LEARNING COURSE

Alternatives to POPs
Annex A

Short-chain chlorinated paraffins (SCCPs)

GGKP, 2024

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POPs listed in Annex A

Parties must take measures to eliminate the production and use of the chemicals listed under Annex A of the Stockholm Convention.

Specific exemptions for use or production are listed in the Annex and apply only to Parties that register for them.

REF: Stockholm Convention

Status of SCCPs under the Stockholm Convention

- In May 2017, by decision SC-8/11, the Conference of the Parties to the Stockholm Convention amended Annex A to the Convention to list short-chain chlorinated paraffins (SCCPs) with chain lengths ranging from C10 to C13 and a content of chlorine greater than 48% by weight.
- Additionally, a limit for the presence of SCCPs in other chlorinated paraffin (CP) mixtures was set at 1% by weight.
- CPs with a SCCP content 1% are therefore considered POPs.

REF: Stockholm Convention - UNEP/POPS/COP.9/INF/21

Short-chain chlorinated paraffins

- Chlorinated paraffins (CPs), or polychlorinated n-alkanes (CA), are complex mixtures of substances with the general molecular formula CxH(2x-y+2)Cly.
- CPs are characterized by the carbon-chain length range of their n-alkanes and by the chlorine content of the product.
- According to their chain length, CPs are categorized into short-chain CPs (SCCPs, C10–C13), medium-chain CPs (MCCPs, C14–C17) and long-chain CPs (LCCPs, C17–C30).

REF: UNEP/POPS/COP.9/INF/21 - UNEP/POPS/POPRC.12/11/Add.3

SCCP production

- CPs are produced by the chlorination of a hydrocarbon feedstock consisting of n-alkanes. The feedstock used determines the carbon chain lengths that are contained in the product.
- Production of commercial SCCP products has decreased globally as jurisdictions have established control measures.
- While historical use of SCCPs was high globally, reductions have been noted in recent years in some countries. More recently, production volumes of CP mixtures that may contain SCCPs have increased.
- CPs (of various chain lengths) are known to be produced in Brazil, China, India, Japan and the Russian Federation.

SCCP uses (as per Annex A)

Specific exemptions

- Additives in the production of transmission belts in the natural and synthetic rubber industry
- Spare parts of rubber conveyor belts in the mining and forestry industries
- Leather industry, particularly fatliquoring in leather
- Lubricant additives, in particular for engines of automobiles, electric generators and wind power facilities, and for drilling in oil and gas exploration, petroleum refineries to produce diesel oil
- Tubes for outdoor decoration bulbs
- Waterproofing and fire-retardant paints
- Adhesives
- Metal processing
- Secondary plasticizers in flexible polyvinyl chloride, except in toys and children's products

REF: Stockholm Convention - UNEP/POPS/COP.9/INF/21

SCCP uses

- SCCPs were, and continue to be, used primarily as extreme pressure additives (i.e., lubricants and coolants) in metalworking applications and in polyvinyl chloride (PVC) plastics.

- SCCPs are also used in paints, adhesives and sealants, leather fat liquors, plastics, and as a flame retardant in rubber, textiles and polymeric materials.

REF: Stockholm Convention - UNEP/POPS/COP.9/INF/21

Waste streams likely to contain SCCPs and recommended management/destruction options

- Releases of SCCPs to the environment may occur at all life cycle stages.
- Major sources of release of SCCPs are likely the formulation and manufacturing of products containing SCCPs, such as PVC plastics, and use in metalworking fluids.
- In the EU, approximately 25 kt of SCCPs are contained in building materials as a “stock” of SCCPs within building and construction applications.
- Disposal of products that contain SCCPs in landfills is not expected to be a major release as CPs would remain stabilized in products.
- Leaching from landfill sites is likely to be negligible owing to strong binding of CPs to soils.
- Releases of SCCPs could occur from the creation of dust during the recycling of plastics and construction and demolition waste, or in the mechanical treatment of rubber prior to incineration.

REF: UNEP/POPS/POPRC.12/11/Add.3

Waste streams likely to contain SCCPs and recommended management/destruction options

- Introducing waste management measures, including controls for products and articles upon becoming waste, would ensure that wastes containing SCCPs at concentrations above the low POP content are disposed of in such a way that the POP content is destroyed or otherwise disposed of in an environmentally sound manner.
- Land application of sewage sludge should be carried out in accordance with applicable regional and local requirements.
- Waste management activities should take into account international rules, standards and guidelines.
- Develop appropriate strategies for identifying sites contaminated with SCCPs.

