CHLORINATED PARAFFINS

1. Introduction

Chlorinated paraffins with the general molecular formula $C_xH_{(2x-y+2)}Cl_y$ have been manufactured on a commercial basis for over 50 years. The early products were based on paraffin wax feedstocks and were used as fire retardants and plasticizers in surface coatings and textile treatments and as extreme pressure–antiwear additives in lubricants. The development of chlorinated paraffins into new and emerging technologies was constrained principally because of the limitations of grades based on paraffin wax and the lack of suitable alternative feedstocks to meet the demands of the new potential markets.

In the early 1960s the petroleum industry employing molecular sieve technology made available a low cost and plentiful supply of normal paraffin fractions of very high purity. This enabled chlorinated paraffin manufacturers to exploit new applications with a range of products specifically designed to meet the technical and commercial requirements.

The principal feedstocks used today are the normal paraffin fractions C10–C13, C12–C14, C14–C17, and C18–C20 together with paraffin wax fractions of C24–C30, precise compositions may vary depending on petroleum oil source. Chlorination extent generally varies from 30 to 70% by weight. The choice of paraffinic feedstock and chlorine content is dependent on the application.

The availability of alpha olefins has enabled some manufacturers to offer a range of chlorinated alpha olefins alongside their existing range of chlorinated paraffins. Chlorinated alpha olefins are virtually indistinguishable from chlorinated paraffins but do offer the manufacturer a single-carbon number paraffinic feedstock and even greater flexibility in the product range.

2. Chemical and Physical Properties

By virtue of the nature of the paraffinic feedstocks readily available, commercial chlorinated paraffins are mixtures rather than single substances. The degree of chlorination is a matter of judgment by the manufacturers on the basis of their perception of market requirements; as a result, chlorine contents may vary from one manufacturer to another. However, customers purchasing requirements often demand equivalent products from different suppliers and hence similar products are widely available.

The physical and chemical properties of chlorinated paraffins are determined by the carbon chain length of the paraffin and the chlorine content. This is most readily seen with respect to viscosity (Fig. 1) and volatility (Fig. 2); increasing carbon chain length and increasing chlorine content lead to an increase in viscosity but a reduction in volatility.

Chlorinated paraffins vary in their physical form from free-flowing mobile liquids to highly viscous glassy materials. Chlorination of paraffin wax (C24–C30) to 70% chlorine and above yields the only solid grades. Physical properties of some commercially available chlorinated paraffins are listed in Table 1.

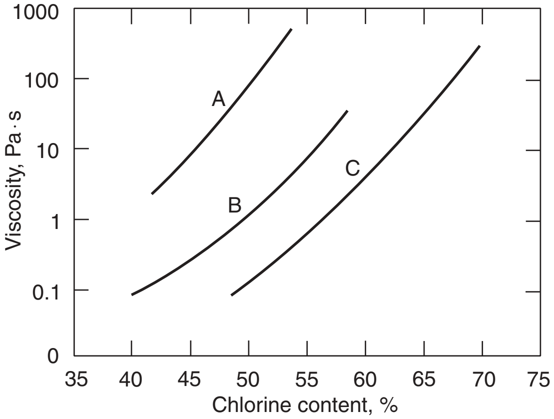

Fig. 1. Viscosity of chlorinated paraffins at 25°C. Paraffin feedstock: A, wax; B, C14–C17; C, C10–C13. To convert Pa·s to P, multiply by 10.

A key property associated with chlorinated paraffins, particularly the high chlorine grades, is nonflammability, which has led to their use as fire-retardant additives and plasticizers in a wide range of polymeric materials. The fire-retardant properties are considerably enhanced by the inclusion of antimony trioxide.

Chlorinated paraffins are relatively inert and exhibit excellent resistance to chemical attack and are hydrolytically stable. They are soluble in chlorinated solvents, aromatic hydrocarbons, esters, ketones, and ethers but only moderately soluble in aliphatic hydrocarbons and virtually insoluble in water and lower alcohols.

