylon – 7

#### TETRACHLOROETHANE

- Solvent for degreasing metals, in paint removers, varnishes, lacquers, photographic films, rust removers, resins and waxes
- Solvent for extraction of oils and fats, preparation of adhesives
- Alcohol denaturant in organic synthesis
- Manufacture of cyanogen chloride, polymers, tetrachloro – alkylphenol
- Soil sterilization as weed killer, insecticide formulations
- Immersion fluid in crystallography
- Solvent for impregnation of furs with chromium chloride

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### Compiled and written by:

Kritika Mathur, Piyush Mohapatra and Dr. Prashant Rajankar

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### For more information, please contact:

#### Toxics Link

H2 (Ground Floor)

Jungpura Extension

New Delhi 110 014

T: +91-(0)11-24328006, 24320711

E: [info@toxicslink.org](mailto:info@toxicslink.org)