REF: UNEP/POPS/POPRC.12/11/Add.3

Alternatives to SCCPs: Metal working fluids in metal processing and other lubricants

SCCPs have been used as lubricants and coolants in metalworking fluids (MWFs), which are liquids that are supplied to a manufacturing process of a metal in a way that allows for increased productivity based on lubricating and cooling effects.

Significant progress has been made by industry through the development of environmentally adapted lubricants (EALs).

Alternatives to SCCPs: Metal working fluids in metal processing and other lubricants

Alternative chemicals			
Sulphur-based substitutes	**Phosphorus compounds**	**Other non-halogenated alternatives**	**Chlorinated organics**
• Zinc dialkyldithiophosphate • Sulphurized polyisobutene, polypropylene and polystyrene • Tertiary nonyl polysulfide (TNPS) • Polyolefin sulphide; • Sulfonated fatty acid esters • Overbased calcium sulphonates • Polysulphides or alkyl sulphide, sulphurized alkenes/olefins, sulphurized hydrocarbons (i.e., • generally di-tertiary alkyl polysulphides, in particular di-tertiary alkyl pentasulphides) – extreme pressure additive	• Alkyl phosphate esters • Phosphate acid esters • Hydrogen phosphites • Phenol, isopropylated, phosphate (ITAP) (3:1) • Tributyl phosphate (TBP) • Triaryl phosphate • Bis(2-ethylhexyl) hydrogen phosphate • Didodecyl phosphite • Dimethyl hydrogen phosphite • 2-Ethylhexyl hydrogen phosphate • Polyethoxy oleyletherphosphate • Zinc dialkyldithiophosphates	• Mineral oils • Alkanol amides (e.g., 2:1 di-ethanolamine (DEA) tall oil fatty acid alkanol amide) • Diisopropyl oleate • Nitrogen compounds • Boundary acid esters • Complex esters • Propylene oxide	• Chlorinated fatty esters and acids • Long-chain chlorinated paraffins (C18+) (LCCPs) • Medium-chain chlorinated paraffins (C14-17) (MCCPs)

REF: UNEP/POPS/COP.9/INF/21

Alternatives to SCCPs: Metal working fluids in metal processing and other lubricants

Alternative materials and techniques

- Use of systems based on gases such as supercritical CO_2, which has the density and solvency of a liquid while maintaining the compressibility and viscosity of a gas.
- Industry has made significant progress developing EALs, which are readily biodegradable, have low toxicity, and perform equally or better than conventional alternatives.
- Synthetic and semi-synthetic lubricants, which are often diluted with water rather than volatile organic compound (VOC) solvents, may serve as alternatives.

Alternatives to SCCPs: Metal working fluids in metal processing and other lubricants

Alternative materials and techniques

a) Material substitution with environmentally adapted lubricants (EALs) in combination with alternative technology:
   - bio-based lubricant formulations (soybean, pine tree, rapeseed, mustard, grape seed, sunflower, coconut, canola, etc.), with or without additives
   - bio-based lubricants in combination with supercritical CO_2
   - oil-in-CO_2 dispersion
   - gas-based lubricant system

b) Material substitution with HIGTO(1) (a modified triglyceride based on rape seed) with a zirconium coating

c) Process change to dry machining (using no cutting fluid)

d) Process change to cryogenic machining (using liquid nitrogen or other liquified gases) (Shokrani et al. 2014)

e) Process change to air delivery of lubricants

f) Process change to oil-free, low viscosity metal-forming lubricants with high solid polymers (HSM)

g) Using synthetic and semi-synthetic lubricants (vegetable-based methyl esters or polymers of various types), which are often diluted with water rather than VOC solvents

Alternatives to SCCPs: Secondary plasticizers in flexible polyvinyl chloride (including tubes for outdoor decoration bulbs), except in toys and children's products

Flexible PVC has many applications such as cable sheeting, in plumbing, conveyor belts, imitation leather, flooring, signage, phonograph records, inflatable products, or tubes for outdoor decoration bulbs.

SCCPs are used in PVC manufacturing primarily where moderate plasticizing and flame retarding properties are required at low cost.

