DEPARTMENT OF THE ENVIRONMENT ENVIRONMENTAL PROTECTION SERVICE PACIFIC AND YUKON REGION

CHARACTERIZATION AND CHEMICAL USE PATTERNS
OF THE PLASTICS, RUBBER AND RESIN INDUSTRY
IN BRITISH COLUMBIA

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ABSTRACT

A characterization of the plastic, rubber and resin industry was undertaken by the Environmental Protection Service in British Columbia in 1984. Approximately 70 plastics, 8 rubber and 43 resin firms were inspected and over 100 firms were asked to fill in a questionnaire regarding chemical use patterns, control equipment and waste products.

Twelve priority and candidate chemicals as identified in the list of chemicals being investigated under the Environmental Contaminants Act, were found to be used in these industries.

Organotin compounds are suspected of being released to the environment from plants extruding polyvinyl chloride products where it is used as a heat stabilizer. Phthalic acid esters were found to be used as plasticisers and several organochlorides were used as anticorrosion and fire retardant additives.

Chlorosulfonated polyethylenes, lead monoxide, various amides and phthalic acid esters were found to be used in the rubber fabrication industry.

The firms producing polyester and formaldehyde resins all had varying degrees of pollution control and treatment. Two firms were discharging material to landfill and one to a remote evaporation lagoon. The major portion of the liquids discharged to the remote lagoon are believed to be lost by infiltration. The greatest volume of waste produced is by the resin industry. This includes waste sludges, tank and reactor residue and off specification product. Most of the solid sludges are stockpiled pending disposal to a suitable secure site.

A preliminary sampling and waste characterization program of two resin plants, two paint plants and one polyvinyl chloride extrusion plant has been undertaken to provide an initial data base. The data will be available in a second volume to this report.

RESUME

En 1984, une caractérisation de l'industrie du plastique, du caoutchouc et de résine fut entreprise par le service de la protection de l'environnement en Colombie Britannique. Approximativement 70 compagnies de plastique, 8 de caoutchouc et 43 de résine furent inspectées et plus de 100 firmes ont rempli un questionnaire traitant des méthodes d'emploi de produits chimiques, de l'équipement de contrôle et des produits de déchets.

Douze produits chimiques prioritaires et d'intérêt potentiel, identifiés dans la liste des produits chimiques étant examines sous <u>la Loi</u> sur les contaminants de l'environnement, furent identifiés comme étant employés dans ces industries.

Des composés organo-étains sont suspectés étre relâchés dans l'environnement d'usines extrudant des produits polyvinyliques où ils sont employés comme un stabilisateur de chaleur. Des esters de l'acide phtalique furent identifies étant utilisés comme plastifiants et plusieurs organochlorures étaient employés comme des additifs d'anticorrosion et de retardateur de feu.

Des polyéthylèmes chlorosulfonés, monoxide de plomb, divers amides et esters de l'acide phtalique furent trouvés comme étant utilisés dans l'industrie de la fabrication du caoutchouc.

Les compagnies produisant des résines de polyester et de formaldéhvde ont tous des degrés variés de contrôle de pollution et traitement. Deux firmes déchargeaient du matériel à un site d'enfouissement et une autre à un étang d'évaporation isolé. La majeure portion des liquides déversés à l'etang isole semblent être perdues par infiltration. Le plus important volume de résidue produit provient de l'industrie du résine. Cela inclut des boues résiduaires, les résidus de réservoirs et de réacteurs, et des produits hors spécifications. La majorité des boues résiduaires solides sont empilées en attente d'être disposées à un site sécuritaire adéquat.

Un programme préliminaire d'échantillonnage et de caractérisation de résidus de deux usines de résine, deux usines de peinture et une usine d'extrusion de chlorure de polyvinyle fut eutrepris pour fournir une base initiale de données. Les données seront disponibles dans un deuxième volume de ce rapport.

