PENTACHLOROPHENOL: An Update to the CWPA and Canadian Wood Treaters

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Abstract

Pentachlorophenol (Penta) was first invented in the early 1930's. Through research and chemical investigations, it was found to be a very effective fungicide and insecticide, which resulted in its early use as a wood preservative before 1940. Due to the severe shortage of Creosote for the war effort, penta became a widespread use wood preservative for millwork/joinery, utility poles, crossarms, lumber and timber, and as its Sodium Salt, for anti-sapstain and mold control, in fresh-cut lumber. It was first registered by the US Government under the Economic Poisons Act of 1910 immediately after its invention and use screening, as a herbicide, fungicide, insecticide, bactericide, and molluskicide. It remained a wide use pesticide, later registered by the USDA, still under the Economic Poisons Act of 1910 when, after the formation of the US EPA by President Nixon in 1972, its registrations were transferred over to the Environmental Protection Agency-Office of Pesticide Programs. It remained a General Use Pesticide, available for public purchase until 1986, when the outcome of the RPAR and the Cancellation Hearings and resultant Settlement Agreement (Chapman Chemical Co. et al.) altered its Registration over to an RUP (restricted use pesticide), and established regulatory limits on its HCB and HxCDD content. In 2008 the USA EPA issued the RED on Penta, deeming its use patterns as a wood pole and crossarm preservative "does not cause any adverse health effects on man or the environment". Today its use patterns around the world are being challenged by Countries that are signatories to the Stockholm Convention, as a PoP (persistent organic pollutant). This review covers the regulatory status of penta and also discusses the very high efficacy of the product when used properly to protect wood, especially wooden utility poles. Today, there are six commercial users in Canada, consuming some 15-20% of the annual production of 16.5 million pounds of penta. Canada has alos opted to opt-out of the Stockholm Commission concerning any future and current penta restrictions or limits for its use as a commercial, industrial wood preservative. It has been listed for use by the CSA in excess of 70 years in Canada.

INTRODUCTION

Pentachlorophenol or "Penta" or PCP (C_6Cl_5OH) is an aromatic hydrocarbon chlorophenol that was described in the scientific literature as early as 1841 and has been commercially produced since 1931. Solutions containing penta in mineral spirits were first used in commercial dip treatments of wood by the millwork industry in 1931. Commercial pressure treatment of poles with penta in heavy petroleum oils began in 1941. Penta was first registered as an active ingredient by the United States Department of Agriculture in 1950 (EPA 2008). Products containing penta as an active ingredient have been used as herbicides, insecticides, fungicides, molluscicides and bactericides.

They have been used in rice and sugar production, in water treatment, as a pre-harvest defoliant in cotton, in adhesives, construction materials, leather and paper. By 1981 over 600 products containing penta were registered for use in the USA. Penta became a restricted-use pesticide in 1987 and is only available to certified applicators. It now has no registered residential uses (Fishel 2005, EPA 2008). It is predominately used to treat utility poles and cross arms. Currently, there are six products containing penta as an active ingredient (EPA 2008). Penta is a broad based pesticide with efficacy against carpenter ants, mold, beetles, beetles, termites, wood rot/decaying fungi, wood stain fungi. Penta is the most documented substance in wood preservation. Before the 1987 Federal register notice that canceled and restricted certain uses, it was one of the most widely used biocides. The salt sodium pentachlorophenate (Na-PCP) was used for similar purposes as PCP and readily degrades to penta. Penta extends the functional life of wood by at least eight times (Wilkinson 1995; Fishel 2005; Freeman 2010).

PERSISTENT ORGANIC CHEMICALS (PoPS)

Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world. Persistent organic pollutants (POPs) are defined as organic substances that: (i) possess toxic characteristics; (ii) are persistent; (iii) bioaccumulate; (iv) are prone to long-range transboundary atmospheric transport and deposition; and (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources (Gon, et al. 2007). POPs persist for long periods of time in the environment and can accumulate and pass from one species to the next through the food chain. POPs generated in one country can and do affect people and wildlife far from where they are used and released because they can be transported by wind and water. To address this global concern, in 2001, the United States and 90 other countries and the European Community signed the treaty, known as the Stockholm Convention which . became effective 2004. Under this treaty, countries agreed to reduce or eliminate the production, use, and/or release of 12 key compounds. Initially co-signatories agreed to outlaw nine of the dozen chemicals, limit the use of DDT to malaria control and curtail inadvertent production of dioxins and furans. Parties to the convention have agreed to a process by which persistent toxic compounds can be reviewed and added to the convention, if they meet certain criteria for persistence and transboundary threat. The first set of new chemicals to be added to the Convention were agreed on in 2009. The Stockholm Convention has five essential aims: eliminate dangerous POPs, starting with the 12 worst, support the transition to safer alternatives, target additional POPs for action, cleanup old stockpiles and equipment containing POPs, Work together for a POPs-free future. The 12 key POPs that were initially targeted by the Stockholm Convention are Aldrin,Chlordane, Endrin, Heptachlor **Dichlorodiphenyltrichloroethane (DDT),** Hexachlorobenzene (HCB) Toxaphene, Mirex, Dieldrin, **Polychlorinated biphenyls, Polychlorinated dibenzofurans, Polychlorinated dibenzo-p-dioxins.**

In 2009, additional chemicals were listed as persistent organic pollutants targeted for ellimination or restricted production. These included.

- Pesticides: chlordecone, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, lindane, pentachlorobenzene;
- Industrial chemicals: hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether, and pentabromodiphenyl ether.

- By-products: alpha hexachlorocyclohexane, beta hexachlorocyclohexane, and pentachlorobenzene.

POP chemicals, often come from certain series or 'families' of chemicals (e.g there are theoretically 209 different polychlorinated biphenyls, differing from each other by level of chlorination and substitution position) (Jones and de Voogt 1999). Hence there are many thousands of individual POPs. POPs have long half-lives in soils, sediments, air or biota. POPs are hydrophobic and lipophilic. In aquatic systems and soils, they partition strongly to solids, notably organic matter, avoiding the aqueous phase. They also partition into lipids in organisms rather than entering the aqueous milieu of cells and become stored in fatty tissue. This confers persistence on the chemical in biota since metabolism is slow and POPs may there-fore accumulate in foodchains. POPs may volatilise from soils, vegetation and water bodies into the atmosphere and because of their resistance to breakdown reactions in air travel long distances before being re-deposited. The cycle of volatilisation and deposition may be repeated many times, with the result that POPs could accumulate in an area far removed from where they were used or emitted. In the atmosphere itself, POPs can partition between particles and aerosols depending on ambient temperature and the physico-chemical properties of the chemical (Jones and de Voogt 1999).

Because POPs can bioaccumulate and magnify in the foodchain, concern centres around their impact on top predator species, including humans. Probably the best documented and clearest evidence of effects have been in birds and marine mammals. Because an extensive array of POPs occur and accumulate simultaneously in biota it is very difficult to say conclusively that an effect is due to one particular chemical, a family of chemicals, their metabolites or indeed several families of chemicals acting synergistically. This makes control of the problem difficult, because scientists and policy makers have been unsure which POP(s) require restriction/regulation.

Factors that apply to POPs but not Penta

While penta is not on the list of the 12, dioxins and furans which are contaminants in penta are included

1. *Poor or non-existent information on past/present regional usage/emission of many POPs*
   Penta is has been widely studied and is the most documented substance in wood preservation. A lot of information is available about use worldwide
2. *Lack of understanding of how POPs cycle and become transported in the deep oceans.*
   Information on how penta and its contaminants partitions in the environment is available due to research that has been done since the 1970's to present.
3. *Uncertainties over the rates of atmospheric reactions for different POPs, uncertainties over the rates of biodegradation in real environmental settings.*
   Rates of penta biodegradation in the environment have been established. The bioaccumulation of penta contaminants is also well elucidated

The one factor that applies to POPs including penta is lack of residue data in air, water, soil and sediments for huge areas of the globe, notably in Africa, Asia, the former Soviet Union and China, South America and the oceans (Jones and de Voogt P 1999).

Penta is only one of many sources of CDDs, CDFs, and HCB in the environment, it is difficult to quantify the portion of the aggregate environmental risk from CDDs, CDFs, and HCB that is attributable to penta use (EPA 2008).

Pentachlorophenol Contaminants as POPs

While pentachlorophenol is not listed on the two lists, by products of penta manufacture or penta impurities are included. The principal impurities of concern are the dioxins with six to eight chlorines including hexachlorodibenzodioxin (HxCDD) and octachlorodibenzodioxin (OCDD). These compounds are inherently toxic, as well as environmentally persistent, and their presence increases the ecological risk associated with the use of penta. In the next sections of this review, we focus on the use of penta and its manufacture. We also focus on properties of penta, its toxicity and the toxicity of its contaminants. A review of literature shows that most of the toxicity, persistence and accumulation in tissues and the environment is attribibuted to contaminants of penta and not penta itself. Contaminants arise during manufacture.

WORLDWIDE PRODUCTION AND USE OF PENTA

Use of Pentachlorophenol worldwide

The use of penta is prohibited in 26 countries around the world, but not in the United States, Mexico and Canada. Penta continues to be used but depending upon the reporting country, the number of banned uses ranges from all uses to few uses. Most reporting countries banned residential indoor uses. Austria, India, Indonesia, New Zealand, Sweden and Switzerland have reported a total ban (FAO 1996). Principal use in the United-States and Canada is now the pressure-treatment of posts, cross arms, utility poles, and fresh water-foundation pilings. In 1997 the manufacturers of penta voluntarily removed groundline/remedial treatment applications from the U.S. EPA registered labels for the product. All non-pressure and non-thermal treatment uses (i.e. spray uses) were deleted from the registrants' labels since 2004. This action left only pressure and thermal treatments with penta. Non-pressure/non-thermal treatments generally lead to higher applicator exposures. Thermal and Butt treating are no longer on the EPA labels today.

Regulations on penta such as a true or perceived ban in certain countries have been triggered by various events such as emotional and political pressures to provide satisfaction to pressure groups (Ozanne 1995). Penta is commonly considered the most documented substance in wood preservation. An extensive body of literature exits on the health effects of penta. Practical conclusions from the enormous amount of work can be drawn to address the various questions raised by the chemical and its derivatives (Ozanne 1995). Beyond Pesticides, formerly NCAMP, has notoriously spread false hoods concerning penta and its toxicity in treated wood for decades.

Production of Pentachlorophenol worldwide

The worldwide production of PCP in 2016(most recent data set) was estimated to be 16.5 million pounds per year, treating some 2 million utility poles annually in the USA, and Canada out of a total 4.2 million pole annual N. American production. Worldwide production level has decreased since 1981 and the penta demand has declined over the last years, mostly due to NaPCP loss of market share and multiple production facilities closed in some countries. In UN-ECE region there is one company manufacturing penta, located in the N. America, located in Matamoros, Mexico. The former production volume in 2009 was indicated at 7,257 tonnes. In most European countries the production of penta ceased in the mid-nineties. Before that time, it was produced in Poland, Germany, the Netherlands, Denmark, Switzerland, United Kingdom, Spain and France. In Spain production stopped in 2003. After production stopped penta was imported to the European market from the United States. In Canada production stopped before 1990. At the moment the one company in North America manufacturing it is KMG Bernuth. Production facilities are located in Tuscaloosa (Alabama), Wichita (Kansas) and Matamaras (Mexico). KMG supplies penta to the wood preservation industry in the U.S, Canada and Mexico. KMG-Bernuth and ISK Biocides produced Na-PCP until 2006, when it stopped production of that product (Jackson 2011). The company's sales of penta in 2009 were valued at $26.2 million. A production plant in Wichita was formerly owned by the Vulcan Materials Company. In 2004, Vulcan Materials sold the assets to Basic Chemical Company, LLC, a subsidiary of Occidental Chemical Corporation, but decided against entering the penta business. In 2005, KMG Chemicals, Inc. a global provider of specialty chemicals acquired assets used in the manufacture and sale of penta from Occidental Chemical Corporation. The equipment included in this acquisition backed-up KMG's then existing penta plant, thereby assuring security-of-supply for penta. KMG had acquired the original penta distribution business in 1984 and built a penta manufacturing plant in Matamoros, Mexico in 1986 (vulcanmaterials.com). Penta revenues were projected to increase by over $3 million per year. Demand for penta and creosote was near record levels during fiscal 2007, driven by continued strong demand for utility poles and rail ties. KMG's penta revenues increased 2% to $28.4 million as compared to fiscal 2006, and creosote revenues were up 42% to $43.6 million. The Railway Tie Association forecasted demand for rail ties to be relatively flat in 2008 and KMG anticipated the same for utility pole demand. The company's penta products include penta blocks, flakes, and solutions of penta concentrate. In the U.S., the company sells penta primarily in Alabama, Arkansas, Georgia, Louisiana, Mississippi and Missouri, but as of today, over four dozen treating plants use penta in 20 states, and Canada. The penta segment constituted 17% of the company's (KMG) net sales in fiscal 2008.

The production process in the United States

Penta manufactured in the United States is produced by the stepwise direct chlorination of phenols in the presence anhydrous aluminum chloride or ferric chloride catalysts at approximately 191°C. However, this process is incomplete. As a result, commercial grade penta is between 84-96% pure. During the process several contaminants including tri- and tetrachlorophenols, other polychlorinated phenols, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are produced too, which are more toxic than the penta itself. However, the most toxic contaminant, 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) is not produced by this process. An alternative production process, used in other countries but not in the United States, involves the hydrolysis of hexachlorobenzene, which can contaminate penta with 2,3,7,8-TCDD. Direct chlorination produces fewer undesirable constituents (Ruder and Yiin 2005).

