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TECHNICAL BULLETIN

What are Chlorinated Paraffins?

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Chlorinated Paraffins (CPs) are straight-chain hydrocarbons that have been chlorinated. Chlorinated paraffins are classified according to their carbon-chain length and percentage of chlorination, with carbon-chain lengths generally ranging from C₁₀ to C₃₀ and chlorination from approximately 35% to greater than 70% by weight. Chlorinated paraffins are made by chlorinating paraffin fractions obtained from petroleum distillation. The three most common commercial feedstocks used are paraffins with carbon number ranges of: Short-chain (C₁₀₋₁₃), Intermediate-chain (C₁₄₋₁₇) and Long-chain (C₁₈₋₃₀).

| Percent of Chlorination (by weight) | | | | | |
|-------------------------------------|-----|-------|-------|-------|-----|
| | <40 | 40-49 | 50-59 | 60-69 | >70 |
| C ₁₀₋₁₃ | A1 | A2 | A3 | A4 | A5 |
| C ₁₄₋₁₇ | B1 | B2 | B3 | B4 | B5 |
| C ₁₈₋₃₀ | C1 | C2 | C3 | C4 | C5 |

These hydrocarbons are reacted with chlorine resulting in chlorinated paraffins of different carbon chain lengths with varying degrees of chlorination. Thus chlorinated paraffins are a group of complex chemical substances. The general formula of CP is C_xH_(2x-y+2)Cl_y. The majority of CP products can be depicted in a 15-cell matrix, as shown above.

Uses and Benefits of CPs

Chlorinated paraffins (CPs) have been widely used in industry throughout the world since their introduction nearly 40 years ago. CPs are needed where chemical stability is highly desired. The primary application of CPs is in industrial cutting fluids, particularly in the manufacture of automobiles and automobile parts. In addition to their use in cutting oils, CPs are also used in a lot of commercial paints, adhesives, sealant and caulks.



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CHLORINATED PARAFFINS IN THE TWENTY-FIRST CENTURY
By Robert J. Fensterheim, MPH
Executive Director, Chlorinated Paraffins Industry Association

Chlorinated paraffins (CPs) are a family of complex substances representing more than 200 commercial products. Use applications for chlorinated paraffins range from extreme pressure additives in lubricants, to secondary plasticizers in paints and plastics, to flame retardants in various plastics and textiles.

Chlorinated paraffins are produced through chlorination of straight-chain paraffin fractions which are typically subdivided into three categories based on their carbon chain lengths:

Short-chain C10-13
Mid-chain C14-17
Long-chain C18-30

The properties of the different chlorinated paraffins can vary significantly depending on their carbon chain length and degree of chlorination.

Mid-chain chlorinated paraffins (MCCPs) represent the largest production and use category in North America (approximately 45%); long-chain chlorinated paraffins (LCCPs) are second (approximately 33%); and short-chain chlorinated paraffins (SCCPs) account for the rest.

Chlorinated paraffins have been the subject of numerous health and environmental reviews. Regulatory attention was first focused on CPs in the United States in the mid-1970s when the US Environmental Protection Agency (EPA) undertook a comprehensive environmental and health review. Starting in the 1990's, Environment Canada began a similar review.

The North American producers of chlorinated paraffins have been working cooperatively to address the various health, environmental and regulatory issues under the auspices of the Chlorinated Paraffin Industry Association (CPIA). 1 (Additional information on CPIA can be found at www.regnet.com/cpia.) CPIA has also been cooperating with the European producers of CPs in addressing various initiatives by the European Union.

The following summarizes the current regulatory status of CPs and highlights that, when properly managed, CPs are safe for use consistent with health and environmental protection goals.

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UNITED STATES

Based in part on the research and advocacy initiatives of CPIA, there are no restrictions in the US on the manufacture, processing or use of any chain length CP. The only regulatory requirement is a reporting obligation for SCCPs. Under the Toxic Release Inventory (TRI) regulations (40 CFR 372), any facility manufacturing or processing 25,000 pounds or more, or any facility using 10,000 pounds or more of SCCPs, is required to file with EPA an annual estimate of their environmental releases. It is significant to note that CPs are specifically exempt from the federal "hazardous" waste Resource Conservation and Recovery Act (RCRA) regulations. While the EPA regulations specify that waste oil containing more than 1,000 ppm halogens is presumed to be hazardous, showing that the source of the halogen is CPs is an effective way to "rebut" the presumption. There are, however, several states that require all waste oils to be managed as hazardous waste and the state of Washington has specifically designated waste oils containing CP as "hazardous" unless the used oil is being sent for re-refinement.