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1.0 CONCLUSIONS

Resin Formulation Plants: There are currently four resin plants in operation in British Columbia producing polyester, urea formaldehyde, phenol formaldehyde and polyvinyl acetate resins. Eight priority and 3 candidate chemicals were identified as being used and they include;

- 1) dibutyl tin oxide
- 2) dibutyl tin dilaurate
- 3) di-n-butyl phthalate
- 4) di-octyl-phthalate
- 5) Bis (2-ethyl hexyl) phthalate
- 6) tetrachlorophenol

- 7) pentachlorophenol
- 8) 1,1,1-trichloroethane
- 9) dimethyl aniline
- 10) di-ethyl aniline
- 11) triethyl phosphate

An estimated 3000 kg of lead napthenate is also used as a drying agent.

It is expected that most of the organotin reaction initiators used in polyester resin are contained in the product matrix and very little is lost during processing. Organotins are handled as a dry powder and may be released from process exhaust streams during reactor loading. An estimated 7.9 m³ of sludge from reactor bottoms, spilled product and sewers is produced each year. In Winfield, B.C., 0.400 m³/yr is disposed to the Glenmore road landfill. Approximately 455 m³/yr of untreated process water (neutralized with sodium hydroxide) is discharged to an open lagoon for disposal by dehydration and infiltration. This water may be a source of release of small quantities of organotins.

Phenol Formaldehyde Plants: At the three phenol formaldehyde resin plants all wastewater is recycled into the process. In the lower mainland, one plant has a biological lagoon treatment system which can oxidize phenolics and discharges to a sanitary sewer which is on the Annacis Island treatment plant collection system. Less than $3.0~\text{m}^3/\text{yr}$ of solid waste is

produced and stockpiled until sufficient volume is collected for shipment. In Kamloops the waste is sent to the Mission Flats Landfill and in the lower mainland they are sent to secure landfill in Oregon or Idaho. The lower mainland plants include waste from a variety of other processes which designates it as special waste.

Urea Formaldehyde Resins: The wastes produced are similar to those for phenol formaldehyde and are included in the volumes given above. There were no priority or candidate chemicals used in these processes.

Polyvinyl Acetate Emulsions: Are produced in the lower mainland and may use phthalate plasticisers in their formulations.

Wastes from the processes, are tank and line washings which are biologically treated before discharge to sanitary sewer. The quantity of plasticiser which is discharged to sewer is not known and is recommended for future qualitative and quantitative analysis. Tricresyl phosphate is also listed in the literature (15) as being used in vinyl acetate production however it was not indicated as being used by any of the producers in the region.

Plastic Pipe and Siding Extruder: There are seven plants extruding acrylonitrile butyl styrene (ABS), polyethylene (PE), polybutylene (PB) and polyvinyl chloride (PVC) pipes and siding. Of these seven, five are extruding PVC products which use 115 900 kg/yr of organotin heat stabilizers and 1 940 000 kg/yr of chlorinated paraffin wax lubricants. These plants are suspected of being the largest source of release of organotins and chlorinated paraffins to the environment by the plastics industry. Preliminary sediment sampling from the storm sewer of one plant showed an average of 180.0 ug/g total tin when background levels were below 2.0 ug/g.

The form of the tin and its environmental availability is not known and it is recommended that further sampling and leachability tests be performed at all five plants. The major cause for release was found to be poor handling of plant wastes and plant hygiene. The lack of dust control

during the unloading of cyclones and bag houses resulted in spillage on plant property and subsequent washdown into storm sewers by storm water runoff.

An unknown quantity of amine ultraviolet stabilizers may be used (1) and modes of environmental release would be similar to organotins.

The quantities of chlorinated paraffins released is not known and routes to the environment are expected to be similar to organotins. Further sampling is recommended to determine environmental levels of these chemicals.

The plants producing PE, ABS and PB products, purchase the resins in preblended pellet form and extrude it directly into piping. Wastes are limited to line startup scrap and off specification piping which is ground to powder and recycled into the process.