Current use of Pentachlorophenol and Consumption volumes of penta treated wood

Current penta consumption for wood preservation concentrates and blocks in North America. In Europe it is presumably no longer used for wood preservation although this cannot be verified for all European countries, especially the ones outside the EU. Utility poles and cross-arms account for more than 90% of penta consumption.

The total amount used in Canada is estimated at 150 tonnes, whereas U.S. consumption was documented by the US EPA to be 5,000 tonnes in 2002. China was once in the penta producing countries outside the UN-ECE region with an annual production volume of 5000 tonnes (Zande 2010, Freeman 2016).

Penta is classified as a Restricted Use Pesticide (RUP) no longer available to the general public and its use and purchase are restricted to certified pesticide applicators. The only currently registered use of penta is for pressure and outdoor construction materials. The majority of penta used in North America is for treatment of utility poles and cross-arms. Utility Poles and Crossarms constitute 90% of market and laminated beams for bridge construction make 5% of market (Zande 2010). Because wood that has been preserved with penta does not become brittle and retains its strength, it is the material of choice in bridge construction (Ritter). In addition, aquatic environments can be exposed to penta when preserved utility poles are used to cross streams and wetlands. In Canada the wood treatment industry consists of about 66 plants in 1999. It is unclear if all these plants use penta as wood preservative. In the U.S. approximately 49 wood preserving plants use penta.

Production and consumption levels of penta have decreased over the years. Legislation and the availability of alternatives account for this decrease. The most prevalent wood preservative utilized for poles in service is penta (>55%). But in 2011, approximately 63% of poles are treated with penta, followed by CCA (16%), creosote (16%), copper naphthenate (3%) and ammoniacal copper arsenate or ammoniacal copper zinc arsenate (1%). Approximately 16.5 million pounds of technical penta are used annually, resulting each year in the penta treatment of an estimated 2 million wood utility poles. Penta is suitable for treatment of Douglas-fir, which is a refractory species, and they cannot be treated with CCA (Jackson 2011). In the lumber and timber market, waterborne salts (primarily CCA until 12/31/2003) have traditionally had the largest share of the market. In 2004, waterborne preservatives were used to treat 11.3 million m^3 of lumber and timber (>99 % of the market) while penta accounted for only approximately 0.08 million m^3 (0.1 %) in this market (Zande 2010). Today, 78% of the residential lumber market is treated with waterborne micronized copper formulations.

The total amount used in Canada in 2013 is currently best estimated at 147 tonnes which is imported from the U.S. This product is used in six (Pressure-vaccum plants in three of the Canada provinces. The U.S. consumption is expected to be much higher. In 2002 over 5,000 tonnes of PCP were used. For that same year about 160 million to 166 million treated wood poles were estimated to be in service in the U.S. An estimated 2-3% of the treated poles are replaced annually. This means that, without reuse or recycling, about 3 to 4 million poles are replaced in the U.S every year (Freeman 2010, Zande 2010).

REGULATIONS GOVERNING PENTA USE IN OTHER COUNTRIES

Penta is the most documented substance in wood preservation. An extensive body of literature exits on the health effects of penta. Practical conclusions from the enormous amount of work can be drawn to address the various questions raised by the chemical and its derivatives (Ozanne 1995). Regulations on penta such as a pure ban in certain countries to provide satisfaction to pressure groups have been triggered by events such as emotional and political pressures.

European Union and National legislation in European countries

Within the EU the marketing and use of substances and preparations, to which penta or its salts and esters have been added intentionally in a concentration equal to or greater than 0,1% by mass is banned since 2000. Some member states were permitted to choose not to apply the total ban until December 31, 2008. It is likely that all EU-members have banned the use by autonomous measures. For outside the EU this is unknown. EU legislation is only applicable to the use of penta within the EU Member States. Some European countries – Norway, Denmark, Germany, Netherlands and Austria – have introduced national legislation on penta in products that is stricter than the harmonised EU legislation. National legislation restricts the presence of penta in products placed on the national market. In the Netherlands the trade and import of articles containing more than 5 mg penta/kg is strictly prohibited since 1997. In the Ukraine penta is included into the list of pesticides banned for usage in agriculture, registration and re-registration. Belgium reports that penta was never authorized as pesticide. In Cyprus penta is restricted under national legislation. In Switzerland the production, import and use of penta have been prohibited since 1986. This general prohibition has been taken over in the Swiss Ordinance on Chemical Risk Reduction since 2005. Additionally, the ban on wood-based materials containing more than 5 ppm of PCP since 2006 was enforced. In the Netherlands the import of consumer products containing more than 5 mg/kg (5 ppm) of Penta or NaPCP is prohibited. In practice, the low maximum concentrations allowed in the Netherlands imply that the use of PCP is as good as prohibited. The prohibition applies to all consumer products, excluding foods and drinks. If a consumer product consists of several parts, the prohibition applies to each part separately (Zande 2010).

Canada

The Canadian Government (PMRA) adopted an identical program to that instituted by the EPA on reregistration of penta. Although there is no penta manufacturing plants in Canada, there are treatment plants that still use penta imported from the United States. As of the writing of this paper, penta plants in Canada producing penta treated items tallies six, including the former DomTar plants now owned and operated by Stella-Jones.

RELEASES OF PENTACHLOROPHENOL IN THE ENVIRONMENT

When penta is produced, used, and when penta treated articles are used or disposed of as waste, penta and its microcontaminants are released into the environment. Wood preservation and hazardous waste handling are the most important sources of penta emissions. In the U.S. approximately 2,600 kg penta was released in 2008, of which 172 kg was released to air, 513 kg to water and 1,865 kg was land filled. The relatively high volatility and mobility of penta and the water solubility of its ionized form have led to the widespread distribution in all environmental sectors, and a long-range dissemination of this compound. Penta will leach from treated wood, volatilise from treated surfaces and may get into waterways (Zande 2010). Penta contamination in the food chain may result from exposure to treated wood or as a result of environmental releases from wood treating operations.

Releases from production facilities

In the case of an annual production of approximately 2000 tonnes of penta, about 18 kg penta, 9 kg of other chlorophenols, 1 kg of chlorobenzenes and 0.2 kg of dioxins are released to air.

The waste remaining from production contains several hazardous substances as well. The waste is generally disposed of by either storage in underground disposal sites or by incineration at high temperatures. Table 1, extracted from the TRI-database, shows disposal releases of penta between 2002-2008. Although data vary over the years, the emission data show that the wood products industry, as well as hazardous waste handling, contribute to a large part to the amounts released.

Year	Industry		Air	Water	Landfills	Other	Total
2002	Wood products		46	293	5030	2	5372
	Hazardous waste/solvent		3	159	121	0	238
	other		11	-	0	0	11
		Total	60	407	5152	2	5621
2003	Wood products		142	270	626	2	1040
	Hazardous waste/solvent		1	159	116	0	231
	other		77	0	0	1	78
		Total	220	384	742	3	1349
2004	Wood products		32	315	917	10	1274
	Hazardous waste/solvent		0	15	7681	0	7696
	other		-	-	-	-	-
		Total	0	330	8598	10	8970
2005	Wood products		31	225	599	3	858
	Hazardous waste/solvent		9	15	230	0	254
	other		25	0	0	6560	6585
		Total	65	241	829	6563	7698
2006	Wood products		26	186	381	0	594
	Hazardous waste/solvent		20	13	119	363	515
	other		0	0	85	0	85
		Total	46	199	584	363	1193
2007	Wood products		33	208	420	366	1026
	Hazardous waste/solvent		8	13	227	0	249
	other		-	-	-	-	-
		Total	41	221	647	366	1275
2008	Wood products		165	489	694	0	1348
	Hazardous waste/solvent		6	24	1107	43	1180
	other		0	0	64	0	64
		Total	171	513	1865	43	2591

Table 1. Disposal of releases of Penta in kg/year in the USA wood industry and hazardous waste solvent recovery and other chemical manufacturers

Documented penta environmental releases have been associated with wood treating operations as evidenced by the number of facilities on the superfund list. Past practices at these superfund sites have resulted in extensive contamination of soils, and groundwater with penta and its impurities and its degradation products. Such practices have included waste water discharge, and storage, process residuals, drippage from treated wood, and waste disposal. Waste water storage, discharge and sludge management have been noted as activities with a high potential for incidental releases of penta or routes of entry of penta into the environment. Introduction of penta into the environment may occur from spills and runoff, and through releases from treated wood by leaching and/or volatilization. These may occur at wood treatment, storage and disposal sites, as well as at the locations of wood usage. Pentachlorophenol may also enter the environment by wastewater discharge or holding pond overflow, both of which may occur at wood treating facilities.

Penta releases from poles in service by bleeding and depletion:

Treated wood typically contains about 130-140 μg/m^3 penta corresponding to concentrations of 0,484 mmol/L in treated wood (Pohleven and Boh 2007). In poles treated to 0.3-0.5 pcf retention, depletion of penta is significant only in the outer ½ inch zone of the pole. Little or no depletion occurs in underlying zones, presumably because there is no liquid hydraulic- flux action present to promote diffusion or capillary migration. Because of the demonstrated tendency for penta to adsorb to soils and the moderately rapid degradation of the compound in the environment, it is not likely that groundwater contamination will result from usage of utility poles, except in situations where the bottom of the pole is directly in contact with the water table or where the leaching occurs from multiple poles in a wood storage or treatment area. Studies have shown that there is no significant releases from penta from poles into surrounding soils. A study of 30 poles showed that releases in soils within 2.5cm of poles averaged 658 mg/Kg and ranged from 0.19-9500mg/Kg. Within 30 cm of the poles it ranged from 0.05-40mg/kg with an average of 3.4mg/Kg. At 150cm an averge of 0.26mg/Kg and a range of 0.03-1.0mg/kg was found. Penta releases to surface water due to open storage of treated lumber into rain water have been shown a range of 0.18-27.5 mg/L which is lethal to juvenile trout. The known acute toxicity to fish is within the range of 0.20-0.6 mg/L , hence there is only a small potential for such releases to cause environmental impact. This author has personally inspected piers, docks and fresh water piling, ranging from 2-40 years old, in Lake Norman, Lake Tillery, and Lake Wylie, and found structurally sound penta treated wooden members, with no obvious effect on aquatic life.

Volatilization: the outer layers of penta treated wood contain up to several hundred mg/kg of penta. Due to volatilization, air levels of penta in proximity to large amounts of treated wood or in confined spaces, may be significantly higher than background levels. Penta has historically been estimated to volatilize from the surface of treated wood roughly at 2% of the total amount of the preservative applied.

Leaching: The leaching of penta out of utility poles may partially depend on the method of application (pressure or thermal treatment). Penta may be leached from the poles as the compound moves with either aqueous solution (as from rain) or with the solvent down the pole, either at the surface or within the pole. Based on experimental data, the main mechanism for the leaching of penta and its micro-contaminants is the downward migration of the oil carrier along the vertical axis of the pole (Gravitational Induced Downward Migration of Oil - GIDMO). Leaching of penta in aqueous solution from rainwater is not considered to be as important as GIDMO, as the replenishment rate at pole surfaces is a limiting factor with respect to the availability of the compound for leaching. Volatilization and leaching in oil borne penta may be simultaneous in the groundline region and also increases with permeability of the wood and original retention. Contamination of subsurface soil found in the vicinity of utility poles may result from the downward movement of penta within the pole, with subsequent leaching from the bottom part of the pole to the soil surface or to the subsoil near the underground portion of the pole, as well as from the downward movement of penta from the surface soils to the subsoil. When leaching of penta from treated poles occurs, the simultaneous leaching of the carrier solvents may affect the mobility of the compound in the soil. Penta applied in oil is rapidly transported from the upper portion of the poles to the underground portion for the first few years of use, and became relatively constant with time (EPA 2008).

Evidence of penta leaching directly into the environment is found in several documents. Levels found differ. In 1992, a study by Environment Canada found penta at high levels in utility and railway ditches, including concentrations of PCP averaging 1060 mg/kg at the base of poles. In a follow-up study, Environment Canada found that penta contaminants were leaching out of penta treated utility poles and railroad ties. A third study conducted for Environment Canada found three poles treated with PCP, that were adjacent to drinking water wells, caused water contamination.

Bleeding: Unrealistically high retentions result in excessive bleeding, excessive migration and preservative loss. Mold and fungal attack during air seasoning may increase depletion of penta-oil after treatment due to increased permeability of the wood resulting in increased liquid and gas flow inward and promoting bleeding and loss of preservative. Bleeding is affected by seasoning condition at time of treatment, viscosity and the surface tension of carrier oil. Poles treated after air seasoning have more oil borne preservative loss than green steam-conditioned ones. Wood that was formerly treated green dries after treatment causing a negative pressure which draws the oil deeper into the wood and reduces the tendency to bleed (Kelso). Poles treated after air seasoning suffer more penta-oil and creosote vapor loss than poles treated green and likewise have more migration of oil downward and outward, while green-treated poles have movement inward. Final steaming of wood reduces bleeding, cleans up, or recovers solvent. It has been found, that an 8 hour final vacuum of 27 in Hg is the most effective agent in reducing bleeding (Freeman 2015, 2016) and making penta treated products meet or exceed the BMP's and AWPA Standard M-20.