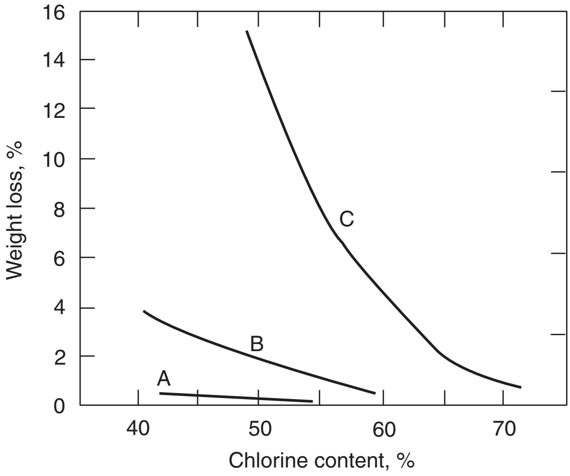

Fig. 2. Volatility of chlorinated paraffins at 180°C after four hours. Paraffin feedstock: A, wax: B, C14–C17; C, C10–C13.

Table 1. **Physical Properties of Selected Commercial Chlorinated Paraffins**

Paraffin carbon chain length	Nominal chlorine contents, %w/w	Color hazen (APHA)	Viscosity,[a] mPa · s (= cP)	Density,[a] g/mL	Thermal stability,[b] %w/w HCl	Volatility,[c] %w/w	Refractive index
C10–C13	50	100	80	1.19	0.15	16.0	1.493
	56	100	800	1.30	0.15	7.0	1.508
	60	135	3500	1.36	0.15	4.4	1.516
	63	125	11,000	1.41	0.15	3.2	1.522
	65	150	30,000	1.44	0.20	2.5	1.525
	70	200	800[d]	1.50	0.20	0.5	1.537
C14–C17	40	80	70	1.10	0.2	4.2	1.488
	45	80	200	1.16	0.2	2.8	1.498
	52	100	1600	1.25	0.2	1.4	1.508
	58	150	40,000	1.36	0.2	0.7	1.522
C18–C20	47	150	1700	1.21	0.2	0.8	1.506
	50	250	18,000	1.27	0.2	0.7	1.512
Wax	42	250	2500	1.16	0.2	0.4	1.506
>20	48	300	28,000	1.26	0.2	0.3	1.516
	70	100[e]	[f]	1.63	0.2		

[a] At 25°C unless otherwise noted.
[b] Measured in a standard test for four hours at 175°C.
[c] Measured in a standard test for four hours at 180°C.
[d] At 150°C.
[e] 10 g in 100 mL toluene solvent.
[f] Solid, softening point = 95 – 100°C.

Although considered to possess good thermal stability, chlorinated paraffins, if held at high temperatures for prolonged periods, first darken in color and then release detectable quantities of hydrochloric acid. Manufacturers often quote a thermal stability index which is a measure of the quantity of hydrochloric acid released expressed as a percentage by weight after heating the product for four hours at 175°C. Degradation of chlorinated paraffins can also be accelerated at elevated temperatures in the presence of iron, zinc, and dehydrochlorination catalysts. The thermal stability of chlorinated paraffins can be improved by the inclusion of epoxidized compounds which typically are epoxy esters, antioxidants of the hindered phenol-type, and metal soaps.

3. Manufacture

Chlorinated paraffins are manufactured by passing pure chlorine gas into a liquid paraffin at a temperature between 80 and 100°C depending on the chain length of the paraffin feedstock. At these temperatures chlorination occurs exothermically and cooling is necessary to maintain the temperature at around 100°C. Catalysts are not usually necessary to initiate chlorination, but some manufacturers may assist the process with ultraviolet light. Failure to control the reactive exotherm during chlorination may lead to a colored and unstable product. The reaction is terminated by stopping the flow of chlorine when the desired degree of chlorination has been achieved. This is estimated by density, viscosity, or refractive index measurements. The reactor is then purged with air or nitrogen to remove excess chlorine and hydrochloric acid gas. Small quantities of a storage stabilizer, typically epoxidized vegetable oil, may be mixed in at this stage or later in a blending vessel.

In general terms, for each ton of chlorinated paraffin produced, approximately one-half ton of hydrochloric acid is generated. Thus materials of construction must be resistant to acid attack. Reactor vessels were traditionally lined with lead or ceramics but glass-lined mild steel is now preferred. Ancillary equipment such as stirrers, pumps, valves, and pipelines should be of corrosion/acid-resistant material. Good housekeeping is vital as minute traces of metal chlorides entering the process can cause dehydrochlorination leading to discoloration of the chlorinated paraffin. A typical system employed in commercial production is shown in Figure 3.

In order to operate an economically viable chlorinated paraffin business, it is essential to have a profitable outlet for the surplus hydrochloric acid, either through direct sales into the market, or preferably via an oxychlorination unit in an integrated vinyl chloride/chlorinated solvent unit, while still maintaining the option of direct sales.