Expanded Polystyrene: There are four plants producing expanded polystyrene products such as insulation, packing and food containers. The plants producing food containers use pigments which are rated as food grade. Pigmented polystyrene is rarely used in insulation production and these products must have a degree of fire retardancy to meet building code specifications. Halogenated alkyl compounds (usually chlorine or bromine) are added as a powder or incorporated into the resin. In British Columbia the manufacturers import the resin with the fire retardant molecules incorporated into the resin structure. Certain food grades of polystyrene will degrade in soil within five years (10) however it is not known how long insulation grades will withstand deterioration as all wastes are disposed to landfill in Langley and Delta. Halogenated compounds in the solid waste disposed to landfill are estimated at 1140 kg/yr.

Extruders and Blow Molders of Plastic Parts: There are an estimated 43 companies in British Columbia which are involved in extruding and/or blow molding of plastic parts and bottles. All the companies (except one)

enforce strict recycle practices due to the high cost of raw materials. Solid plastic waste disposal to landfill is estimated at less than 100 000 kg/yr. Some plastics such as PVC require organotin heat stabilizers to prevent metal adhesion during processing and shut down. If a PVC extruder is to be shut down for servicing or over a weekend, a load of high organotin polymer concentrate is injected into the feed to fill the extruder. The high tin plastic will prevent charring and sticking in the extruder but must be discarded after startup. Most operations run twenty-four hours/day and there is no estimate of the amount of this type of waste as production varies greatly with present economic conditions.

Plastic Film Extruders: There were seven plastic film extruders identified in the Lower Mainland/Vancouver Island region. The materials used include polypropylene, cellophane, low density P.E., linear low density P.E., and high density P.E. Most of the films produced are for food packaging and material handling is controlled in such a manner as to prevent contamination. Cuttings and off specification film is recycled and total wastage is estimated at 27 100 kg/yr which includes polymer and 5 000 kg of additives such as slip and antiblock agents, ink solids and pigments.

Firms Manufacturing with Polyester Resins: Forty-one firms manufacturing with polyester resins were identified in British Columbia.

Approximately 60% to 70% of manufacturing activity occurs in the Okanagan/Winfield area and 30% to 40% in the Lower Mainland/Vancouver Island region. The two types of manufacturing are filler and fiber reinforced products. Anticorrosion storage tanks and piping use chlorendic based resins with organotin initiators. Most filler reinforced applications use orthophthalic or Isophthalic acid (or anhydride) based resins and some formulations may use organotin initiator complexes.

An estimated 14 000 m³ of solid waste is produced each year which includes residual resin, resin and fiber overspray, trimmed resin with fiber and/or filler. The fillers used are calcium carbonate or silica

powders. There is considerable dust generation during the trimming and grinding of the finished products. This dust was seen to spread beyond the plant boundaries of most operations and may be the most significant route to the environment of contaminants such as organotins, heavy metal pigments and chlorendic anydrides. (The quantity of organotin is expected to be low.) An estimated 800 kg of dimethyl aniline which is a candidate chemical is used as a catalyst in some applications.

Styrene monomer which is used as a resin diluent is released as a vapour directly to atmosphere.

Further soil and stormwater runoff sampling is required to determine the extent of contamination by any of these chemicals.

Rubber Manufacturers and Distributers: One hundred firms handling or producing rubber materials were identified in British Columbia. Sixteen of these were involved in blending and manufacturing with raw materials, the remainder being distributers or using cutting and cold bonding processes. The rubbers used include styrene butadiene, polychlorobutadiene, polybutadiene and acrylonitrile rubber. Polyurethane foam rubber is manufactured from glycols and 2,4 or 2,6-toluene diisocyanate. Hard polyurethanes use methyl diisocyanate.

Priority chemicals used include approximately 800 kg/yr of dibutyl phthalate, 1500 kg/y of di-octyl phthalate and less than 400 l/yr of stannous octoate catalyst. Waste rubber is produced from cleaning old rubber coatings (using cutting tools or blast shot) from mining, logging and pulpmill equipment and grinding rubber from tires. All the rubber tire grindings produced in B.C. (approximately 1 500 000 kg/yr) is recycled into rubber mats. 190 000 kg/yr of old machinery rubber grindings is disposed to landfill and 115 200 kg/yr is incinerated.

The 13 firms actively processing rubber consume approximately $58\ m^3$ water/day as steam and cooling water. Water which contacts the rubber is discharged to sanitary sewer. Cooling water is passed through jacketed systems and discharged to storm sewer.