Releases of Pentachlorophenol from waste handling

As Table 1 shows, hazardous waste handling contributes to a large extent to penta releases. When treated wood poles become waste, this generates an ongoing source of emissions of penta, dioxins, furans and HCB. Approximately 1.5 million poles treated with penta become waste assuming no reuse or recycling. After service life articles treated with penta are either incinerated, disposed of in landfills, reused or recycled. Releases from land filled articles are mainly in leachate. According to the Agency for Toxic Substances and Disease Registry, 445 hazardous waste sites in the U.S. have been contaminated with penta. Once land filled, treated poles may still leach penta and microcontaminants into the environment. Therefore, incineration under controlled conditions is preferred over disposal to landfills (Zande 2010).

When penta treated articles are burned, dioxins and furans may be formed, depending on operating conditions. Uncontrolled conditions – like in open fire or in barrel burning may result in higher dioxin and furan emissions than incineration under controlled conditions.
Penta containing waste should preferably involve controlled high-temperature combustion; at 910 ºC. High temperatures are needed to reduce the formation of dioxins and furans.

Disposal of penta waste

Two types of waste are generated through the use of penta: wood treated with penta and industrial waste generated through the application of penta. Disposal requirements differ for each type of waste. Discarded penta treated lumber is disposed in either construction and demolition landfills, municipal solid waste landfills, or industrial non-hazardous waste landfills. Many state and local governments may have specific regulations, guidelines.

The Resource Conservation and Recovery Act (RCRA) applies to wastes generated at facilities where wood preservatives are used to treat wood. Because penta is a "chlorophenolic formulation", waste generated from its use is classified as hazardous waste. Thus, wood treaters using penta would be hazardous waste generators and are subject to the applicable requirements under RCRA (EPA 2008). EPA and Utility Solid Waste Activities Group (USWAG) developed a set of comprehensive guidelines for Handling treated wood in service and after service to ensure safety for workers or consumers. EPA and PMRA/Canada agencies continue to evaluate the potential impacts of land disposal of discarded penta treated wood.

ENVIRONMENTAL CHEMISTRY AND DISTRIBUTION OF PENTACHLOROPHENOL

Current releases of penta are limited, as indicated by the Toxics Release Inventory (TRI). Levels of penta in environmental media have decreased. Because penta was used for a wide range of domestic, agricultural, and industrial purposes for more than 60 years, the compound was ubiquitously distributed in the environment (Pohleven and Boh 2007). Its occurrence in aquatic and terrestrial food chains was established (Fishel 2005). Pentachlorophenol may be released to the environment as a result of its manufacture, storage, transport, or use as an industrial wood preservative for utility poles, cross arms, and fenceposts, and other items that consumes about 90% of its production. Certain key properties of chemicals control their fate in the environment and, if these are known, environmental chemists can make predictions about their fate and behaviour. These properties include aqueous solubility, vapour pressure, partition coefficients between water: solid (analogous to the measured octanol: water partition coefficient, KOW) and air: solid or liquid (analogous to the measured octanol: air partition coefficients KOA; and Henry's law constants, KAW), and half-lives in air, soil and water (Jones and de Voogt 1999). In general, the environmental fate and transport of penta in soil and water depends on the pH of the systems. The chemical behavior and the physical properties of penta will depend on whether it exists primarily as the phenol (under more acidic conditions) or the phenolate anion (under basic conditions). Penta is released into the atmosphere via volatilization from treated wood and can be transported back to surface waters and soils via wet and dry deposition. Chemicals with a log Kow value greater than 4.0 are likely to bioaccumulate in organisms and food chains. The log Kow for penta is 5.01. Bioaccumulation of penta in in the food chains has been demonstrated. Penta is readily and completely absorbed following inhalation, oral and dermal exposure.

Air: Penta is a relatively volatile compound, while its sodium salt in nonvolatile. In the atmosphere, volatilized penta may undergo photolytic degradation or may react with photo-chemically produced hydroxyl radicals. Atmospheric penta associated with particulate matter or moisture will be lost from the atmosphere through wet deposition. Based on the low Henry's law constant, volatilization from aqueous systems is not a significant mode of transport in the environment.

Water: Penta is hydrolytically stable in water at pH 4-6.5. This precludes hydrolysis as a major degradation process in the environment. Chemical degradation of penta in water will occur mainly through photo-degradation, but penta use in marine environments is mostly due to alkaline Ca salt formation, or some Na salt formation, and marine uses of penta should not be promoted, mostly due to efficacy and not due to potential marine pollution.

In surface water, penta will rapidly photo-degrade when exposed to direct sunlight, with more rapid degradation occurring with increased pH (when the compound is dissociated). Pentachlorophenol is expected to bioconcentrate because of its low water solubility, but the bioconcentration factor will be dependent upon the pH of the water since penta will be more dissociated at higher pH's. If released in water, pentachlorophenol will adsorb to sediment, photodegrade (especially at higher pHs) and slowly biodegrade. The low water solubility and moderate vapor pressure would suggest that evaporation from water is not rapid, especially at natural pHs where penta is present in the dissociated form (pKa= 4.74). Penta does not appear to oxidize or hydrolyze under environmental conditions; however, photolysis of the dissociated form in water appears to be a significant process. A measured photolysis half-life has been reported to be 0.86 hrs. Various studies have documented the rapid dissipation or degradation of penta in shallow waters and either showed or suggested that photolysis is the main mode of degradation in aquatic systems. In three separate limnocoral experiments, Liber et al. (1997) assessed the fate and effects of a commercial formulation containing 4.8% Penta. Results showed that initial dissipation of penta from the water implicated photolysis as the primary degradation mechanism and it did not accumulate in the sediments to any significant extent (< 0.1% of applied mass), but sediment-associated residues did dissipate at a considerably slower rate than residues in the water column. About 97 to >99% of the applied penta had dissipated from the water of treated enclosures by the end of the experiments, i.e. 42-63 days. In addition, results strongly suggested that the environmental conditions under which a study is conducted, especially water depth, can drastically affect the persistence and fate of the compound (Liber et al.1997).

Soil and wood: Wood treated with penta may release the compound through volatilization, bleeding, or leaching. Additionally, penta may be photo-degraded on the wood surface, making degradates available for leaching. Releases to soil can result in slow biodegradation and leaching into groundwater. Penta has a tendency to adsorb to soil and sediment; calculated Koc= 1000, measured sediment Koc= 3,000-4,000. Adsorption to oxidized sediment is higher than to reduced sediment. Adsorption to soil and sediment is pH dependent; stronger under acid conditions. The Koc values for the total dissociated phenol was calculated to be 1250 and 1800 for light and heavy loam, respectively, while for the undissociated species, the Koc is 25,000. Penta does biodegrade in soil but requires several weeks for acclimation. Half-life in soil is approximately weeks to months, depending on pH, temperature, concentration, and amount of available oxygenation. In an artificial stream, microbial degradation became significant after 3 weeks and accounted for 26-46% removal (US EPA, Beltsville Study data).

The environmental risk assessment indicates that typical concentrations of penta in terrestrial and aquatic environments from wood treatment uses are not expected to be of sufficient quantity or duration to adversely impact terrestrial or aquatic organisms.

TOXICITY OF PENTACHLOROPHENOL

Technical grade, pure powdered or flake-form penta is toxic to all forms of life because it is an inhibitor of oxidative phosphorylation. At low concentrations it causes uncoupling of oxidation and phosphorylation cycles in tissues and at high concentrations, inhibit mitochondrial and myosin adenosine triphosphatase, inhibits glycolytic phosphorylation, inactivates respiratory enzymes and causes gross damage to mitochondria (Ozanne 1995).

The results are accelerated aerobic metabolism, increased heat production, and loss of membrane electrical resistance (FAO 1996). Humans will be occupationally exposed to technical-grade penta during production and formulation, via inhalation and dermal contact primarily in situations where they manufacture or apply this preservative. The general population can be exposed primarily from ingesting food contaminated with penta, and rarely to dermal contact with penta treated wood. Because of trace impurities produced during the penta manufacturing process, notably hexachlorodioxins (HCDDs), the use of penta has been subject to intense regulatory scrutiny since the 1970's (Wilkinson, 1995). Hundreds of reports and publications on the environmental effect and toxicity of these compounds and the relative safety of formulated penta products can be found in the literature. Penta treated wood poses no adverse human health effects, unless used interiorly in a home or the wood burned for fuel in a home fireplace, stove or heater. Commercial burning or destruction of penta treated wood in 600 hp boilers, or larger, has been permitted by the US EPA since 1986.

Acute toxicity

The acute toxicity of pentachlorophenol is low for dermal toxicity (Toxicity Category IV) and primary dermal irritation (Toxicity Category III) but shows higher toxicity for acute oral toxicity and primary eye irritation (Toxicity Category II). No dermal sensitization was observed with the technical test material. Table 2 below summarizes the acute toxicity of penta. Studies cited are older data, in which the test material may contain measureable concentrations of contaminants such as hexachlorodioxins and hexachlorobenzene.

Study Type	**Results**	**Toxicity Category**
Acute oral	LD50=155mg/kg (M) LD50=137mg/kg (F)	II
Acute dermal toxicity	LD50>3980mg/kg	IV
Acute Inhalation toxicity		I
Primary eye inhalation	Corneal involvement at day 7 post instillation	II
Primary dermal irritation	Moderate irritation at 72 hours post application	III
Dermal sensitization	No sensitization observed using Buehler method	NA
Acute Dietary (all populations)	Acute endpoint of 30 mg/kg/day was selected from a developmental toxicity study in rats	
Chronic Dietary (all populations)	A chronic endpoint of 1.5 mg/kg/day, the LOAEL from a chronic toxicity study in dogs	
Dermal (short- and intermediate-term)	NOAEL = 30 mg/kg/day from a developmental Toxicity study – rats	
Dermal (long-term)	LOAEL = 1.5 mg/kg/day. LOAEL = 1.5 mg/kg/day from a Chronic Toxicity study – dogs	
Inhalation	Inhalation risks for occupational exposure were not performed because most values derived from the biomonitoring study in workers were below the level of quantitation, thus implying that the majority of worker exposure is through dermal contact with penta.	

Table 2. Summary of Acute toxicity and Toxicological Endpoints data for penta

Carcinogenicity of penta

Penta was classified as a B2 carcinogen (suspect human carcinogen) in 1990, based on animal studies that showed that liver tumors, pheochromocytomas, and hemangiosarcomas observed were penta treatment-related. These tumors were observed from a study conducted by the National Toxicology Program using pure penta or a technical grade formulation, Dowicide EC-7.

Ruder and Yiin (2005) assessed mortality in a cohort of 2122 workers from the National Institute for Occupational Safety and Health (NIOSH) Dioxin Registry who were involved in the production of penta to determine if the cohort had increased risk of cancer mortality, compared to the general US population. The study found an excess of cancers of a priori interest, non-Hodgkin lymphoma and leukemia, providing some support for the carcinogenicity of penta. The limitation of the study is a lack of detailed information on other exposures such as lifestyle choices or previous and subsequent employment that could affect mortality.

Teratogenic effects of pentachlorophenol

Most developmental toxicity studies on penta show no teratogenic effects, but in one single, non-repeated study, Welsh et al. (1987), showed toxic effects of penta in offspring that occurred at dose levels below those producing maternal toxicity.

POTENTIAL OF BANNING PENTACHLOROPHENOL USE IN NORTH AMERICA

The socioeconomic impacts resulting from a ban on penta consumption could affect the North American industry pole industry most. The existing electrical transmission and distribution system in the U.S. and Canada is mainly supported by wood poles, of which about half is treated with penta. Alternative wood preservative chemicals as well as alternate materials for poles are generally available and applicable. An important aspect for selecting an alternative is the dependability of the product. Wood poles have a proven track record. Some alternatives either have not existed for the requisite period of time or have not been used for pole applications long enough to consider it proven. This may counteract with the fact that alternatives are in use for several years in European countries, where the marketing and use of penta containing products is prohibited. According to the European industry trade association representing the pressure treated wood industry about 6.5 million m^3 of pressure treated wood per year is supplied by the wood preservation industry. About 11% is preserved with creosote, 71% with waterborne preservatives and 18% with light organic solvent preservatives. In addition, steel and concrete are widely applied in Europe, at a negative life cycle effect compared to penta and at costs ranging from 2.7 x to 8 x the costs of penta poles. Recently the EEI and EPRI have published findings where burying conductor underground is not only 8 times more expensive than going overhead but, in some cases, cause such a devastating blow to the natural environment by digging, trenching, and soil compression, that recovery of the environment can take multiple years, if at all possible.

Costs of implications for treating plants

Cost implications of phasing out penta gradually will and can affect the wood treatment industry and electric utility industry the most. Implementation of alternatives, either chemical or non-chemical, will consequently have economic effects and will require additional investments (Zande 2010). About 50 to 100 penta using wood preservation facilities in North America exist. A possible unavailability of penta would have a significant effect on these companies, as they would have to shift capacity from penta treatment to other treatments. The treatment plants will have to upgrade equipment to accept new formulations. Additional investments will be required in most facilities to increase capacity or to expand their plants to treat using other alternatives.

Wood treatment plants that shift to alternatives that are more corrosive, such as ACQ, would have to change their fittings at a substantial cost (Becker et al. 2008). In the USA, over 31 PT plants switched to Copper Naphthenate following the 1986 closing of the RPAR and the Settlement Agreement (EPA, 2009).