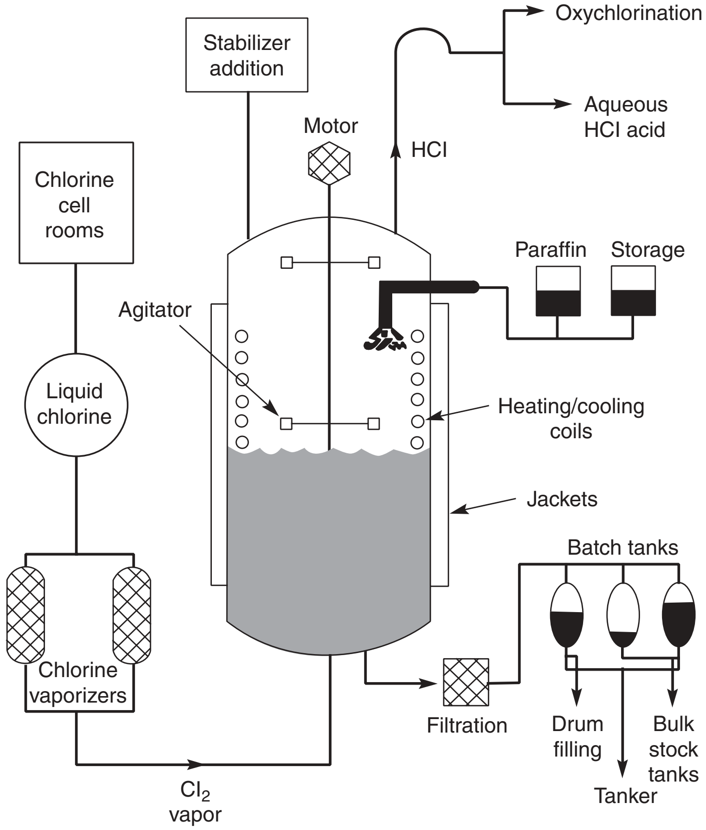

Fig. 3. Chlorinated paraffin manufacture.

4. Shipment and Storage

Liquid chlorinated paraffins are shipped in drums usually lacquer-lined mild steel or polyethylene and in road or rail barrels. Where appropriate larger quantities can be shipped by sea either in deck tanks of conventional cargo ships or in chemical parcel tankers for larger consignments.

The high viscosity of a number of grades generally precludes consideration of bulk supplies unless special transport, heating, pumping, and storage can be made.

Road and rail barrels are usually constructed of stainless steel or lacquer-lined mild steel and may require some provision for heating during cold weather. This is best achieved by submerged coils circulating hot water at about 40°C or low pressure steam, but care must be taken to ensure the surface temperature of the coils does not rise excessively otherwise discoloration of the product may occur.

The main points to be considered when designing a bulk storage installation are (*1*) the viscosity of all grades of chlorinated paraffin varies sharply with a change in temperature; (*2*) chlorinated paraffins should not be exposed to temperatures in excess of 40°C for prolonged periods of time; (*3*) chlorinated paraffin stability can be affected by contact with zinc and iron, therefore tanks of mild steel should generally be lined and galvanized steel avoided. Stainless steel, lacquer, or glass-lined mild steel tanks are recommended. The preferred linings are of the heat-cured phenol—formaldehyde type; and (*4*) chlorinated paraffins swell certain types of rubber and therefore rubber joints should be avoided. Polytetrafluorethylene joints are recommended.

As for storage tanks, stainless steel and lacquer-lined mild steel are suitable materials of construction for pipe lines. For pumps, valves, etc, various alloys are suitable, including phosphor bronze, gun metal, Monel, stainless steel, and certain nickel steel alloys. Alloys with high proportions of zinc and tin together with copper and aluminum are not recommended.

5. Economic Aspects

U.S. Producers of chlorinated paraffins are listed in Table 2.

Demand for Chlorinated paraffins in 2000 was 42.9×10^6 kg (97×10^6 lb), in 2001 demand was 42.5×10^6 kg (96×10^6 lb). Expected demand in 2005 is 42.9×10^6 kg (97×10^6 lb). Demand equals production plus imports (negligible).