Alternatives to SCCPs: Secondary plasticizers in flexible polyvinyl chloride (including tubes for outdoor decoration bulbs), except in toys and children's products

Alternative chemicals			
Inorganic substances	**Organophosphorus flame retardants**	**Organohalogen substances**	**Phthalates (generally, including phthalates esters)**
• Alumina trihydrate • Aluminum trihydroxide (ATH), used in conjunction with antimony trioxide • Aluminum trioxide • Antimony trioxide (or Antimony oxide) • Zinc borate	• Cresyl diphenyl phosphate (CDP) • Tertbutylphenyl diphenyl phosphate (TBPDPP) • Isopropylphenyl diphenyl phosphate (IPPDPP) • Phosphorus-based compounds (in general) • Tricresyl phosphate (TCP)	• Long-chain chlorinated paraffins (C18+) (LCCPs) • Medium-chain chlorinated paraffins (C14-17) (MCCPs)	• Di-isononyl'phthalate (DINP) • Di-isodecyl phthalate (DIDP) • Bis(2-ethylhexyl) phthalate (DEHP) • Butyl benzyl phthalate (BBP) • Di-isoundecyl phthalate (DIUP)

Other available alternatives:

- Other phtalate-like alternative: Tri-octyl trimellitate
- Polymeric additives: Acrylic polymers

REF: UNEP/POPS/COP.9/INF/21

Alternatives to SCCPs: Secondary plasticizers in flexible polyvinyl chloride (including tubes for outdoor decoration bulbs), except in toys and children's products

Alternative materials and techniques

Material substitution with other elastic polymers has been identified as an alternative material that can replace the use of PVC applications containing SCCPs:

- Polyethylene
- Polypropylene
- Rubber
- Ethylene vinyl acetate (EVA)

Alternatives to SCCPs: Secondary plasticizers in flexible polyvinyl chloride (including tubes for outdoor decoration bulbs), except in toys and children's products

- Analysis of alternatives to SCCPs suggests that, in many cases, the overall technical characteristics of the PVC product (e.g., flexibility and stability) would improve with the use of alternatives.
- Flame retardancy can be achieved through the use of alternate techniques, such as using inherently flame-resistant materials, flammability barriers and product re-design could improve with the use of alternatives.
- As a result of using alternatives to SCCPs, cost implications may arise for reformulation, re-approval and on the price of the finished product.

Alternatives to SCCPs: Rubber (spare parts of rubber conveyor belts, production of transmission belts in the natural and synthetic rubber industry)

- SCCPs are exempted as spare parts of rubber conveyor belts in the mining and forestry industries and in the production of transmission belts in the natural and synthetic rubber industry.

- Alternatives to SCCPs for use in conveyor belts are available and include alternative chemicals and alternative materials or techniques.

Alternatives to SCCPs: Rubber (spare parts of rubber conveyor belts, production of transmission belts in the natural and synthetic rubber industry)

Alternative chemicals			
Phosphate esters are viable alternatives in applications where a non-flammable plasticizer is needed (there are a range of organophosphorus flame retardants available)	**A range of inorganic alternative additives or combination of inorganic and organic additives can be used for some application**	**Other halogenated additives**	**If only the plasticizing property are needed than Phthalates (generally, including phthalates esters) can be used as alternatives**
• Cresyl diphenyl phosphate (CDP) • Tertbutylphenyl diphenyl phosphate (TBPDPP) • Isopropylphenyl diphenyl phosphate (IPPDPP) • Tricresyl phosphate (TCP) • Phosphorus based compounds (in general)	• Antimony trioxide (ATO) (or antimony oxide) • Aluminum trihydroxide, used in conjunction with antimony trioxide (ATO) • Borate and phosphate esters • Calcium sulphonates • Sulphonated fatty esters • Zinc borate • Acrylic polymers	• Medium-chain chlorinated paraffins (C14-17) (MCCPs) • Long-chain chlorinated paraffins (C18+) (LCCPs) • Alicyclic chlorinated compounds	• Bis(2-ethylhexyl) phthalate (DEHP) • Butyl benzyl phthalate (BBP) • Di-isononyl phthalate (DINP) • Di-isodecyl phthalate (DIDP) • Di-isoundecyl phthalate (DIUP)

REF: UNEP/POPS/COP.9/INF/21

Alternatives to SCCPs: Rubber (spare parts of rubber conveyor belts, production of transmission belts in the natural and synthetic rubber industry)

Alternative materials and techniques

SCCPs can be avoided by using inherently flame-resistant materials or flammability barriers, or by otherwise redesigning the product such that chemical flame retardants are not needed.