Cost implications for consumers

Consumers presumably will not experience a significant impact from a ban on penta in the pole market since several alternative chemicals are available, unless their utility decides to go underground; burying of conductor could potentially alter monthly billing state costs from $300/monthly to greater than $2500/monthly, should the utility decide to pass along 100% of their increased costs and absorb zero. However, given the fact that penta has a large share in the market, there could be significant production shortages as wood treatment plants and producers transition from penta to the alternatives. This could lead to fluctuation in prices that could adversely affect consumers. Penta is the preferred preservative for cross arms; however, ACZA and ACQ may be suitable alternatives for this use as they can be used to treat Douglas fir which is used in the majority of cross-arms. Other than chemical alternatives, a small percentage of the market may also go to alternatives to treated wood, such as plastic and composite lumber or concrete. These alternatives are substantially more expensive than treated wood, but some consumers have opted for these because of their non-toxicity and durability (Becker et al. 2008). Today, the only product capable of replacing penta for 100% of its wood pole and crossarm useage is Copper Naphthenate, but recent research by Nicholas, Freeman and others, indicate DCOIT or CTL (chlorothalonil) in heavy oil may represent another two potential highly effective alternatives for penta.

Cost implications for governments or state budgets

The costs of a ban on penta for the EU member states are zero, since this is already the case in the EU. Replacement has already taken place. The costs for Canada and the U.S. depend on the actions taken. Replacing wood poles by alternate materials will considerably reduce the annual volumes of hazardous waste that is either disposed in landfills or incinerated. Treatment of hazardous waste involves governmental costs for monitoring and control. These costs will drop significantly when treated poles are replaced by alternate material poles. Since consumption volumes in North America are relatively high, a switch to alternatives needs investments and will require time.

Certain Penta Attributes

1. **Ease of use and proven efficacy**: advantages of penta are that it can be dissolved in oils having a wide range of viscosity, vapor pressure and is easy to handle and use. Penta also has proven efficacy: the results of pole service and field tests on wood treated with 5% penta in a heavy petroleum oil are similar to those with coal-tar creosote. In terms of cost, it was rated the least expensive of the three major preservatives (Hatcher 1980) at least before rising cost of petroleum. Chemical and non-chemical alternatives also vary in efficacy. In many cases, efficacy is the determining factor for selecting the preservative and/or material used. In the short-term, a product treated with an alternative preservative may offer comparable efficacy compared to a product treated with a penta however, comparable efficacy may or may not be observed over the entire expected lifespan of the product (e.g. a utility pole may require replacement much sooner, than if it had been treated with penta).

Because certain alternatives do not offer the same level of efficacy and because the end products themselves (e.g., utility poles) may not last as long as penta, they also cannot be considered as direct replacements. Today, only CuNap fits this bill of attributes as well as penta.

2. **Pole worker safety**: Although many chemical and non-chemical alternatives exist, many are not truly interchangeable due to safety, environmental, efficacy, and/or economic considerations. In the case of utility poles, the material selected can affect the maintenance personnel's safety. Although steel utility poles may result in less human or environmental exposure to penta, they also increase the likelihood of electrocution for workers. For poles treated with chemical alternatives, certain alternatives make poles more slippery and therefore harder to climb which may also affect worker safety. Although the risk of electrocution and slippage cannot be compared quantitatively to potential environmental exposure.
3. **Well understood environmental effects**: Alternatives also vary in their potential effects on the environment. The potential short and long-term environmental impacts of many chemical and non-chemical alternatives are unknown. Penta on the other hand, has been the subject of numerous toxicity, exposure, environmental fate, and ecological effects studies. Because there are varying amounts of information on each alternative, it is difficult to quantitatively or qualitatively estimate the potential environmental impacts of alternatives; however, the potential environmental impacts of penta and its micro-contaminants are relatively well understood, compared to certain chemical and non-chemical alternatives.
4. **Performance in extreme conditions**: penta treated crossarms are less likely to warp, crack, twist (causing stress on the wires), or drip than some of the alternatives. Utility and public works companies require products proven to be capable of withstanding extreme conditions for long periods of time. Penta's flexibility lowers the chances of ice and windstorm breakage, penta's moisture resistance properties reduce checking and pole twist and penta poles resist undetected burning (afterglow) when exposed to grass or brush fires.
5. **Economic Considerations**: Finally, economic considerations almost always impact decisions regarding project materials. Included in economic considerations are initial costs (e.g., cost of wood treatment), lifespan and maintenance costs of the product, and disposal costs. Penta has easy maintenance and generally offers lower initial costs than many alternatives, offers documented and predictable lifespan, and in many cases can be disposed of in municipal landfills. Because certain alternatives, although lower in initial costs, do not offer the same resistance and/or do not last as long as pentachlorophenol treated products, they also cannot be considered as direct replacements. Economic considerations are particularly relevant to utility and other public works uses because increased costs are frequently passed on to the public.
6. **Recycling and disposa**l: after removal from service, penta poles still provide a long-term cost benefit because they can be re-used, recycled or safely disposed of in landfills in accordance with state and local requirements. Nearly 70 percent of out-of-service poles are either remanufactured and re-used as utility poles or used as fence posts or to support farm lighting. Penta treated products can also be burned for energy recovery in some combustion units and industrial boiler

Non-Chemical alternatives for Penta wood preservation

Non-chemical alternatives include replacement of wood by steel, concrete, fibre reinforced composite, naturally resistant wood, and some other alternatives.

Concrete poles*:* The main disadvantages of concrete poles are higher installation and freight costs due to weight, and poor Life Cycle analysis. Design and installation to prevent electrocution of raptors is important which leads to additional costs. Concrete is subject to degradation in saltwater regions. Also freeze/thaw cycles may cause degradation of the material (Becker et al. 2008). They also impact the environment severely negatively in 5 of the 6 potential green areas (Smith et al).

Steel poles*:* Corrosion can be a problem with steel poles, primarily below the ground line. This can be prevented by coating or galvanising the steel. Steel poles have less insulation characteristics, so additional insulation is needed. They are more costly than wood poles. Gaffs which are used to climb wood poles are not usable with steel poles. Steel poles therefore need to be designed with permanent or removable steps (Becker et al. 2008). They also impact the environment severely negatively in 5 of the 6 potential green areas (Smith et al).

Fiberglass reinforced composite (FRC) poles*:* FRC poles are more easily damaged, so that the surface of FRC must be carefully protected during transportation and installation. As steel poles, they require steps for linemen to climb the poles. Installation costs are significantly higher than that of wood poles (Becker et al. 2008). They also impact the environment severely negatively in 5 of the 6 potential green areas (Smith et al).

Decay resistant wood*:* Can potentially be used without chemical treatment. The main disadvantage is the high cost and environmental degradation of their narrow harvesting area. (Becker et al. 2008)

CONTAMINANTS OF PENTACHLOROPHENOL AND UNINTENTIONAL EMMISIONS

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and chlorobenzenes are formed as impurities during the manufacturing process of penta. The range and concentrations of the impurities vary depending upon the manufacturing method and upon process conditions. PCP can be manufactured by direct chlorination of phenols or by hydrolysis of hexachorobenzene. Formation of dioxins and furans may be promoted by conditions which favor the formation of chlorine or other halogen radicals. Contaminants of great concern are the PCDD, PCDF and hexachlorobenzene HCB (Zande 2010). Physical and chemical properties and toxicity of the contaminants vary with the degree of chlorination. The dioxin/furan contaminants of penta present a unique case for purposes of risk characterization. Up to 17 CDD/CDF congeners are produced as contaminants in the manufacture of technical grade penta. All of these contaminants have chlorine substitution in at least the 2,3,7, and 8 positions. Thus, all must be considered in the risk assessment for the contaminants of pentachlorophenol (EPA 2008). These compounds are inherently toxic, as well as environmentally persistent, and their presence increases the ecological risk associated with the use of penta. However, penta is only one of many sources of these compounds in the environment making it difficult to quantify the portion of the aggregate environmental risk that is attributable to penta wood treatment uses. Chlorination of phenolic compounds during water treatment produces detectable levels of penta. Table 3 below summarizes analyses from a variety of sources of the contaminants in technical grade penta and purified penta.

Contaminant	Technical grade (85-90%)	Purified (>99%)
CHLOROPHENOLS		
Trichlorophenols	1000	-
Tetrachlorophenols		
2,3,4,6 tetrachlorophenol	49,000	0.25
2,3,4,5 tetrachlorophenol	9,000	0.073
Total	40,000-80,000	500
Other chlorophenols	20,000-60,000	-
DIBENZOFURANS		
Pentachlorodibenzofurans	40	-
Hexaachlorodibenzofurans	90	-
Heptachlorodibenzofurans	400	-
Octachlorodibenzofurans	29-260	-
DIOXINS		
Tetrachlorodioxins (not 2,3,7,8 TCDD)	0.035-0.12	-
Pentachlorodioxins	0.03	-
Hexachlorodioxins	1-173	0.00001
Heptachlorodioxins	119-1000	1.8
Octachlorodioxins	40-47,000	0.0002-3.0
Total dioxins	1900-2625	<7
HEXACHLOROBENZENE	56-270, less than 75 after 1986	0.0014
PHENOXYPHENOLS		
Heptachlorophenoxyphenols	12000	4.8
Octachlorophenoxyphenols	28,000	300
Nonachlorophenoxyphenols	15,000	500

Table 3: List of contaminants detected in technical grade penta and purified penta (All values in mg contaminant/Kg product)

Possible influence of the presence of chlorodioxins in penta treated wood was evaluated by Alliot (1975). He concludes that penta does not contain 2,3,7,8 TCDD which is by far the most toxic and dangerous chlorodioxin at very low doses. TCDD is tetarogenic and embryotoxic at very low doses. OCDD at 3-1000ppm, representing the most abundant chlorodioxin, is an impurity of technical penta, however, it is so low in toxicity and common solubility, it appears, almost like beach "sand" in commercial production, sometimes at levels approaching 0.50% w/w.. OCDD has no teratogenic action and is practically non-toxic at the doses at which it is found in penta. A small proportion of HxCDD (1-100ppm) is found in penta but it is 1,000-10,000 times less toxic and less teratogenic than TCDD. 2,7 DCDD and OCDD have no teratogenic, embryotoxic or acnegenic action. They can be considered of no danger even at highest proportions which have been found in certain penta samples (Alliot 1975). The acute toxicity of HCDD is nearly the same as that of penta, hence this is the impurity that most influences penta toxicity and other health effects. In the 1970's Dow Chemical Company introduced a preservative, Dowicie EC7 in which dioxin levels had been reduced two orders of magnitude using more expensive production techniques but the product was uncompetitive against rival non-decontaminated brands (Dickson 1980), due to its high insolubility. It seems that after purification, solvent solubility is greatly reduced.

Contaminant Releases from waste and contaminated sites

PCDD and PCDFs may enter the when the utility poles are removed from service and are disposed in landfills. Annually, nearly 1 million additional utility poles are replaced (3% replacement rate) on land and in water annually. EPA has estimated that the utility poles in service contain approximately 374 kg of dioxin toxicity equivalents (I-TEQs). The PCDD and PCDFs in these poles may be released into the environment via volatilization and leaching.

When penta treated wood is disposed of in landfills, these microcontaminants leach into the environment. Penta treated wood in the waste phase must be treated as hazardous waste. Highly contaminated areas from former production facilities or treatment plants may still cause an impact on the environment via transport to air and water. In Sweden relatively, high levels of penta contaminants have been detected at contaminated sites, where preservation of wood has taken place.

Persistence and accumulation of penta contaminants in animal and human tissues

The specific dioxin congener profiles present in penta have been shown to persist for decades after exposure. While absorbed penta is excreted primarily in urine, with elimination half-lives of between 4 and 72 days, the PCDD/F contaminants of penta are believed to have elimination half-lives of up to ten years. Measurement of penta in urine or plasma, therefore, provides an estimate of current exposure while the chemical is in use whereas the measurement of dioxin in serum provides an estimate of exposure in previous decades. The higher chlorinated PCDD/F like TCDD appear to be highly persistent in humans with half-lives ranging between 4 and 12 yr. Flesch-Janys (1996) report on an investigation on the elimination of 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in a group of 43 exposed workers. The median half-life was 7.2 years for 2,3,7,8-TCDD while the estimates were between 3.7 years for 1,2,3,4,6,7,8-HpCDD (hepta-chlorinated) and 15.7 yr for 1,2,3,7,8-PCDD. For the furans it was 3.0 years for 1,2,3,4,6,7,8-HpCDF and 19.6 years for 2,3,4,7,8-PCDF. Increasing age and percent body fat were associated with increasing half-life for most of the congeners. In the USA production of penta, NO 2,3,7,8 TCDD has ever been found, at the detection limit of 0.001 PPM.

To determine whether past occupational penta exposure was the source of current body burden of dioxin, McLean et al. (2008) tested 94 former sawmill workers randomly selected from surviving members of a cohort enumerated for a mortality and cancer incidence. They tested whether penta exposure had resulted in elevated serum dioxin levels twenty years after its use. 71 workers had been exposed to penta while 23 were non-exposed, based on job title and work tasks performed at the penta plant. They compared age-adjusted dioxin levels in the exposed and non-exposed groups, examined the effect of exposure duration and intensity, and compared congener profiles with those found in the commercial grade penta used at the time. Mean levels in exposed workers were elevated when compared with the non-exposed, with levels of 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD being two to three times higher. The congener profiles in serum were consistent with those in penta solutions, and dioxin levels increased with both employment duration and estimated exposure intensity. Generally serum dioxin levels in the former New Zealand sawmill workers remained elevated twenty years after exposure to penta ceased. Significant age variations were observed with higher serum concentrations measured in older people reflecting higher historical exposures and the fact that these compounds are only slowly metabolized and excreted from the body. The dioxin congener profiles present in the serum samples of the exposed study participants are consistent with the profiles found in penta solutions in used in the past showing the predominance of 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD. Duration of exposure in the sawmilling industry had a strong influence on the excess serum dioxin levels. Those with more than ten years exposure had average excess levels of the specific higher chlorinated dioxin congeners that were 200-400% of the background levels in the ‘non-exposed’ group.