CANADA

There are presently no restrictions in Canada on the manufacture, processing or use of any chain length CP. Like the TRI reporting in the United States, reporting of certain CPs (alkanes, C6-18, chloro, CAS# 68920-70-7; alkanes, C10-13, chloro, CAS# 85535-84-8) is required in accordance with the National Pollutant Release Inventory (NPRI). Facilities in Canada that manufacture, process and otherwise use the specified CPs in an amount greater than 10 metric tons, are subject to this rule. Small facilities whose employees work less than 20,000 hours are exempted from this requirement. In 1993, Environment Canada classified SCCPs as "toxic" under the Canadian Environmental Protection Act based on animal carcinogenicity studies. There has been no follow-up action, since the concern identified was very limited. Environment Canada is continuing to investigate whether SCCPs should be listed as "toxic" to the environment given their acknowledged toxicity to aquatic life when discharged without proper management.

CPIA has advocated that Environment Canada initiate a Life Cycle Management Program (LCMP) as an effective response to its concerns over environmental release of SCCPs. CPIA has identified the ILMA/ORC Guide, "Management of the Metal Removal Fluid Environment" as a useful starting point for developing such a program. CPIA is soliciting metalworking fluid formulators and users interested in working on the development of a metalworking fluid LCMP. This effort is intended not only to achieve a positive outcome in Canada with respect to SCCPs, but also to support continued use of mid- and long-chain CPs throughout North America.



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EUROPE

CPIA is closely monitoring, and as appropriate, responding to the European Union's risk assessment and risk management initiatives with regard to CPs. The European Union concluded that the release of SCCPs into the environment poses a risk to aquatic organisms and therefore has decided to impose "marketing and use restrictions" on the use of SCCPs in metalworking and leather finishing. The United Kingdom has begun to assess MCCPs, as part of the European Union's ongoing review of existing substances. That assessment is scheduled for completion in 2002. CPIA is actively working with the United Kingdom and the European producers to ensure no restrictions.

CPIA is also working directly with the United Kingdom to address LCCPs under the International Council of Chemical Associations (ICCA) High Production Volume (HPV) Initiative.

COMPANY RESTRICTED LISTS

Beyond formal government oversight, some companies have their own initiatives to prohibit or restrict the use of certain compounds. CPIA actively monitors these initiatives and has successfully worked with different companies to ensure the continued use of CPs in North America. Metalworking fluid formulators are encouraged to contact CPIA if they become aware of any circumstances calling for restrictions on the use of CPs.

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1 CPIA represents the major North American manufacturers of chlorinated paraffins, which includes: Dover Chemical Corporation; Ferro Corporation, Petroleum Additives; and, Pioneer Americas, Inc.

CP FAQ's

What are Chlorinated Paraffins (Cps)?

They are a group of chemicals manufactured by chlorination of liquid n-paraffin wax and contain from 30 to 70% chlorine. They are largely inert, almost insoluble in water and have extremely low vapor pressure. Most commercial products are liquid and range from relatively low to extremely high viscosity. There are also solid types containing 70-72% chlorine.

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For any given feedstock, increasing the chlorine content results in products with higher viscosity and density. Chlorinated paraffins are miscible with many organic solvents such as aliphatic and aromatic hydrocarbons, chlorinated solvents, ketones and esters.

How do the various commercial products differ? The range of chlorinated paraffins available are generally grouped into a number of distinct 'families' depending on the chain-length of the feedstock, ie:

short-chain based on C10-13 paraffin

medium-chain based on C14-17 paraffin

long-chain based on C18-20 or wax

(average chain length approximately C25)

This distinction is important when considering toxicity or environmental effects as it has been found that these can vary depending on both the chain length and to a lesser extent the chlorine content of the product.

Liquid grades of chlorinated paraffin are produced from each of these feedstock types. The solid grades (with 70-72% chlorine content) are made from a wax feedstock.

Manufacture and use of Chlorinated Paraffins

How are Chlorinated Paraffins produced? Chlorinated paraffins are manufactured by chlorinating, normally in a batch process, of liquid n-paraffin or molten wax. The reaction is exothermic and leads to the generation of by-product hydrochloric acid. After removing residual traces of acid, finished batches are stabilized by addition of a small proportion of expoxidized vegetable oil.

What quantities of Chlorinated Paraffin are produced? Total world production of chlorinated paraffins is believed to be approximately 300 kt/year.

Who are the major producers? Major producers are Ineos Chlor, Hoechst AG and Caffaro in Europe, OxyChem and Dover Chemicals in the USA. There are numerous producers in Asia, principally in India, China, Taiwan and Japan.

(Hoechst have announced their intention to cease production of chlorinated paraffins by the end of 1998).

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What are the major applications for Chlorinated Paraffins?