SCCP-free alternative conveyor belt types with inherent flammability include:

- PVC solid woven and
- chloroprene (CR) multi-ply

Alternatives to SCCPs: Rubber (spare parts of rubber conveyor belts, production of transmission belts in the natural and synthetic rubber industry)

As a result of using alternatives to SCCPs, cost implications may arise as a result of reformulation and re-approval, which may affect the price of the finished product.

Transitional costs could be high for flame retarded conveyor belts given that the research needs and testing requirements could be more arduous than in other applications given the safety requirements surrounding underground mining.

Alternatives to SCCPs: Leather industry, in particular fatliquoring in leather

- The fatliquoring step is the last stage of leather preparation.
- The leather industry has used SCCPs as inexpensive bulking agents in fat liquors.
- They are not considered critical to leather processing, so several countries have completed the phase-out of SCCPs in this application, no relevant cost implications are expected as a result of a phase out of SCCPs for this specific use.

Alternatives to SCCPs: Leather industry, in particular fatliquoring in leather

Alternative chemicals		
Non-halogenated alternatives	**Nitroalkanes**	**Organochlorine alternatives**
• Mineral oils • Combination of mineral oils and animal oils or vegetable oils	• Sulfonated fatty acid esters • Alkyl phosphate	• Medium-chain chlorinated paraffins (C14-17) (MCCPs) • Long-chain chlorinated paraffins (C18+) (LCCPs)

Alternatives to SCCPs: Leather industry, in particular fatliquoring in leather

Alternative materials

The following natural oils can be used:

- Vegetable oils
- Natural animal oils
- Combination of animal and vegetable oils

Alternatives to SCCPs: Waterproofing and fire-retardant paints

- SCCPs are used as plasticizers and flame retarding agents in paints which often function at the same time as coatings.

- Applications include road marking paints, anti-corrosive coatings for metal surfaces, paints/coatings for swimming pools, manure pits, water tanks and fish pond coatings, decorative paints for internal and external surfaces, and textile printing inks.

REF: UNEP/POPS/COP.9/INF/21

Alternatives to SCCPs: Waterproofing and fire-retardant paints

Alternative chemicals

- Medium-chain chlorinated paraffins (C_{14-17}) (MCCPs)
- Long-chain chlorinated paraffins (C_{18+}) (LCCPs)
- Boron- and silicon-based compounds (e.g., phosphorous-boron-nitrogen compounds)
- Diisobutyrate compounds
- Other organophosphorus flame retardants
- Phosphate esters
- Phosphorus-based compounds
- Phthalates (generally, including phthalates esters)
  - Butyl benzyl phthalate (BBP)
  - Di-isoundecyl phthalate (DIUP)
- Polyacrylate esters

Alternatives to SCCPs: Waterproofing and fire-retardant paints

Alternative materials

Replacing paints requiring plasticizers with epoxy-based paints eliminates the need for SCCPs.

For road marking, paints can be replaced with thermoplastic products, which do not contain SCCPs and provide improved durability.

Alternatives to SCCPs: Waterproofing and fire-retardant paints

- It is speculated (with a high degree of uncertainty) that the substitution of SCCPs in paint and coating applications could result in a 7% increase in the cost of acrylic paint.

Alternatives to SCCPs: Adhesives/sealants

- While for adhesives an exemption has been granted, there is no particular exemption for sealants. SCCPs are used as plasticizers and flame retardants in the production of adhesives and sealants. Since sealants might be used as adhesives, SCCPs might still be used in the production of sealants.
- Generally, alternatives to SCCPs in sealants are various phosphate esters.
- Alternate types of sealants and adhesives are available that are not formulated using SCCPs as the plasticizer.
- The difference between an adhesive and a sealant can be difficult to define as some are used as adhesives and vice versa. Generally, sealants are considered to be materials that are installed into a gap or joint to prevent water, wind, dirt, or other contaminants from passing through the joint or crack. Adhesives, on the other hand, are used to transfer loads and are typically designed with much higher tensile and shear strength than sealants.