High risk tasks like mixing penta solutions cleaning sludge from dip tanks and handling treated timber on a sorting table were all associated with excess exposure, with higher levels of PCP exposure and of serum dioxin levels but that maintenance work was not necessarily a source of exposure.

Collins et al. (2008) examined the serum dioxin levels of 98 long term workers at a plant with chlorophenol units. They examined the serum lipid adjusted levels of chlorinated dioxins and furans, and four coplanar PCBs. Workers who worked in the penta units had mean lipid adjusted levels for 123478-HxCDD of 14.8 ppt, 123678-HxCDD of 156.4 ppt,123789-HxCDD of 23.7 ppt, 1234678-HpCDD of 234.6 ppt, and OCDD of 2,778.2 ppt significantly higher ($p < 0.05$) than the reference group (unexposed workers) levels for the same congeners of 7.5, 71.8, 8.0, 67.5, and 483.2 ppt, respectively. All furan levels were not significantly different than the reference group. They found distinct patterns of dioxin congeners many years after exposure. Penta workers had higher levels dioxins than the reference group (unexposed workers) a finding that is consistent with other serum studies of penta workers (Flesch-Janys et al. 1996; Schecter et al. 1996; Coenraads et al. 1999).

Toxicity of Dioxin/Furan and Hexachlorobenzene

Dickson (1980) reports a study on three groups of heifers given feed containing penta. The groups were separately given feed containing analytical penta prepared in the lab, technical penta containing dibenzodioxin and dibenzofuran contaminants and feed containing the mixture. Results indicated a number of dose related effects; low body eight, anaemia, unexpected lesions in the heifers exposed to contaminated penta compared to those exposed to the analytical penta. Clearly the toxic effects attributed to penta were actually due to the impurities. Some of the effects observed in humans (or the severity and dose-response characteristics of effects) may be related to the impurities. Several studies over the years have confirmed this finding.

The concept of toxic equivalency factors (TEFs) was developed to facilitate risk assessment of exposure to chemical mixtures of CDDs and CDFs. Individual TEFs are assigned to the various congeners of CDDs and CDFs based on assigning relative values in relation to 2,3,7,8-TCDD, which is assigned a TEF value of 1.0, it being the most potent congener. Multiplying the exposure concentration of individual congeners by their respective TEFs yields a toxic equivalency, which, when summed for all the components of the mixture, gives the toxic equivalency quotient (TEQ) for that mixture. The toxicity of **o**ther dioxins and furans relative to that of 2,3,7,8-TCDD ranges from 0.0001 to 1 (Ruder and Yiin 2005). Human health effects associated with exposure to HCB include skin lesions, nerve and liver damage as short-term effects. Long-term effects from lifetime exposures include damage to liver and kidneys, reproductive effects, benign tumors of endocrine glands, and cancer.

Occupational exposure to PCDD/Fs is associated with biochemical abnormalities that may persist for years after serum PCDD/F levels have declined. In a cross-sectional study, of 1167 participants Chang et al. (2012) compared serum PCDD/F levels and biochemical examinations of retired Na-PCP workers and other inhabitants living near a Na-PCP plant that closed 25 years ago and had discharged contaminated wastewater into a nearby pond that supplied seafood in Tainan, Taiwan.

Although the occupational exposure to dioxins of the retired workers ended when the plant closed 25 years ago, distinct ‘‘fingerprints’’ of dioxin congeners in their serum were found. Examination of these fingerprints showed evidence of higher dioxin and furan levels in Na-PCP workers with a significantly higher proportion of PeCDD, HxDD and PCDD/F versus the general population. Specifically, serum dioxin levels were: general population: 22.9 ± 10.0; retired Na-PCP workers who moved: 27.9 ± 21.3; residents eating a normal diet: 45.8 ± 41.9; residents eating a polluted diet: 71.3 ± 81.4; retired Na-PCP workers eating a normal diet: 95.8 ± 102.5; and retired Na-PCP workers eating a polluted diet: 109.6 ± 94.5 pg ($P< 0.001$). Blood biochemical examinations showed overall abnormalities of glucose, triglycerides, blood urea nitrogen (BUN) and creatinine in retired Na-PCP workers or residents were significantly higher than the general population. These trends were consistent with those seen elsewhere (Schecter et al. 1996; Coenraads et al. 1999) resulting from exposure to dioxins. The adverse health effects caused by dioxins persisted even after the serum dioxin levels had declined or was eliminated for many years. However, a genuine cause-effect relationship between exposure to penta or its associated by products and blood biochemical levels has not been confirmed. The association between insulin resistance, metabolic syndrome, and exposure to PCDD/Fs has recently been reported (Chang et al. 2010a,b, 2011) but a genuine cause-effect relationship has not been established.

Carcinogenic effects of pentachlorophenol contaminants

The International Agency for Research on Cancer (IARC) classifies 2,3,7,8-TCDD as a known “human carcinogen”. This means that, based on the weight of all of the evidence (human, animal, mode of action), 2,3,7,8-TCDD meets the criteria that allows EPA and the scientific community to accept a causal relationship between 2,3,7,8-TCDD exposure and cancer hazard. Other dioxins are characterized as “likely” human carcinogens primarily because of the lack of epidemiological evidence associated with their carcinogenicity, although there is a strong inference based on toxic equivalency that they would behave in humans as 2,3,7,8-TCDD does. The IARC and EPA have both classified HCB as a B2 (suspect human) carcinogen, having inadequate evidence of human carcinogenicity and sufficient evidence for animal carcinogenicity based on data sets that showed induction of tumors of the thyroid, liver, and kidney in three rodent species treated with technical grade penta or Dowicide EC-7. HCB is widely distributed throughout the global ecosystem because if its mobility and resistance to degradation. It has been detected in all environmental media and in numerous of living organisms including insects, aquatic biota, birds and mammals. HCB has also been shown to bioaccumulate in both aquatic and terrestrial organisms.

Penta manufactured in the USA/Mexico has no TCDD, but studies of penta exposures in Europe and New Zealand, where the PCP manufacturing process could be contaminated with 2,3,7,8-TCDD, occupational exposure was associated with increased risk of brain cancer, lymphomas, soft-tissue sarcomas, and non-malignant respiratory disease morbidity (Cordier et al. 1988; Cooper and Jones, 2008; McLean et al. 2009a).

Teratogenic effects of pentachlorophenol contaminants

Developmental toxicity studies on penta show no teratogenic effect but, the contaminants hexachlorodioxin and 2,3,7,8 tetrachlorodioxin are considered teratogenic chemicals.

Due to this reason combined with the knowledge that hexachlorodioxin is a contaminant of penta, the warning labels on penta formulations with respect to potential teratogenic effects have remained.

Risks of pentachlorophenol contaminants

Dietary risk: Dietary intake is generally recognized as the primary source of human exposure to CDDs and CDFs and HCB. Residue data are available for meat, fish, dairy products, eggs and fruits and vegetables. Residue data are reported in terms of both parts per trillion (ppt) and in terms of toxicity equivalents for both CDDs and CDFs. The only residues, reported for environmental media and these commodities, were for the octachlorodibenzodioxin congener and ranged from 0.6 - 8 ppt and HCB residues are trace amounts (0.01 ppm range).

Occupational risk of contaminants: EPA determined that there are potential worker risks of concern with the currently registered uses of penta due to contaminats. Total potential cancer risks for all four handler scenarios assessed are of concern (i.e. risks greater than 1.0×10^{-6}). Handler exposure to penta results in potential exposure to CDDs and CDFs during handler operations in pressure treatment plants. Occupational handler cancer risk estimates have been calculated for dioxin/furan and most of the assessed occupational handler scenarios exceed the Agency's level of concern for potential worker cancer risks. A cancer risk estimates greater than one in a million (1.0×10^{-6}) is of concern.

PMRA REREGISTRATION OF PENTACHLOROPHENOL

In 1978, the PMRA, following suit with the US EPA, instituted a regulatory proceeding that considered cancellation of all penta pesticide registrations but, after extensive review declined to do so. Instead in 1986, the EPA and PMRA put in place measures to ensure penta in wood preservation would not cause risks to the public or environments and also put in place measures to enforce them (Wilkinson 1995).

PMRA took action that required higher chemical purity and addition of more requirements for the protection of workers involved in the usage of Penta. These regulatory actions required:

(i) Restriction of the use of penta to commercial applicators.
(ii) Reduction of hexachlorodibenzodioxin (HxCDD) in penta formulations to 4 ppm for any single batch, with a monthly average not to exceed 2 PPM, and to below limits of detection for 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD)
(iii) Initiation of a consumer awareness program for treated wood.
(iv) Use of a teratogenicity /fetotoxicity label warning on penta products.
(v) Initiation of additional steps to protect workers in wood treatment plants.

Since then new studies on penta have confirmed that while the danger is actual, the appropriate mechanism for addressing penta concerns <u>is not to ban the important uses, but to ensure that those uses are properly managed to minimize exposures</u> (Ozanne 1995).

Federal law directs the both the EPA and the PMRA to periodically re-evaluate older pesticides to ensure that they meet current standards for safety, health and environmental risks based on existing labels and uses.

The US. Penta taskforce organized in 1988 was in response to the FIFRA act that required registrants of older pesticides to develop certain data on their products. In 2005 penta, CCA, and creosote underwent the re-registration process. Re-registration involves a thorough review of the scientific database of a pesticide and additional information received through the public docket before a Reregistration Eligibility Decision (RED) is published containing the risk assessment and regulatory decision (Elkassabany 2005). The process ensures that older pesticides meet current standards for health and environmental risks based on existing labels and uses. Penta underwent an extensive data review process resulting in its re-registration by the U.S.

The rigorous reregistration process ***showed that use in pressure treatment of wood did not pose an unacceptable risk to man or the environment*** because of the contained exposure and much of the toxicity of penta is attributed to its impurities. An enormous amount of work has been carried out in many countries on penta and its derivatives. The increased knowledge of the toxicology of penta has contributed to penta being the most documented substance in wood preservation. Regulations only based on intrinsic properties of substances, appear totally blind. The risk/benefit approach applied to penta has involved specifications on impurities, classification of the dangers, identification of the most suitable form to minimize the risk, voluntary limitations of use for sensitive applications, rules of handling waste and finally a standard of specifications socially acceptable worldwide (Ozanne 1995).

In 2008, the EPA determined that the toxicological database for penta had sufficient information to allow its for reregistration (Freeman 2010, Wilkinson 2010, USEPA-2008). In 2008, the EPA completed the human health and environmental risk assessments for penta and determined that the economic and societal benefits that penta use contributes the society outweigh the risks. Eliminating these uses could result in reliance on products with greater safety risks, reduced effectiveness and higher costs that could be passed on to the general public. The review for penta determined that the pesticide meets the "no unreasonable adverse effects" criteria of FIFRA and that the data and information available was sufficient to support re-registration for the professional use as wood preservative (Elkassabany 2005). EPA required that risk mitigation measures be implemented, label amendments made, and data gaps and confirmatory data requirements satisfied. Safe design and operation of timber treatment plants minimizes release into the environment. *Use in wood preservation did not pose an unacceptable risk to man or the environment because of the contained exposure* (Fitzpatrick and Mackie, 1995). The appropriate mechanism for addressing penta concerns is not to ban the important uses, but to ensure that those uses are properly managed to minimize exposures (Ozanne 1995).

EPA determined that penta was eligible for re-registration provided mitigation measures and associated label changes identified in the REDs are implemented (EPA 2008; Fitzpatrick and Mackie 1995; Elkassabany 2005). In its risk assessments, the EPA identified risks of concern associated with occupational exposure and ecological exposure to penta. The data and available information was sufficient to support re-registration for the professional use as wood preservative. Such use did not pose an unacceptable risk because of the contained exposure (Fitzpatrick and Mackie 1995). The Penta manufactured today in the U.S. and Mexico has reduced toxic characteristics due to regulatory mandates.

Penta is a restricted-use pesticide, meaning the product or its uses are restricted "to use [and purchase] by a certified pesticide applicator or under the direct supervision of a certified applicator" (Jackson 2011).

The use of penta as a wood preservative is not expected to pose an acute or chronic risk to birds and mammals. Due to limited exposure, the use of penta treated wood in service, such as utility poles, is not likely to result in long lasting impacts to the aquatic ecosystem, including aquatic invertebrates and fish. No aquatic acute or chronic levels of concern are exceeded for freshwater invertebrates and fish or for estuarine/marine fish from application to utility poles. The application of penta to utility poles is not expected to pose an acute risk to estuarine invertebrates. No chronic estuarine/marine aquatic invertebrate studies were available for penta. However, based on data from a freshwater invertebrate chronic study, no chronic aquatic levels of concern are exceeded for estuarine invertebrates from application to utility poles. Acute levels of concern are not exceeded for vascular and non-vascular aquatic plants from application to utility poles.

Additionally, wood treatment plants have adopted best management practices, i.e. recommendations for the design and operation of wood preservation facilities, which reduce environmental releases of penta and associated contaminants. The registrant is requested to submit batch analysis data on pentachlorobenzene and tetrachlorobenzenes as well as a revised specification sheet to confirm that the change in manufacturing process has been implemented at the commercial level.