One application for chlorinated paraffins is as a plasticizer, generally in conjunction with primary plasticizers such as DOP, DINP etc in flexible PVC. The use of chlorinated paraffins in PVC imparts a number of technical benefits, of which the most significant is the enhancement of flame retardant properties this is particularly of benefit in PVC flooring and cables.

Chlorinated paraffins are also used as plasticizers in paint, sealants and adhesives where the main advantages over alternatives are their inertness and the enhancement of flame retardant properties. Higher chlorine content grades are used as flame retardants in a wide range of rubbers and polymers systems, where they are often used in preference to potentially more toxic phosphate and bromine-based additives.

The other major outlet for chlorinated paraffins is in the formulation of metalworking lubricants where they have long been recognized as one of the most effective additives for lubricants used in a wide range of machining and engineering operations.

In all of these applications there is a long history of safe use and some major customers have been using chlorinated paraffins for over 50 years.

Toxicity

Are Chlorinated Paraffins toxic?

The toxicity of any material is normally expressed in terms of both its acute and chronic effects; for chlorinated paraffins these relate, respectively, to short-term (normally single dose) exposure and longer term or repeated exposure to lower levels (such as might be experienced in the workplace).

Results from animal studies clearly show that chlorinated paraffins are of very low acute toxicity. Various different grades have been tested and doses of 4 to 10g/kg show no signs of toxicity. This would be equivalent to drinking a single dose of about 250-600 ml of liquid Chlorinated Paraffin for an average person.

In longer-term studies, it has been found that chlorinated paraffins produce toxic effects on the kidney and liver of exposed animals. The highest dose which can be given without showing an effect (the no-effect concentration or NOEC) is 10mg/kg/day for rats. This amount is many orders of magnitude higher than the highest exposure likely to be encountered in industrial conditions and conditions under which people are likely to be exposed in everyday life.

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Are there any effects if I come into contact with Chlorinated Paraffins?

The three routes by which any chemical can enter the body are by ingestion (via the mouth), inhalation and skin contact. During industrial use, we are normally concerned only with the latter two and since vapor pressure is very low, exposure by inhalation is minimal (but see Q3 for more information). For most workers, skin contact is the most likely source of exposure to chlorinated paraffins and again studies have shown that skin (and eye) irritation is low and that chlorinated paraffins are not absorbed significantly through the skin. Limited information from human studies indicates that the degree of skin irritation produced by chlorinated paraffins is very low.

There have been reports that workers exposed to metal-working lubricants may suffer from allergic reactions or skin sensitization. There is no evidence that this is caused by the chlorinated paraffins in the lubricants. Animal studies, together with evidence from humans, have confirmed that chlorinated paraffins do not have the potential to be skin sensitizers.

Are Chlorinated Paraffins volatile and what if I breathe in fumes?

All chlorinated paraffins have very low vapor pressure; short-chain grades have the highest volatility and for a 50% chlorine content grade, this has been measured as 0.000213 hPa at 40°C (ie about 0.16 x 10³mm Hg). This is an extremely low value and therefore under normal conditions of use the quantity of Chlorinated Paraffin likely to be inhaled is extremely small. However, if chlorinated paraffins are heated during handling, some fuming may be experienced. These fumes may contain a small proportion of HCl (which is irritant) and it is recommended that in these circumstances adequate ventilation is provided.

In the engineering industry, aerosol mists can be produced during use of metal working fluids and these mists may contain a proportion of Chlorinated Paraffin. It has been calculated that exposure to chlorinated paraffins in this way does not present a risk provided that the Occupational Exposure Standard for oil mists (5mg/m³) is met.

Are Chlorinated Paraffins carcinogenic?

Lifetime animal studies have been carried out with two grades of Chlorinated Paraffin. One of these (a short-chain grade with 58% chlorine) caused tumors in rats and mice. Male mice exposed to a long-chain with 40% chlorine showed an excess of tumors at one site. However, it has been shown that the mechanisms by which chlorinated paraffins cause these tumors to be formed are specific to rodents and therefore of no relevance for human health. Furthermore chlorinated paraffins have been clearly shown to be non-genotoxic. Based on all of this evidence it is concluded that the carcinogenic findings in animals do not give rise to concern for human health.

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If Chlorinated Paraffins are not carcinogens why have they been classified as such in some countries?

The basis for classification differs from country to country. Some countries give less weight to the more recent mechanistic studies which indicate that the animal results are of little relevance for man.

In the USA, the short-chain (C12), 58% chlorine product is the only one to be classified and labeled as a carcinogen. However, some suppliers have decided to label other short-chain products.

In Germany, the MAK Commission has classified virtually all chlorinated paraffins as IIIB (ie suspect carcinogens). However, they have not been included in the list of substances (TRGS 905) required to be labeled. The German authorities await an EU decision, which is expected to be made later this year following recommendations from the UK government.