Rubber Recyclers: Rubber recyclers process in excess of 4 000 000 kg of waste rubber into protective flooring for use in agricultural, industrial and commercial applications and as marine and loading dock protective bumpers. There are no significant amounts of waste produced except for miscellaneous scrap screened from the waste rubber grindings which is disposed to landfill and cooling water which is discharged to storm sewer or open ditches.

Epoxy and Polyester Resin Distributers: Epoxy resin, polyester resin, qel coat and pigment distributers handle resins for corrosive and passive applications, blend gel coat resins and handle additives such as fillers, promoters, catalysts, mold release agents, cloths, fibers and tools. Mixing operations are performed under explosion proof conditions in the shipping containers or in mixing tanks for repackaging. Waste acetone is produced during cleaning operations and is disposed by evaporation, or used as a base solvent for sundeck coatings or redistilled. Minimum resin wastage occurs due to the high cost of \$800.00 to over \$1000.00 per barrel.

The areas where further investigation is required is in testing water and sediment samples for the release of organotins from PVC producers and polyester resin fabricators and characterization of waste effluents from polyester, urea and phenol formaldehyde resin producers. Background level analysis of water and sediment for the priority and candidate chemicals identified as being used in the province is lacking.

2.0 INTRODUCTION: ENVIRONMENTAL CONTAMINANTS ACT, PRIORITY AND CANDIDATE CHEMICALS

The Environmental Contaminants Act list of priority and candidate chemicals includes certain chlorinated hydrocarbons, phthalic acid esters, organotins, aromatic amines, halogenated diphenyl ethers, halogenated toluenes, nitrophenols and organophophorous compounds. Chemicals listed are those of particular interest to the departments of the Environment and National Health and Welfare for special investigation to determine commercial/industrial use patterns, concentrations in the environment and health effects. Some of these chemicals were identified as being used in the plastic, rubber and resin industry and this report examines their use in British Columbia.

2.1 Characterization of the Various Industry Groups

Characterization of the broad range of firms involved in the Plastic, Rubber and Resin Industry required the consolidation of the available production and environmental information. Sources for the documentation of companies in operation included:

- a) Municipal telephone directories
- b) Trade indices
- c) Federal environmental files
- d) Provincial environmental files
- e) Province of B.C. Business Opportunities Sourcing System (BOSS) Index

The companies identified were then grouped into six different classes:

- 1) Plastics, general
- 2) Plastics, raw materials
- 3) Plastics, scrap dealers
- 4) Rubber, general
- 5) Resins

A computer file was created, containing the company's name, address, telephone numbers, drainage basin codes, and municipality. Each municipality or city was mailed a printout of the companies believed to be operating in their jurisdiction for confirmation, additions or deletions and request for environmental data relative to the operation. In most cases the list was referred to the business license office and very little environmental information was available. Several lower mainland municipal offices are converting to a computer data base with the capacity to store similar information. It was also found that some municipal fire departments are performing chemical inventories from a fire prevention and safety perspective. Future inventories should consider this source of information.

2.2 Industry Questionnaire

In co-operation with the Industrial Programs Branch in Ottawa an industry questionnaire was developed and tested by submission to several companies to fill out and comment. The Industrial Programs Branch was also responsible for contacting industry and trade associations such as the Canadian Paints and Coatings Manufacturers Association regarding the survey of their members in the Pacific Region. After several revisions of the questionnaire, company officials were contacted by phone to determine;

- a) if they were actively involved in manufacturing with the chemicals of concern
- b) the contact person to receive the questionnaire. This was very important to assure that the questionnaire was dealt with quickly by the most qualified person and reduce chances of it being lost.
- c) an appointment to examine the facility first hand, observe handling procedures, answer inquiries regarding the questionnaire.

2.3 Site Inspection

Approximately 115 companies were contacted and 90 were visited over a seven month period. These included: 63 - General Plastics firms;

4 - General Resin firms; 23 - Paint and Ink firms (see Ref. #29). The large number of visits were made to ensure that most variations in production were included, that none of the companies would feel that they were singled out and that a fair assessment would be made of the industry.