Reregistration of penta in Canada

The Canadian Government adopted an identical program to that instituted by the EPA. Health Canada Pest Management Regulatory Agency (PMRA) reevaluated Penta and reached the following conclusions. Potential risks of concern associated with the continued use of penta are identified as: (i) occupational cancer and non-cancer risk from dermal exposure to penta, (ii) occupational cancer risks from dermal exposure to dioxin/furan resulting from penta use. The PMRA also reached the following conclusions: Penta does not meet all Track 1 criteria and is not considered a Track 1 substance (Toxic Substances Management Policy Track 1 substances under the Canadian Environmental Protection Act), (ii) Penta does not form any transformation products that meet all Track 1 criteria.

The PMRA is currently participating in the UN Convention on Long-range Transboundary Air Pollution (LRTAP) process to gather additional information on pentachloroanisole, a transformation product of pentachlorophenol. Technical grade active ingredient pentachlorophenol contains the following Track 1 contaminants: hexachlorobenzene, chlorinated dibenzodioxins, chlorinated dibenzofurans. The PMRA in Canada may choose to "opt out” of the recent decision by the Stockholm Convention, and allow continued use of penta for wooden poles and crossarms, without designating it a POP.

EFFICAY (INTRODUCTION)

Pentachlorophenol, also known as penta or PCP, had its wood preserving properties discovered in the 1930s and the production for wood preserving began on an experimental basis then. Trade names include: Forpen®, Penta®, Pentacon®, Penwar®.

Penta is a standardized oil-borne preservative listed in the AWPA Book of Standards under P8-1. Principal use in the United-States and Canada is now the pressure-treatment of railroad ties, posts, cross arms, utility poles, and wharf pilings. Penta extends the functional life of wood by at least eight times (Wilkinson 1995; Fishel 2005). It is dissolved in petroleum or other organic solvents to allow adequate wood penetration.

Pure penta exists as colorless crystals with a sharp phenolic smell when hot but little odor at room temperature. Impure penta is dark gray to brown and exists as dust, beads, or flakes. The sodium salt dissolves easily in water, but penta itself does not. The two forms have different physical properties but are expected have similar toxic effects (ATSDR 2001). Treated wood typically contains about 130-140 $\mu g/m^3$ penta corresponding to concentrations of 0,484 mmol/L in treated wood (Pohleven and Boh 2007). Advantages of penta are that it can be dissolved in oils having a wide range of viscosity, vapor pressure and color, and it is clean and easy to handle and use. It is highly effective against wood destroying organisms. In terms of cost, it is rated the least expensive of the three major preservatives (Hatcher 1980) at least before rising cost of petroleum. Due to continual increase in petroleum costs and possible reduced availability of petroleum in the future there has been a need to find treating processes which will keep the industry competitive and profitable in the face of competition from other materials (Hatcher 1980).

PHYSICAL AND CHEMICAL PROPERTIES

The physical/chemical properties of penta are well characterized (Table 4). It is freely soluble in organic solvents, slightly soluble in cold petroleum ether, carbon tetrachloride and paraffins and is inflammable. Technical penta used in wood preservation contains toxic impurities. Those of regulatory concern penta’s microcontaminants (FAO 1996).

Property Value	**value**
Physical state	Light tan to white needle-like crystals. Crystalline, aromatic compound
Water solubility (at 20°C)	14 mg/litre (pH 5), 2 g/litre (pH 7), 8 g/litre (pH 8)
Log octanol–water partition coefficient	3.56 (pH 6.5) 3.32 (pH 7.2)
Melting point	191ºC (anhydrous), 174ºC (monohydrous).
Vapour pressure	2 × 10-6 kPa at 20°C
Boiling point	309-310°C (decomposition)
Density	1.987 g/cm3
pKa	4.7 at 25°C

Table 4. Physicochemical properties of penta (WHO 1987)

HISTORY

The wood preserving properties of penta were discovered in the 1930s. Water-repellent solutions, containing penta in solvents of the mineral spirits type, were first used in commercial dip treatments of wood by the millwork industry in1931. Commercial pressure treatment of poles with penta in heavy petroleum oils began in 1941, and considerable quantities of various products soon were pressure treated. Penta became a restricted-use pesticide in 1987 and is only available to certified applicators. It now has no registered residential uses (Fishel 2005; EPA 2008).

Before the 1987 Federal register notice that canceled and restricted certain uses, penta was registered as an herbicide, defoliant, mossicide, and disinfectant. It was then one of the most widely used biocides (EPA 2007). In 1947 nearly 3,200 metric tons of penta was reported to have been used in the U.S. by the wood preserving industry. As of 2002, about 11 million pounds of penta was produced. It may not be used in residential, industrial, or commercial interiors except for laminated beams or building components in ground contact and where two coats of sealer are applied. It may not be used in farm buildings where there may be contact with animals or in beehives.

Because penta was used for a wide range of domestic, agricultural, and industrial purposes for more than 60 years, the compound is ubiquitously distributed in the environment (Pohleven and Boh 2007). Its occurrence in aquatic and terrestrial food chains has been established (Fishel 2005). Penta continues to be used but depending upon the reporting country, the number of banned uses ranges from all uses to few uses. Most reporting countries banned residential indoor uses. Austria, India, Indonesia, New Zealand, Sweden and Switzerland have reported a total ban (FAO 1996).

In 1997 the manufacturers of penta voluntarily removed groundline/remedial treatment applications from the U.S. EPA registered labels for the product. All non-pressure and non-thermal treatment uses (i.e., spray uses) were deleted from the registrants' labels since 2004. This action left only pressure and thermal treatments with penta. Non-pressure/non-thermal treatments generally lead to higher applicator exposures.

MODE OF ACTION

Penta is toxic to all forms of life because it is an inhibitor of oxidative phosphorylation. Often used in combination with an insecticide, penta/NaPCP at low concentrations causes significant uncoupling of oxidation and phosphorylation cycles in tissues. At high concentrations it inhibits mitochondrial and myosin adenosine triphosphatase, inhibits glycolytic phosphorylation, inactivates respiratory enzymes and causes gross damage to mitochondria (Ozanne 1995). This results in accelerated aerobic metabolism and increasing heat production. It also causes loss of membrane electrical resistance (FAO 1996).

STANDARDS AND SOLVENTS FOR PENTA

The standard AWPA P8 defines the properties of penta wood preservative. Penta solutions for wood preservation shall contain not less than 95% chlorinated phenols, as determined by titration of the hydroxyl group and calculated as pentachlorophenol. The performance of penta and the properties of the treated wood are influenced by the properties of the solvent used (Ibach 1999). AWPA P9 standard defines solvents and formulations for organic preservative systems.

i. **AWPA P9- Hydrocarbon solvent Type AP (Type A or HSA)** The heavy petroleum solvent included in P9-A is preferable when the wood is used in ground contact and for bridge applications and pole use. The solvents are petroleum oils [like # 2 distillate] and hydrocarbon solvents (No. 2 diesel, and blends of diesel oils with auxiliary solvents that are intended to stay in the wood due to the high boiling characteristics. The heavy oils remain in the wood for a long time but do not usually provide a clean or paintable surface. They are designed to provide permanent penta solvency in wood and physical properties that will minimize the depletion rate of penta from wood.

ii. **AWPA P9- Hydrocarbon solvent Type C-** A system of light naphtha (mineral spirits or HB VMP naphtha) with a high-boiling and non-water soluble high viscousity auxillary solvent with ability to dissolve nearly its own weight of penta. It is used when treating glulam before gluing. These co-solvents must have ability to prevent migration and blooming as the light carrier solvent evaporates and migrates to the surface. The light naphtha may be either recovered in the cylinder by a solvent recovery process or left to evaporate from the wood.

HEAVY PETROLEUM SOLVENTS CHARACTERISTICS

Petroleum solvents used with penta have continually changed over the years. When penta as first used in wood preservation, only straight-run distillates having 5% solvency were available. Later cracking, aromatization and solvent refining of diesel increased the solvency and provided more stable oils. Hydro treating increases the stability, yields higher grade products, and stabilizes color but it lowers penta solvency through reduction of the olefinic content. Heavy oils contribute to sludge and emulsions and do not produce clean treatments. Sulfur compounds, olefins and nitrogen compounds in the oils are reactive under conditions of heat, moisture, acidity and catalytic action of penta. Blending heavy oils with oxygenated co-solvents and use of trace amounts of antioxidants and stabilizers that prevent catalytic polymerization creates solvents meeting various needs such as: light and uniform color, solvent power to carry preservative in wood at the concentration used for adequate penetration into wood, permanency of treatment, resistance to emulsification and sludging during storage and treating, lower corrosiveness, lower cost and finally lower environmental and industrial hazard. Avoiding emulsions is important to prevent deposits on the surface.

Loss through volatilization, leaching, blooming, bleeding, migration and decay can all be reduced by proper design of the carrier system. AWPA P9 recognizes that the higher boiling constituents are also the more viscous and more permanent. If the high solvency of a carrier is combined with a tendency of the carrier to migrate due to its volatility, viscosity and surface tension, then depletion of the preservative is considerable. Majority of the solvency of a carrier should be in the permanent portion of the carrier. Permanency is a function of high-boiling constituents, high viscosity and high interfacial tension (Arsenault 1973). Loss of penta from pole sections is greater in low interfacial surface tension oils than from high interfacial surface tension oils. If too little solvency is available in the more permanent portions of a solvent or if the solvency power is lost by evaporation, or leaching, after treatment, the preservative may be carried to the wood surface causing depletion. Co-solvents for penta solvents are normally the non-swelling type because swelling agents are water miscible. Water solubility must be low enough so as not to cause preservative drop-out before penetration is accomplished (Arsenault 1973).

RETENTION

Retentions required after treatment must be the amount needed to protect plus an amount lost through migration and depletion. Studies with penta wood have shown that decay tends to start when the outer zone has retention lower than 0.20 pcf. Pole line inspections have confirmed this (Arsenault 1973). Penta/LPG treatment and penta-petroleum treatment both require a minimum retention of 0.70 pcf in the outer ½-in. zone to prevent deterioration of wood poles (DeGroot 1984).

Other depletion studies have shown that initial retentions should be 13-14 pcf creosote and 0.6-0.8 pcf penta for effective protection in ground contact for effective protection and provide for depletion. Loading to higher levels, than those demanded by practical standards, results in waste, undesirable surface appearance, bleeding, and increased depletion. Excessive final steaming will lower the surface retentions of organic wood preservatives by steam distillation and it will also lower the distribution gradient. It removes approximately 19% of the penta and 25% of the solvent uniformly over the cross section resulting in a cleaner surface. The lowering of the gradient can be adjusted for by slightly over treating or increasing the penta concentration in treating solution. This lowers loss of penta in service by exudation and solvent migration.

EFFICACY AND COMPARISONS TO OTHER PRESERVATIVES

USA and CANADA

Tests on poles in service and field tests on wood treated with 5% penta in a heavy petroleum oil show efficacy similar to that of coal-tar creosote (Davidson 1977; Ibach 1999). Creosote at 4.9-5.1 Ib/ft^3 and 5% penta in heavy petroleum has shown service life of over 35 years against Formosan termites in saucier Mississippi and Lake Charles, Louisiana. Penta had a slightly better performance in Mississippi (Crawford et al. 2000).

Davidson (1977) gives an evaluation of the effectiveness of various wood preservatives, in treated southern yellow pine fence posts installed at saucier Mississippi an AWPA hazard zone 5 since 1949. In 2005 Freeman and co-workers reassessed the condition of the treated wood posts, and statistically calculated the expected post life span (Table 5). The study used SYP fence posts with an average diameter of 4-5 inches. In estimating service life prior to 100% failure, average service life was approximated by the time when 60% of the posts in a group have failed. Freeman et al. (2005) evaluated the posts by a standard 50 Ib lateral load pull test. After 53 years many of the posts failed upon to the stress load. Table 6 shows some of the preservatives, retention, posts remaining, and percentages of posts that passed or failed the test. It was determined that penta in oil, creosote, and copper naphthenate in oil, provided life spans calculated to exceed 60 years. Creosote, with low residue, (clean creosote) did not perform as well, giving a service life of 37 years from the 1977 inspection, and 45 years in the 2005 evaluation. Penta treated posts, in P9-Type A oil (# 2 fuel oil) treated to a retention of 0.30 pcf penta, (75% of the AWPA standard retention) had a typical calculated service life of 74 years in the 2005 evaluation and an even better performance when dissolved in aromatic residue.

Preservative	**Predicted service life (Davidson et al.1977)**	**Predicted service life (Freeman et al. 2005)**
Ammoniacal copper arsenate (ACA)	42	59.5
Coal-tar creosote, straight run, low residue	37	45.7
Coal-tar creosote, straight run, medium residue	40	54.0
Coal-tar creosote, medium residue, low in fraction from 235° to 270° C, crystals removed	40	71.7

Copper naphthenate (5%)-petroleum	42	72
Pentachlorophenol (5%)-petroleum oil (No. 2 distillate)	42	74
Pentachlorophenol (5%)-petroleum oil (Wyoming residual)	36	
Penta 5% in Petroleum Oil		55.5
Penta 5% in #4 Aromatic Res.		119.4
Penta 3% In #4 Aromatic Res.		122.1
untreated controls	3.6	2.4

Table 5. Average service life of penta, creosote and Cu-Nap pole stub/large diameter posts in Mississippi.