ENVIRONMENTAL ISSUES

Do chlorinated paraffins damage the environment?

There is no evidence that the low levels of chlorinated paraffins which have been shown to occur in the environment have any adverse effect. However results from laboratory experiments indicate that short chain grades are toxic to some sensitive species and may be of potential concern in areas where higher levels of such chlorinated paraffins are present.

The overall assessment of environmental impact is often based on measures of persistence, bio-accumulations and toxicity and each of these topics is addressed in subsequent questions.

Q2 Have Chlorinated Paraffins been detected in the environment?

Very low levels of chlorinated paraffins have been found in the environment. Analysis of rivers in industrialized parts of the UK has shown levels in the range 0 to 5 ug/l (ie. parts per billion), with the more toxic short-chain chlorinated paraffins typically accounting for one-quarter to one-third of the total amount present. Higher levels typically 0 to 10 mg/kg have been found in sediments collected close to industry. In areas remote from industry chlorinated paraffins were either found at much lower levels or could not be detected at all.

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Are Chlorinated Paraffins persistent? Or do they biodegrade?

Chlorinated paraffins are considered to be persistent. They have been shown to break down under the action of bacteria and this biodegradation takes place relatively slowly and none of the grades tested was judged to be 'readily biodegradable'. The rate of biodegradation was found to be higher for grades with lower chlorine content and where bacterial had become acclimatized to chlorinated paraffins for example in the immediate vicinity of a production site.

Do Chlorinated Paraffins bio-accumulate?

Laboratory tests have been carried out to measure the levels present in fish exposed to chlorinated paraffins compared to those present in the water; this ratio is called the bio-concentration factor (BCF). In tests carried out with trout, the BCF was found to be approximately 8000 for short-chain grades, whilst for mid and long-chain grades it was only about 50. These values are very much lower than for substances such as PCDs and chlorine-based pesticides (dieldrin, DDT etc). Studies have also shown that there is no bio-magnification of chlorinated paraffins by fish; the levels of chlorinated paraffin in fish eating food dosed with the product were no higher than those in their diet.

Are Chlorinated Paraffins toxic to fish and other aquatic species?

Only the short-chain grades have been shown, in laboratory tests, to have any measurable toxicity to aquatic life. Tests so far carried out on mid and long-chain chlorinated paraffins indicate that they have a lower order of toxicity than the short-chain grades.

Although short-chain chlorinated paraffins do exhibit some toxic effects to aquatic life after long term exposure to concentrations close to their solubility in water, these are higher than the levels found in the environment.

In the light of this information, what action is being taken to reduce the environmental impact of Chlorinated Paraffins?

From the information presented above, it can be concluded that any environmental risk is limited to short chain chlorinated paraffins. Even for these grades, the levels measured in the environment do not appear to present a major risk. The UK government has been preparing a risk assessment report on short-chain chlorinated paraffins within the framework of the EU Existing Substances Review and the outcome of this is likely to be known by the end of the year.

In the meantime, the Oslo and Paris Commissions have reached a decision to phase out the use of short-chain chlorinated paraffins in most applications by the end of 1998 (although both the UK and Portuguese governments have decided not to enforce this decision). European producers of chlorinated paraffins are also voluntarily taking steps to reduce sales of these grades to the metalworking industry which is believed to present the greatest risk of impact on the environment.

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There have been reports recently of various chemicals acting as estrogen mimics in the environment; do Chlorinated Paraffins have this effect?

There is nothing in the biological profile of chlorinated paraffins to suggest that they would have this effect.

Regulatory Position

Are Chlorinated Paraffins classified as dangerous? The mid and long-chain grades are not classified either for transport or supply under any of the categories of toxicity, physical properties or environmental effect.

The short-chain grades have been provisionally classified by the European producers as 'Dangerous for the Environment'; they are also categorized by IMO as 'Severe Marine Pollutant' and are therefore now placed in UN class 9 for road/rail transport in Europe.

Waste Disposal, Incineration and Dioxins Issues

What advice is given for disposal of wastes containing chlorinated paraffins? Basic information is given in the Material Safety Data Sheets provided for each grade. More detailed advice on the handling of both liquid and solid wastes can be found in fact sheets recently published by Euro Chlor (the group within CEFIC representing the European Chlor-Alkali industry).

Where recovery of chlorinated paraffins from wastes is not a viable option, disposal by either incineration or (where allowed) landfill are recommended.

Will incineration of Chlorinated Paraffins give rise to dioxins? Although the formation is dioxins is theoretically possible whenever materials containing chlorine are burned, studies with PVC and other waste streams both with and without chlorinated paraffins present have not shown any increase in dioxin formation in the presence of chlorinated paraffins. Published reports are referenced in the fact sheets.

[Chlorinated Paraffins Industry Association](#)

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