Table 2. **U.S. Producers of Chlorinated Paraffins and Their Capacities**[a]

Producer	Capacity, $\times 10^6$ kg ($\times 10^6$ lb)
Dover Chemical, Dover, Ohio	40.8 (90)
Keil Chemical, Hammond, Ind.	23.7 (50)
Total	*63.5 (140)*

[a] Ref. 1.

Exports are estimated to be about 4.9–7.3 × 10^6 kg (11–16 × 10^6 lb) in recent years (1).

Growth is expected at 0% since applications are mature. Environmental pressure exists against chlorinated materials although no future regulations directly related to chlorinated paraffins is anticipated (1).

The European Union was to adopt restrictions on the use of short chain chlorinated paraffins for metal working and leather finishing. The United States Environmental Protection Agency completed its investigation and concluded there was no need to restrict short-chain chlorinated paraffins in any of its uses (1).

Prices have remained over the period 1996–2001 at $0.32/kg ($0.70/lb), 50% chlorine, list drum T.1. del.

In the United States approximately 50% of the chlorinated paraffins consumed domestically are used in metal-working lubricants. Approximately 20% are consumed as plastic additives, mainly fire retardants, and similarly 12% in rubber. The remainder as plasticizers in paint (9%), caulks, adhesives, and sealants at 6%, miscellaneous uses account for 3% (1).

6. Health and Safety Factors

A substantial body of information on the toxicological and environmental effects of chlorinated paraffins has been compiled over the past 20 years, and research is still continuing in both areas.

The acute toxicity of chlorinated paraffins has been tested in a range of animals and was found to be very low (2). A comprehensive study (3) demonstrated that the toxicity of chlorinated paraffins was related to carbon chain length and to a lesser degree chlorine content. The shorter chain-length chlorinated paraffins were more toxic than the longer chain chlorinated paraffins.

Subchronic studies in mice, rats, and rabbits determined the liver as the primary organ for attack by chlorinated paraffins. Mutagenicity, and reproductive and teratology studies revealed no abnormal effects. However, the National Toxicology Program (NTP) in the United States concluded that there was sufficient evidence of carcinogenicity from lifetime studies in rats and mice with one chlorinated paraffin having chain length of 12 carbon atoms and chlorine content 58% by weight. It is listed in the *Fifth Annual Report on Carcinogens.* Parallel studies on a long-chain chlorinated paraffin of average chain length (23 carbon atoms and 42% chlorine) showed no statistical increase in tumors. The NTP studies were reviewed by the International Agency for Research on Cancer (IARC) who concluded that the short-chain chlorinated paraffin was a possible human carcinogen (Cat II B). More recently, an extensive series of experiments (4) have been conducted to study further the biochemistry of the carcinogenic effects of the short-chain chlorinated paraffin C12 and 58% chlorine in rats and mice. The results support an earlier hypothesis (2) that the mechanism responsible for the occurrence of tumors in the liver of rats and mice is of a nongenotoxic nature and is associated with liver growth. This work shows that the effect is accompanied by peroxisome proliferation, and these effects are unlikely to occur in humans.

Because of the nature of some applications in which chlorinated paraffins are used, skin contact is inevitable and therefore an important potential route into the body. Skin absorption studies (5) have shown that chlorinated paraffins are very poorly absorbed through the skin and should not cause significant systemic concentrations.

7. Environmental Aspects

In general, chlorinated paraffins biodegrade; the rate is determined by chlorine content and carbon chain length. Microorganisms previously acclimatized to specific chlorinated paraffins show a greater ability to degrade the compounds than nonacclimatized organisms. Mammals and fish have been shown to metabolize chlorinated paraffins (6).

The acute toxicity of chlorinated paraffins to mammals, birds, and fish is very low (6), but over longer periods of exposure certain chlorinated paraffins have proved to be toxic to some aquatic species. However, the very low water solubility of chlorinated paraffins has made studies on aquatic species complicated. Laboratory experiments in which the chlorinated paraffins had been artificially solubilized showed only the short-chain grades to be toxic at low concentration; other longer-chain grades showed no adverse effects on the majority of aquatic species tested. The degree of solubilization achieved in the laboratory is unlikely ever to be experienced in the environment and is of doubtful environmental relevance (7).

In the United States further information and advice is readily available from the Chlorinated Paraffin Industry Association (CPIA) based in Washington D.C.