Chemical	**Ret. (TOTAL)**	**% Remaining**	**Fail**	**Pass**
Ammoniacal copper arsenate ACA	0.34	64	4 (25%)	12 (75%)
CuNap 5% Cu in Petroleum	6	68	4 (24%)	13 (76%)
Boliden Salt B	0.7	60	1 (7%)	14 (93%)
Penta 5% in #2 Distillate	6.3	68	0 (0%)	17 (100%)
Penta 5% in #4 Aromatic Res.	5.9	88	1 (5%)	21 (95%)
Penta 3% In #4 Aromatic Res.	6	100	2 (8%)	23 (92%)
Penta 5% in Petroleum Oil	6	64	6 (38%)	10 (63%)
Penta 5% Cu Nap in Petro	6.2	92	2 (9%)	21 (91%)
Creo Straight Run High Res	6	72	2 (11%)	16 (89%)
Creo Straight Run Low Res	5.9	28	4 (57%)	3(43%)
Control	0	0	0	0

Table 6. Preservative retention, posts remaining and percentages of pass, fail posts evaluated.

Other efficacy studies include those by Johnson and Thornton (2000), who report data from stakes of *Pinus radiata* sapwood and *Eucalyptus regnans* exposed for 35 years at three Australian sites (Innisfail, Sydney, Walpeup). After 35 years, 5% penta in furnace oil (128 kg/m^3) performed as well as Australian K.55 (blend) creosote oil and much better than 5% penta in diesel fuel oil (128 kg/m^3). Penta has been shown to provide adequate protection after 18 years in roofing shingles of western wood species treated by simple dipping and brushing (Scheffer et al., 1997). Highley et al. (1993) showed that length of dipping in penta whether 3 or15 minutes gave similar results. No benefit of longer dipping was observed and there was no evidence that incorporation of water repellant improves effectiveness of penta.

Crawford et al. (2000) present results of a long-term stake test initiated in 1938 by the Forest Products Laboratory. Replicate stakes of southern pine sapwood treated with several preservatives were installed in test sites at Saucier Mississippi, Madison Wisconsin, Bogalusa Louisiana, Jacksonville Florida; and the Canal Zone, Panama. In 1967 another stake installation that included 11 standard wood preservatives was made in at Lake Charles, Louisiana is infested by *Coptotermes formosanus*. Table 7 summarizes the efficacy comparison at the Mississippi site. Penta in heavy oil, performed as well as creosote and ACC with service life above 35 years. Performance of penta in mineral oils and that of Tributyltin oxide (TBTO) was inferior with service life below 20 years. TBTO generated a lot of attention as a possible alternative to penta but is less effective, is detoxified by microorganisms and degrades at elevated temperatures (Johnstone 1986). The performance of *P.radiata* samples impregnated with a range of light organic solvent preservatives or CCA salt in and above ground revealed that TBTO performed poorly compared to penta which gave relatively good protection under both hazard conditions and that CCA was most effective. In this study TBTO contributed only slightly towards fungal protection when combined with penta and could be rated as relatively unsuccessful without fortification with penta (Johnstone 1986).

PRESERVATIVE	RETENTION (lb/ft^3)	AVERAGE LIFE (YEARS)	REMARKS
ACID COPPER CHROMATE	0.25	11.6	
	0.51	-	70% failed after 55 years
	0.75	-	50% failed after 55 years
	1.54	-	22% failed after 35 years
CHROMATED COPPER ARSENATE	0.14		No failures after 22 years
COPPER-8-QUINOLINOLATE Stoddard Solvent (mineral oils).	0.12	7.8	
COPPER-8-QUINOLINOLATE	0.03	27.3	
AWPA P9 Heavy Oil	0.12	-	No failures after 37 years
COPPER NAPHTHENATE	10.3 (0.012)		15.9
(No. 2 Fuel Oil).	10.2 (0.029)		21.8
	10.6 (0.061)		27.1
	9.6 (0.082)		29.6
CREOSOTE, COAL-TAR	4.6	21.3	
	8.3		50% failed after 46 years
	13.2		20% failed after 54-1/2 years
	16.5		10% failed after 60 years
PENTA	0.38		80% failed after 38-1/2 years
Stoddard solvent (mineral spirits)	4.00	13.7	
	8.00	15.5	
PENTA	4.10		89% failed after 50 years
Heavy gas oil (Mid-United States)	7.90		80% failed after 50 years
PENTA	4.20	21	
No. 4 aromatic oil (West Coast)	8.20		70% failed after 50 years
PENTA	0.11		90% failed after 38-1/2 years
AWPA P9 (heavy petroleum)	0.29		No failures after 38-1/2 years
	0.29		No failures after 38-1/2 years
TRIBUTYLTIN OXIDE			
Stoddard solvent	0.015	6.4	
	0.045	7.4	
	7.90	7.0	
AWPA P9 (heavy petroleum) 3%	8.00	20.8	
AWPA P9 (heavy petroleum) 6%	8.00	24.0	

Table 7. Long term stake test performance with various wood preservatives in Mississippi. (Retention values in parentheses are based on preservative oxides or copper metal)

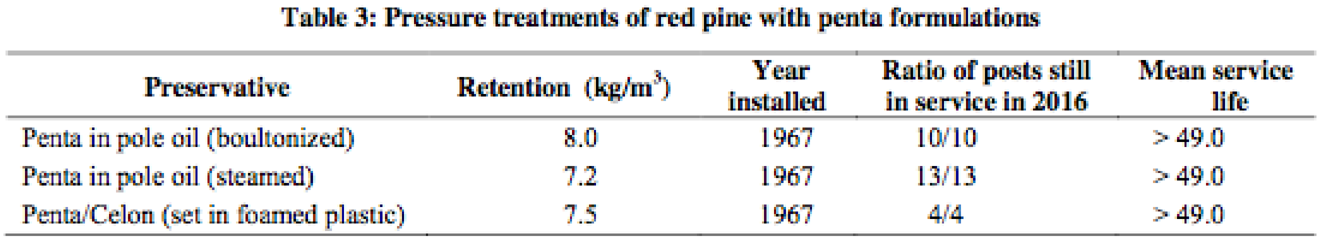

Table 3: Pressure treatments of red pine with penta formulations

Preservative	Retention (kg/m^3)	Year installed	Ratio of posts still in service in 2016	Mean service life
Penta in pole oil (boultonized)	8.0	1967	10/10	> 49.0
Penta in pole oil (steamed)	7.2	1967	13/13	> 49.0
Penta/Celon (set in foamed plastic)	7.5	1967	4/4	> 49.0

Table 7A. (Adapted from Stirling, 2017-in press)

Nicholas and Freeman (2000) compared the performance of CuNap and penta pine stakes against decay and termite attack at two test sites in Mississippi using four different petroleum oils meeting AWPA P9-A as carriers. The efficacy of CuNap, at a retention of 0.05 pcf Cu, was found equivalent or slightly better than penta at 0.40 pcf after ten years exposure. The type of carrier oil had an effect on the performance but was variable for type of preservative and test site. A summary of the results is shown in Table 8 and Figure 9. All of the CuNap formulations performed better than comparable penta formulations except in the diesel/KB3/B11 and base oil formulations, for which the performance of CuNap is slightly lower than for penta at the Saucier test site. The depletion rate of penta was somewhat greater than that for CuNap. The depletion rate plays a major role in the performance of treated wood.

Career oil	**Preservative Initial Retention (pcf)**	**Average % loss after 2-years exposure**	
		Above ground	Below ground
Ashland	Cu Nap. (0.049).	20.3	30.1
	Penta (0.383)	8.4	39.2
CA Shell	Cu Nap. (0.045).	20.6	17.1
	Penta (0.383)	14.7	39.4
Base Oil L	Cu Nap. (0.049).	17.9	21.8
	Penta (0.396)	11.2	43.2
Diesel/KB3/B11	Cu Nap. (0.051).	8.0	18.8
	Penta (0.394)	31.9	19.1

Cu Nap retention and depletion values are based on Cu Content

Table 8. Average % Depletion of Cu-Nap and Penta in stakes treated with several different carrier oils exposed at saucer for 2-years.

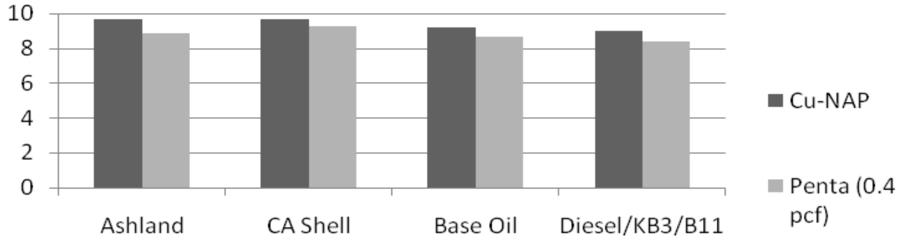

Figure 9. Comparative decay ratings of Cu-Nap and Penta treated Stakes using different carrier oils and exposed at Dorman MS. for a year.

Creosote-penta solutions were evaluated by many workers and were shown to have superior wood preserving properties. In 1950's utility companies used creosote that contains about 2% w/w penta but, experience showed that the solution was highly corrosive to storage and pressure vessels, piping, and pumps. Corrosion inhibitors such as orthophosphoric acid and cathodic protection systems showed no significant improvement. Removing tar base impurities from creosote prior to preparation of the formulation by washing with a mineral acid (30% sulfuric acid) or extraction with monopyridinium sulfate reduced corrosivity to about 15-20% of that of conventional creo-penta solutions (Albright and Leach 1971). The formulation is not commercially used anymore.

FACTORS AFFECTING PERFORMANCE OF PENTA

Factors affecting the performance of penta in treated wood include, conditioning method, solvent type (carrier solvent), amount of oil in solvent, presence of co-biocide, soil type, and soil chemistry of site of installation of the treated wood.

Effect of Carrier Solvent on Penta Performance

The importance of the carrier on performance of penta is well documented (DeGroot 1984, Nicholas 1988, Nicholas et al. 1994, Lowrimore 1994 and most recently by Nicholas and Freeman (2000 and Crawford et al., 2000). The influence of carrier oil properties on the performance of wood preservatives serves as the basis for the AWPA P9-A. In this standard physical property such as viscosity, specific gravity, penta solvency and distillation range of the carrier oils must meet specified criteria in order to be acceptable because they influence the plant operation and performance of the treated wood.

In a comprehensive review of stake tests installed in 1938 (Crawford et al., 2000) showed that in stakes treated with penta at similar retention, better performance is obtained with solvents containing heavy solvents such as heavy gas oil, lube oil extract, No. 4 aromatic oil, and AWPA P9 heavy petroleum solvent than with volatile LPG or light oils such as Stoddard solvent (mineral spirits). Table 10 shows results of average service life of penta treated stakes in Mississippi and Louisiana. Tributyltin oxide and copper-8-quinolinolate also show better performance with the heavy petroleum solvent than the light oils as shown in Table 10.

Carrier solvent affects penetration and permanency of the preservative in wood and affects biocide depletion rate. With regard to performance, the major factor is the effect of the carrier on depletion rate of the biocide. In penta-mineral spirits treatments without stable auxillary solvents, washing, vaporization and leaching could cause soft rot organisms and basidiomycetes to penetrate deeper (Arsenault 1973). Increasing penta solvency in the carrier oil results in a trend of improved decay resistance and less loss of penta by volatilization (Arsenault 1973). Oils with higher distillation temperatures, higher viscosity, higher surface tensions, and higher aromaticity perform better. The effectiveness of oil carriers is positively correlated with boiling point and average molecular **w**eight. (Lowrimore 1994). Higher boiling petroleums retard but do not prevent decay. A solvent with lower volatility is expected to provide an advantage in allowing a longer time for penetration following treatment and in suppressing loss of a volatile preservative (Highley et al., 1993). Table 10 is a summary of average service lives of penta stakes in various solvents in Mississippi and Louisiana test sites from the review by Crawford et al. (2000).

Inherent toxicity of the carrier oil to decay organisms influences the performance of the preservative. Aromatic oils are more toxic than paraffinic oils and aromatic content may make a difference in service life of treated wood. Lowrimore (1994) separated three P9-A petroleum solvents (California shell oil, Ashland oil and Base oil L) into four fractions each (saturates, neutral polycyclic, aromatics, bases and acids) by adsorption chromatography and tested each fraction against decay fungi. California oil the most viscous had the highest proportion to remain above 500°F. The first fraction to elute in all three carriers was composed of saturated aliphatics and constituted more than 87% of each oil. It exhibited no appreciable fungitoxic properties.

Oil or preservative	Location	Retention Ib/ft^3	Total (%) stakes removed after 50 years	Average life (years)
5% penta in Stoddard solvent (mineral spirits).	MS	4.0	100	13.7
	LA	4.0	100	8.8
5% penta in fuel oil	MS	4.0	100	14.9
	LA	3.8	80	12.5
5% penta in Heavy thermal side out	MS	4.0	100	14.0
	LA	4.0	100	10.6
5% penta in Diesel oil	MS	4.1	100	17.0
	LA	4.1	50	>50
5% penta in catalytic gas-base oil	MS	4.2	100	16.3
	LA	4.1	12	>50
5% penta in No. 300 fuel oil	MS	4.0	100	14.6
	LA	4.1	37	-
5% penta in No. 400 fuel oil	MS	4.2	100	13.9
	LA	4.2	78	12.5
5% penta in light gas oil	MS	4.0	100	15.6
	LA	4.2	50	>50
5% penta in heavy gas oil	MS	4.1	89	>50
	LA	4.1	-	-
Untreated controls	MS	-	100	2.2
	LA	-	100	2.8

Table 10. Condition of stakes pressure treated with penta in various petroleum oils 50 years after treatment in Mississippi (Saucier) and Louisiana (Bogalusa).