Five of these companies were selected for a preliminary sampling program to characterize wastes and determine possible routes of transport of priority chemicals to the environment. Two paint and coatings plants, two resin plants and one plastics plant were selected on the basis of;

- a) size
- b) process operations being typical for the industry
- c) use of priority or candidate chemicals as defined in the Environmental Contaminants Act

2.4 Types of Companies Operating in British Columbia

Fourteen types of plant operations (with minor variations on each type) were identified after the plant visits and are divided as follows.

- 1) Paint and coatings manufacturers (see Ref. #29)
- 2) Resin manufacturing including:
 - polyester resins
 - phenol formaldehyde resins
 - polyurethane resins
 - polyvinyl acetate
 - alkyd resin
 - clear coatings
- 3) Polyurethane foam manufacturers
- 4) Polyvinyl chloride, Acrylonitrile-butyl-styrene, Polybutylene, and polyethylene pipe extruders
- 5) Polystyrene expander/molders
- 6) Extruders and blowmolders of plastic parts and bottles
- 7) Plastic film extruders

- 8) Polyester resin fabricators
- 9) Rubber vulcanizers/applicators
- 10) Rubber recyclers
- 11) Polymer resin, pigment/additive suppliers
- 12) Paints and coatings solvent suppliers

3.0 RESIN PRODUCTION IN BRITISH COLUMBIA

There are four resin manufacturers in British Columbia. The resins produced include:

- 1) Polyester resins for the powder and fiber reinforced resin industry.
- 2) Urea formaldehyde resins for foam insulation and protective coatings.
- Phenol formaldehyde resins for glues used in the plywood and veneer industry.
- 4) Polyvinyl acetate and polyvinyl alcohol based resins for the coatings industry.

Table 3.1 outlines the estimated production of each resin. The following priority and candidate chemicals were identified as being used in this industry:

- 1) dibutyl tin oxide
- 2) dibutyl tin dilaureate
- 3) di-n-butyl-phthalate
- 4) di-octyl-phthalate

- 5) Bis(2-ethyl hexyl)phthalate
- 6) tetrachlorophenol**
- 7) pentachlorophenol**
- 8) 1,1,1-trichloroethane

**These chemicals have been removed from the priority list and further details on their use can be found in DSS report contract #065B.KE603-4-0375, Inventory and Characterization of Pesticide Formulations and Distributers in British Columbia, March 31, 1985. They are used in other coatings formulations not related to the manufacture of polyester resins.

Candidate chemicals identified include:

- 1) dimethyl aniline
- 2) diethyl aniline
- 3) triethyl phosphate

Table 3.2 lists the raw materials which were identified as being used in the industry.

TABLE 3.1 ESTIMATED ANNUAL PRODUCTION OF RESINS IN BRITISH COLUMBIA

CHEMICALS	PRODUCTION (k	g/y)
Polyester resins Urea Formaldehyde Phenol Formaldehyde Poly Vinyl Acetate Poly Vinyl Alchohol	< 5 000 000 < 11 000 000 < 52 000 000 1 < 2 500 000 N/D	(E) (E) (E) (E)