REF: UNEP/POPS/COP.9/INF/21 - UNEP/POPS/POPRC.12/11/Add.3

Alternatives to SCCPs: Adhesives/sealants

Alternative chemicals		
As alternative plasticizers for polysulphides		**As alternative plasticizers for polyurethane formulations**
• Medium-chain chlorinated paraffins (C14-17) (MCCPs) • Long-chain chlorinated paraffins (C18+) (LCCPs) • 2,2,4-trimethyl-1,3-pentanediol • Alkyl sulphonic acid esters of phenol or cresol • Di-2-ethylhexyl adipate • Glycolate esters • Hydrogenated terphenyls • Polyacrylate esters • Phosphate esters	• Phthalates (generally, including phthalates esters): i. Di-isononyl phthalate (DINP) ii. Di-isodecyl phthalate (DIDP) iii. Bis(2-ethylhexyl) phthalate (DOP aka DEHP) iv. Butyl benzyl phthalate (BBP) v. Di-isoundecyl phthalate (DIUP)	• Dibenzoate • Dipropylene glycol

REF: UNEP/POPS/COP.9/INF/21

Alternatives to SCCPs: Adhesives/sealants

Alternative materials and techniques

- Urethane or silicone sealants, which do not contain SCCPs, can replace polysulphides or other sealants. In silicone sealants, polydimethylsiloxanes are used as plasticizers.
- SCCP plasticizers in dam sealants can be replaced with high molecular weight plasticizers, which are less prone to leaking monomers and additives.

REF: UNEP/POPS/COP.9/INF/21

Alternatives to SCCPs: Adhesives/sealants

- For substitution of SCCPs in sealant and adhesive applications, some producers would require up to two years to identify and test alternatives and reported that the cost to end users may increase by 5%; however, other companies have reported no apparent loss in performance or increase in cost.

Alternatives for uses of SCCPs **not exempted** by the Convention

- As a niche application, SCCPs have been used to provide a flame retardant, waterproof and rot-proof finish to heavy textiles, such as military tents. This use has not been exempted in the Convention since alternatives to SCCPs in textiles are available. Some countries might still use SCCPs in textiles.

Alternatives for uses of SCCPs **not exempted** by the Convention

Alternative chemicals		
Replacement for SCCPs in textiles		
• Acrylic polymers • Aluminum trihydroxide (ATH), used in conjunction with antimony trioxide • Antimony trioxide (or Antimony oxide)	• Phosphorus-based compounds: i. Cresyl diphenyl phosphate (CDP) ii. Tertbutylphenyl diphenyl phosphate (TBPDPP) iii. Isopropylphenyl diphenyl phosphate (IPPDPP) iv. Phosphorus based compounds (in general) v. Tricresyl phosphate (TCP) vi. Phosphate esters vii. Other organophosphorus flame retardants	• Halogenated flame retardants i. Bis (tribromophenoxy) ethane ii. Dibromostyrene iii. Ethane, 1,2-bis(pentabromophenyl) (EBP), used in conjunction with antimony trioxide iv. Ethylenebistetrabromophthalimide v. Hexachlorocyclodecane vi. Brominated Phthalates (generally, including phthalates esters) a. Tetrabromophthalate ester (TBPH) b. Tetrabromophthalate diol c. Tetrabromophthalic anhydride vii. Tribromophenyl allyl ether viii. Medium-chain chlorinated paraffins (C14-17) (MCCPs) ix. Long-chain chlorinated paraffins (C18+) (LCCPs)

REF: UNEP/POPS/COP.9/INF/21

Alternatives for uses of SCCPs **not exempted** by the Convention

Alternative chemicals

The use of flame retardants depends to some extent on the textiles:

- Halogenated flame retardants mixed with antimony trioxide can be used on wool, cotton, polyester, polyamide fibers and blends (upholstery fabrics and roof insulating fabric)
- Brominated flame retardants mixed with antimony trioxide can be applied on polyester and cellulosic fibers, modacrylic fibers, non-wovens for drapery, upholstery and textile coatings
- Organophosphorus compounds, such as tris(isopropylphenyl) phosphate, are suitable for cellulosic, nylon and polyester fibers (upholstery fabric, garments, flexible ducting)

Alternatives for uses of SCCPs **not exempted** by the Convention

Alternative materials and techniques

Alternative materials and techniques to the use of SCCPs in textiles include replacing the flame retarded textiles with less flammable fabrics and materials.

- Natural fabrics and materials include:
  - Leather
  - Wool
- Synthetic fabrics
  - Modacrylics
  - Aramide

Inherently flame-resistant materials can be used for example, by designing polymer backbones with very high heat and flame resistance, or by using metal instead of textiles.

Final remarks

- It has been demonstrated that technically feasible alternatives are commercially available for all known uses of SCCPs.
- Although it is expected that producers of SCCPs and chlorinated substitutes will face losses, it is also expected that these losses will be outweighed by corresponding gains for producers of alternatives.