The second fraction (benzene eluted) was of moderate yield (7.4, 12.6 and 16.7% for California shell, Ashland, and base oil L respectively) and contained neutral polycyclic aromatics. This was the only fraction that reached a toxic threshold for inhibiting decay fungi. Yields of the third and forth fractions were relatively minor and played no role in inhibiting fungi. Overall performance of the oils were Base oil L> Ashland>>California shell. California shell gave the poorest performance most likely because it contained the least amount of the second fraction. Elemental analyses showed all oils were similar in carbon, hydrogen and oxygen but differ in nitrogen and sulfur content. Sulfur has fungicidal activity in elemental and organic forms and fungi utilize nitrogen as a food source. Base oil and Ashland oil contain higher levels of sulfur and undetectable levels of nitrogen, another explanation why the performance of Base oil L> Ashland>>California shell.

The data in Figure 11, Nicholas and Freeman (2000), show the toxic threshold values (pcf) for 8 oil types based on a pure culture basidiomyce test. Base oil gave the best performance in this data too with the lowest threshold values of 1.7pcf against *T. versicolor* and 4.2 pcf against *G. trabeum*.

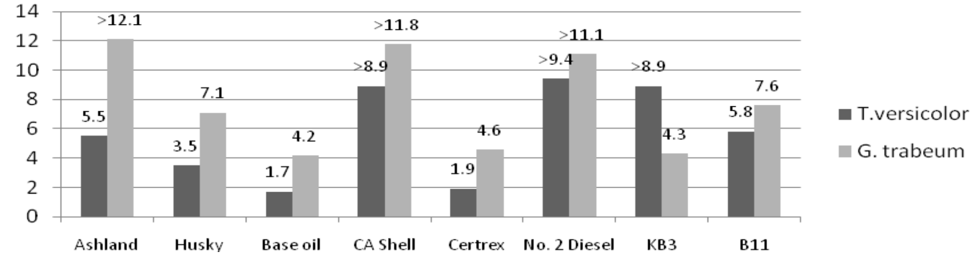

Figure 11. Approximate Toxic Threshold Values (pcf) of Several Oils Exposed To Fungi In A Soil-Block Test

Nicholas and Freeman (2000) report on a more recent study of the three carrier oils; California Shell oil, Base oil L (Lillyblad Petroleum Inc), Ashland oil (Ashland Petroleum). They also included 17% No. 2 Diesel Oil + 2% KB3 + 1% B11 (KB3 & B11 from Eastman Chemical Products). All oils were diluted with toluene (20% oil and 80% toluene) and used in a soil block test using SYP sapwood against brown-rot *Gloeophyllum trabeum* and white-rot *Trametes versicolor*. Field stakes (AWPA E 7) were installed in Dorman Lake, MS and Saucier, MS. Wood treated with the oil carriers alone initially performed reasonably well against both wood decay fungi and termites, but the activity decreased rapidly after about six years exposure. Each oil performed differently. The data in Figures 3 and 4 demonstrate that the carrier oils provided some degree of protection. At Dorman Ashland oil had the worst performance. After the 6th year California Shell Oil had better performance most likely because a previous study Lowrimore (1994) showed that it is the most viscous, has the highest proportion to remain above 500°F increasing its permanence in wood.

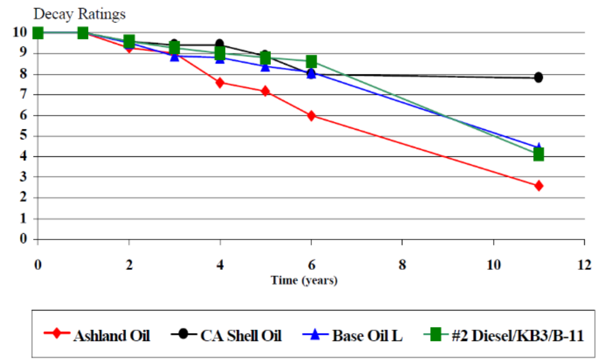

Figure 12. Average decay ratings-Stakes treated with Carrier oils after exposure at Dorman.

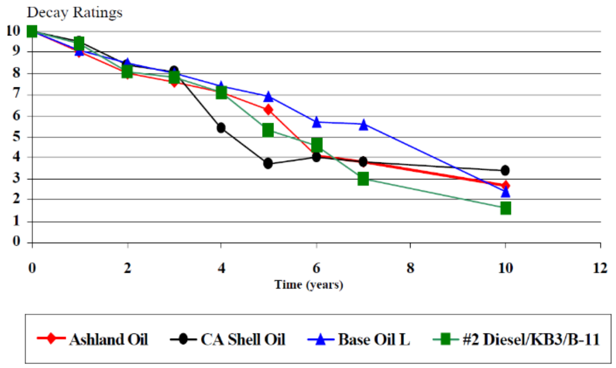

Figure 13. Average decay ratings- Stakes treated with Carrier oils after exposure at Saucier

Barnes et al. (2007) analyzed stubs treated with penta in seven oil types labeled A to G (Table 14) and set at a depth of 30-inches in a test plot set in DeQueen, Arkansas in 1960. Periodically, the pole stubs were pulled, evaluated for decay and termite attack (Figure 15) and bored for preservative assay. Steamed posts performed better than air-dried material, presumably due to the sterilization effects of pre-treatment steaming. Type D with the lowest aromatic fraction, gave the poorest performance irrespective of conditioning method. Oils A and B exhibited the best performance, and both had high aromatic content. The paraffinic fraction apparently had no effect on performance.

Oil	A	B	C	D	E	F	G
Composition & Properties	(% by vol)						
Aromatic light fraction	100	90	75	20	---	---	---
Aromatic heavy fraction	---	10	25	---	---	---	---
Paraffinic light fraction	---	---	---	80	60	100	---
Paraffinic heavy fraction	---	---	---	---	40	---	---
Waxy petroleum fraction with high pour point	---	---	---	---	---	---	100
Treating solution concentration (% w/w)	4.99	4.90	4.86	4.86	4.86	5.38	5.02
Specific gravity, oil only @ 60° F	0.982	0.982	0.965	0.882	0.881	0.863	0.908
Penta solvency, max @ RT (% w/w)	14	13	10	8.2	5.3	7.8	13.8

Table 14. Composition and characteristics of treating solutions used

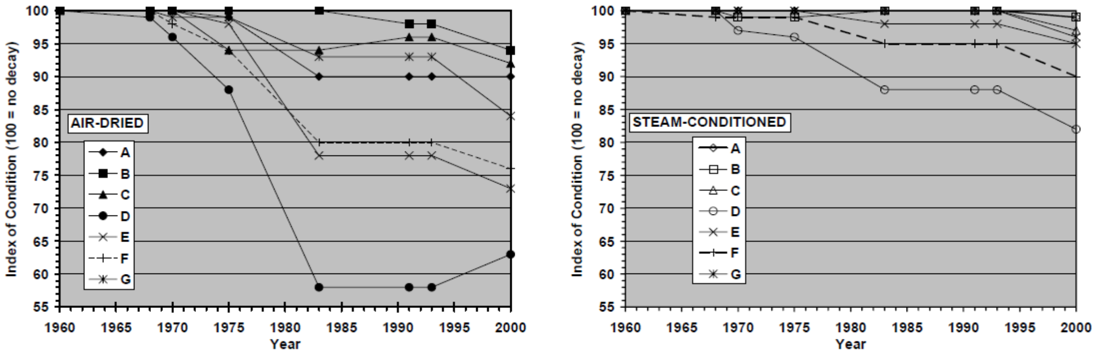

Figure 15. Effect of treatment solution

The penetration properties of penta and creosote oil-borne wood preservatives are improved by adding 15-16.6% N, N-dimethylamide acid (DMA) at 100-5,000ppm of preservative as part of the formulation (Johnston 1980). Suitable N, N-dimethylamides of straight chain carboxylic acids are those prepared from acids containing 18 carbon atoms and having at least one carbon to carbon double bond. Acids within this category include: linoleic, linolenic, oleic, ricinoleic or mixed acids. Adding DMA decreases time required to obtain adequate preservative penetration, results in less treating time and increase in overall plant efficiency (Johnston 1980).

Effect of Wood Species and Fungal Species on Penta Performance

Differences in performance of penta between species may be partly explained by the magnitude of adhesion of the oily preservative to wood. In hardwoods bordered pits, and tyloses hold oil in vessels helping retain it in wood. The narrow lumens in fibers retain liquids better resisting internal pressure and gravitational forces that encourage migration (Arsenault 1973).

Early soft rot attack on cellon treated poles is associated with the depletion of penta to below threshold retentions in the outer fibres (outer annual ring). Soft rots generally penetrate wood with the fungal hyphae lying within the thickness of the secondary walls of the longitudinal wood elements.

Since oil solutions do not penetrate the cellwall, prevention of soft rot attack by oil borne preservatives must depend on high surface concentrations of preservatives, vapor pressures of preservatives and water insolubility. Mechanical washing, vaporization, and leaching could cause early failure in such treatments.

Mineral solvents result in cellwall penta treatments which stabilize the preservatives so that mechanical washing, leaching and vaporization are minimized. Thus, swelling type co-solvents such as methyl alcohol, result in better service life than isopropyl ether co-solvent. In pine efficacy was improved with penta in a swelling system against white rot *Polystictus versicolor*, but with brown rot *Coniophora cerebella* and soft rot *Chaetomium globosum*, the swelling solvent system with penta and CuNap showed no advantage. Inhibition of white rot would be more effective by swelling–type penta solvents systems because the susceptible lignin deep in the cellwall would be in intimate association with the preservative. Brown rot would be expected to attack the cellulose near the surface of the cellwall (Arsenault 1973). Another study showed that only wood treated in the green state with swelling agents exhibited cellwall impregnation. In the dry state the wood did not exhibit swelling. Small amounts of water added to the swelling type solvents, increase their ability to enter the cellwall because the water acts as the opening wedge in preceding the larger molecular size solvent into the cellulose matrix through hydrogen and diffusion. Swelling results in more uniform retentions and distribution (Arsenault 1973).

ANALYSIS OF PCP IN TREATED WOOD

In the past two decades, the use of x-ray fluorescence spectroscopy (XRF) for the determination of chlorine for analysis of penta has become commonplace. However, some treating plants and inspection agencies still use the older Volhard chloride (lime ignition) method (AWPA 2006). The Volhard method, of back-titrating Chloride derived from Penta is over 150 years old. As part of a study on the effect of oil composition on the durability of penta-treated wood, pole stubs from a forty-year-old exposure in an AWPA Hazard Zones 3-4 (DeQueen, Arkansas installed in 1960 and decommissioned in 2000) were analyzed for preservative content using both methods. A linear regression of lime ignition values (LI) vs. XRF values was established for each of the seven oil carriers and for all oils combined. The best coefficient of determination (R2) was for Oil B with a composition of 90% aromatic light fraction + 10% aromatic heavy fraction. The oil with the worst fit with an R2 of 91% was the 80/20 mix of paraffinic light fraction to aromatic light fraction. When the data for all oils were combined, an R2 of almost 98% was obtained. This extremely good fit to the data over a range of oils with widely varying properties is an assurance of the validity of XRF analysis for quality control and other purposes (Barnes et al. 2007).

Bioassays using the fungus *Aspergillus niger* have been shown to respond to penta and indicated a good relationship between the amount of retained preservative in the wood and the circular area free from sporulated mycelium around preserved specimens, observed on agar substrate (Moreschi 1982). Penta specimens reveal an excellent correlation coefficient between mycelia growth and preservative content. The species does not respond to CCA in the same manner. *Aspergillus niger* as considered the most appropriate species for this purpose because its fast growth and symmetry of the TZE presents a reasonably accurate and easy approach to estimate amount of penta in treated wood (Moreschi 1982).

Capillary gas chromatography method with electron capture detection is another widely applied method of assaying penta (usually methylated or acetylated) after acid extraction to diethyl ether. The detection limit is 0.005-0.01 μg/litre. Other methods include gas chromatography with atomic emission detection, GC-MS using selected ion monitoring and HPLC (WHO 1997).

Summary and Conclusions

Penta remains a very viable wood preservative today. It continues to be the favored wood preservative for wooden poles in the USA and in N. America, in a recent Lineman only poll.. Its recent re-regsitration by the US EPA/PMRA (2009) has recently been completed. Penta provides long service life for properly treated, preserved and quality controlled wooden items, especially for the utility industry.

The dioxin/furan contaminants of penta present a unique case for purposes of risk characterization. Research has clearly established that the toxic effects attributed to penta are actually due to the impurities. It is these contaminants that meet all the POP criteria. Penta is the most documented substance in wood preservation. An extensive body of literature exits on the health effects of penta and its contaminants. The most toxic of the Penta impurities is TCDD which has has not been identified in any sample of penta produced in the United States. The US EPA put in place mearsures to limit the amount of these impurities in Penta years before the reregistration was due. Because of the demonstrated tendency for Penta to rapidly degrade in the environment, there is no risk of accumulation. The rigorous process undertaken by the EPA to re-register penta showed that use in pressure treatment of wood did not pose an unacceptable risk to man or the environment because of the contained exposure and much of the toxicity of penta is attributed to its impurities which have been limited in current formulations used. In summary, there are adequate controls for human and environmental exposure and specific approved uses for Penta that do not pose risk and should be allowed to continue. The environmental risk assessment indicates that typical concentrations of penta in terrestrial and aquatic environments from wood treatment uses are not expected to be of sufficient quantity or duration to adversely impact terrestrial or aquatic organisms.

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