TABLE 3.2 ESTIMATED MAXIMUM ANNUAL CONSUMPTION OF RAW MATERIALS IN THE RESIN INDUSTRY OF BRITISH COLUMBIA

CHEMICAL	ANNUAL CONSUMPTION
Resourcinol	250 000 1/yr (E)
Urea	17 000 000 kg/yr (E)
Pheno1	$10\ 000\ 000\ m^3/yr\ (E)$
Methanol	17 000 000 1/yr
Formaldehyde (35%-45% soln.)	42 000 000 1/yr
Melamine Formaldehyde	4 500 000 kg/yr (E)
Ethylene Glycol	< 60 000 1/yr (E)
Diethylene Glycol	300 000 kg/yr (E)
Propylene Glycol	900 000 kg/yr (E)
Dipropylene Glycol	< 10 000 kg/yr
Maleic Anhydride	< 500 000 kg/yr
Phthalic Anhydride	< 2 000 000 kg/yr
Isophthalic Acid	< 300 000 kg/yr
Adipic Acid	6 000 kg/yr
Propion Aldehyde	N/D
**Dimethyl Aniline	< 1 000 kg/yr
**Diethyl Aniline Paraffin Wax	< 4 000 kg/yr < 4 000 kg/yr
*Chlorinated paraffin wax	N/D
Tert-butyl-catechol	< 500 kg/yr
Hydroquinone	< 500 kg/yr
Chlorendic Anhydride (21)	N/D
Styrene Monomer	< 2 300 000 1/yr
Methyl Styrene monomer	< 10 000 1/yr
Acetone	22 000 1/yr (E)

TABLE 3.2 ESTIMATED MAXIMUM ANNUAL CONSUMPTION OF RAW MATERIALS IN THE RESIN INDUSTRY OF BRITISH COLUMBIA

(Continued)

CHEMICAL	ANNUAL CONSUMPTION
Poly-methyl-methacrylate	1 000 kg/yr (E)
Hexachlorocyclopentadiene (21)	N/D
*Dibutyl tin Oxide	300 kg/yr (E)
*Dibutyl tin Dilaureate	100 kg/yr (E) 11 500 kg/yr (E)
Cobalt Napthenate	11 500 kg/yr (E)
Copper Napthenate	200 kg/yr (E)
Cobalt Octoate	3 000 kg/yr
Copper Octoate	N/D
Lead Napthenate	< 3 000 kg/yr
Zinc Napthenate	N/D
Iron Napthenate	< 5 000 kg/yr
Zinc Acetate	< 500 kg/yr
*di-n-butyl phthalate	< 5 000 kg/yr
Cadmium Red	< 500 kg/yr
Cadmium Yellow	< 400 kg/yr
Cadmium Orange	< 400 kg/yr
Chromium Green	< 100 kg/yr
Chromium Yellow	< 400 kg/yr (E)
Carbon Black	20 kg/yr (E)
Moda Flow	N/D
Mold Wiz	N/D
Aluminum Powder	200 kg/yr (E)
Si05	60 000 kg/yr (E)
Clay	
Walnut Shell Flour	75 000 1 / /5)
Wood Flour	75 000 kg/yr (E)
M3X-10 (Trade Name)	. 600, 000, 7.4
Toluene	< 600 000 1/yr
Xylene	< 200 000 1/yr
Denatured Ethanol	< 28 000 1/yr
*1,1,1-Trichloroethane	< 16 000 1/yr
*Tetra chlorophenol (See Note)	< 150 000 kg/yr
*Pentachlorophenol (See Note)	< 350 000 kg/yr
*Methylene Chloride	< 9 000 1/yr
Dowicil 75	< 500 1/yr
Polyurethane (Oil Modified)	N/D
Soya Lecithin	< 5 000 1/yr

TABLE 3.2 ESTIMATED MAXIMUM ANNUAL CONSUMPTION OF RAW MATERIALS IN THE RESIN INDUSTRY OF BRITISH COLUMBIA

(Continued)

CHEMICAL	ANNUAL CONSUMPTION	
*Tri-ethyl phosphate	N/D	
Methyl Ethyl Ketone Peroxide	(Distributed)	
2,4-toluene di-isocyanate	N/D	
Sulphuric Acid	< 5 000	
Phosphoric Acid	N/D	
Acetic Acid	10 000 l/yr (E)	
Sodium Hydroxide	100 000 kg/yr (E)	
Nitrogen	$18\ 000\ m^{3}/yr\ (E)$	
Styrene Butadiene Rubber	5 000 kg/yr (E)	

^{*}Priority Chemical **Candidate Chemical

- (E) Estimated value based on best available data, actual value may be less.
- N/D Known to be used in small quantities, insufficient data to estimate.
- Note These chemicals are used in wood preservation formulations at the same plant site where resins are formulated. For more information see the report DSS Contract #065B.KE603-4-0375, "Inventory and Characterization of Pesticide Formulators and Distributers in British Columbia", March 31, 1985.