8. Applications

Chlorinated paraffins are versatile materials and are used in widely differing applications. As cost-effective plasticizers, they are employed in plastics particularly PVC, rubbers, surface coatings, adhesives, and sealants. Where required they impart the additional features of fire retardance, and chemical and water resistance. In conjunction with antimony trioxide, they constitute one of the most cost-effective fire-retardant systems for polymeric materials, textiles, surface coatings, and paper products. Chlorinated paraffins are also employed as components in fat liquors used in the leather industry, as extreme pressure additives in metal-working lubricants, and as solvents in carbonless copying paper.

8.1. Plasticized PVC.

Chlorinated paraffins are employed as secondary plasticizers with fire-retardant properties in PVC and can be used as partial replacements for primary plasticizers (qv) such as phthalates (8) and phosphate esters (9).

By selection of those chlorinated paraffins specifically developed for the PVC industry to match the properties of primary plasticizers, reductions in costs can be achieved without significant change in properties. However, certain aspects can be improved by the inclusion of chlorinated paraffin such as flame resistance, chemical and water resistance, low temperature performance, and the viscosity aging stability in plastisols.

8.2. Metal-Working Lubricants. A range of chlorinated paraffins are used as components of straight and emulsifiable metal-working lubricants as well as gear oils for industrial and automotive applications. In heavy-duty industrial gears, hypoid gears, metal cutting, and allied operations where high pressures and rubbing action are encountered, hydrodynamic lubrication cannot be maintained. In order to maintain lubrication under such conditions, extreme pressure (EP) or antiwear additives must be added to the lubricant. Such additives contain one or more of the elements of chlorine, sulfur, or phosphorus. Chlorinated paraffins are cost-effective extreme pressure additives and are either used alone or in combination with additives containing sulfur and/or phosphorus according to the application. High chlorine content lubricants are used for severe metal-forming operations such as deep drawing and stamping. This area is the principal outlet for chlorinated paraffins in the United States, accounting for approximately 50% of total sales.

The selection of chlorinated paraffin and the level of additives to a lubricating oil depends on the type of application and the severity of the operation. An approximate guide for the formulation of straight-cutting oils for metal-working is as follows:

Fluid type	*Additives*
heavy-duty broaching	60% chlorine + 10% fatty acid
very heavy-duty cutting	30% chlorine + 1% sulfur + 10% fatty acid
medium to heavy-duty	5 − 10% chlorine + 1 − 0.5% sulfur + 1 − 5% fatty oil
light to medium-duty	2 − 5% chlorine + 0.2% sulfur + 1 − 5% fatty oil

Metal-forming operations such as deep drawing, stamping, wire drawing, etc, are extremely severe and require large amounts of chlorinated paraffins; often the high chlorine containing grades are preferred. In some applications a mid-range chlorine content grade may be used neat. After deep drawing and stamping of mild steel, components are frequently left unprotected in storage. This can result in corrosion problems. For these applications chlorinated paraffins containing corrosion inhibitors and special stabilizers are available.

8.3. Paints. Chlorinated paraffins are used as plasticizers for paints based on many types of resins, particularly chlorinated rubber and vinyl copolymers. Chlorinated rubber-based paints are employed in aggressive marine and industrial environments and vinyl copolymer principally for the protection of exterior masonry. The excellent chemical resistance of chlorinated paraffins and their ability to withstand prolonged contact with water makes them ideally suited as plasticizers for the most demanding applications.

8.4. Adhesives and Sealants. Various grades of chlorinated paraffins are used as nonvolatile inert fire-retardant plasticizers and modifying resins in adhesives and sealants (10). They find wide application in polysulfide, polyurethane, acrylic, and butyl sealants for use in building and construction. The low volatility high chlorine types are also employed in sealants for double- and triple-glazed windows.

8.5. Flame-Retardant Applications. The flame resistance of polyolefins, unsaturated polyester, rubber, and many other synthetic materials can be improved by the inclusion of chlorinated paraffins. The solid 70% chlorine product is the preferred choice in most polymeric systems, but the liquid grades are widely used in rubbers, polyurethane, and textile treatments.

Chlorinated paraffins and modified types are used as solvents in carbonless copying paper production based on the encapsulation of a solution of reactive dyes. Chlorinated paraffins fullfill the technical requirements for a solvent including excellent solvency for the dyes; they do not react with the dyes nor encapsulation material, are immiscible with water, and have low volatility and low odor.

8.6. Fat Liquors for Leather. The addition of a chlorinated paraffin to a sulfated or sulfonated oil offers alternatives to natural oils as fat liquors for leather.

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