4.0 POLYESTER RESIN FORMULATION

There are six basic types of Fiber Reinforced Plastic Resins (FRP) used in British Columbia. They are Orthophthalic, Isophthalic, Chlorendic, Bisphenol A, Vinyl and Furan resins. Only the first two are manufactured in the region the other four are imported in varying grades by FRP distributers. Orthophthalic resins are based on diacids or anhydrides with carboxylic acid groups in the ortho position such as phthalic acid or anhydride. These resins provide minimum corrosion resistance and are used as general purpose resins.

Isophthalic resins are based on acids or anhydrides in the meta position such as isophthalic acid. These resins are usable up to temperatures of 80°C (180°F), in corrosion applications such as weak acids, alkalis, water, and solvents including gasoline and oil (21).

Chlorendic resins are heat resistant and are based on hexachloro-cyclopentadiene acid (HET) (or chlorendic anhydride) and stable glycols such as neopentyl glycol (21). The Bisphenol A resins are formulated by reacting 2,2-Bis (p-hydroxyphenyl) propane with propylene oxide to form a glycol and is reacted with fumeric acid to produce a polyester (20, 21). This resin is stable in strong acids or bases but not for solvent or oxidising applications (21). Chlorendic and Bisphenol resins require glass lined reactors due to the corrosive nature of the reactants and are not produced in B.C. (22).

Vinyl esters are based on methacrylated epoxies and are used for acids, alkalies, hypochlorites and solvents. Furan resins are based on polymer derivatives of furfural alcohol and are resistant to strong acids and alkalis containing chlorinated organics.

4.1 Polyester Resin Production Process

Polyester resins are blended and produced according to the fiberglass manufacturers specifications at the end use. The resins contain additives to control flexibility/rigidity, bond/matrix strength, durability, corrosion/abrasion resistance, impact strength, resistance to biological and ultraviolet degradation and workability of the raw resin. The basic polyester reaction involves the dehydration and polymerization of a dicarboxylic acid and dialcohol or an anhydride and a dialcohol. The following reactions are typical of the process.

Eg. (1) Adipic Acid (1, 4 - butane dicarboxylic acid) and diethylene glycol.

Eg. (2) Maleic Anhydride and diethylene glycol

Powdered or flaked reactants are preweighed, blended and charged to a batch reactor with the appropriate glycol (or glycols). A batch cook will take 8 to 12 hours to complete depending on catalysts and the degree of polymerization required. A two reactor system may be used where Reactor #1 is charged and initiated while Reactor #2 is being emptied, thinned to the proper consistency and blended with additives (if required). The

finished resin is packaged in 204 L (45 gal) metal drums and stored for shipping to fiberglass manufacturers. Condensed water vapour contaminated with raw materials is the major process discharge.

Dry reactants are blended according to the required batch recipe. Solids include:

- anhydrides or diacids to form the ester.
- powdered dibutyltin oxide or dibutyltin dilaureate as reaction initiators.
- paraffin wax as sealants

The exact amounts of each reactant are weighed and added to the reactor through a chute and dusts are controlled by filtration through a baghouse or, vacuum hood to an incineration unit (see Figure 4.1).

Liquid reactants are added according to batch recipes and include:

- polyols such as diethylene glycol, ethylene glycol, propylene glycol, dipropylene glycol and aldehydes for esterification.
- di-methyl-aniline, di-ethyl-aniline as intermediate dyestuffs to react with cobalt or other pigments (22, 23).
- triethyl phosphate which is used as an ethylating agent.
- styrene monomer (usually added at the end of a cook to dilute the resin.

The reactor consists of a large tank (up to 20 000 l or more) with raw material delivery ports and access hatch mounted at the top. A condensate vent releases byproduct water vapour to a condensor to reflux some water and styrene back to the reactor. Excess vapour is vented to strippers/ condensors which condense the remaining water vapours and wash with caustic to remove fumes and acids. Excess purge gas is vented to the atmosphere while byproduct water is neutralized to pH 7 in a titrator before discharge to a holding tank or sump. The finished cook is highly viscous and is drained or pumped to a thinning tank for the addition of

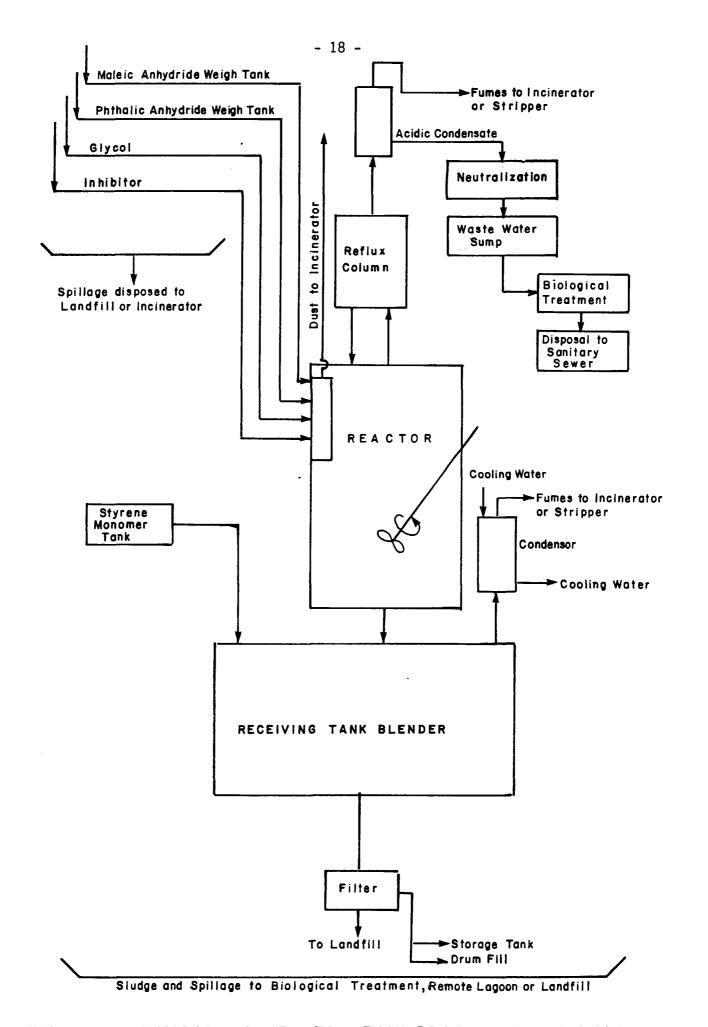


FIGURE 4-1 TYPICAL POLYESTER RESIN PROCESS FLOW CHART

styrene or alpha methyl styrene monomer. Some residual water is drained from the thinning tanks to the neutralization tanks and subsequently discharged to a sump or treatment system.

4.2 Additives to Resin

Additives to resin include metallic soaps, pigments, antioxidants, fillers, flow agents and internal lubricants.

4.3 Metallic Soaps

Metallic soaps are added to promote curing of the resin when it is exposed to an initiator such as methyl ethyl ketone peroxide.

These include: Cobalt napthenate (12%)

Cobalt octoate

Copper napthenate (8%)

Copper octoate
Lead napthenate
Zinc napthenate
Iron napthenate

4.4 Pigments

Pigments are added to the resins only if a continuous color is required through the cross section of the formed product. Separate polyester resins called "Gel Coats" are formulated and are painted onto the mold surface before resin and fiberglass laminates are applied. (A wax or silicon compound is first applied to the mold to ensure that it releases from the final product). Titanium oxide is a white pigment and is the major color used. Small amounts of pigments can be added to the white gelcote resin to achieve the desired tint. Other pigments include cadmium reds and yellows, chrome green and yellows and carbon blacks. A wide range of pigments are used and most are proprietory trade formulas which are not known for exact content.

4.5 Antioxidants and Fillers

Antioxidant and filler pigment include aluminum and carbon black which provide bulk and also inhibit ultraviolet radiation which reduces excessive crosslinking and brittleness in the finished product.

4.6 Flow Agents and Internal Lubricants

Flow agents and internal lubricants such as Moda Flow and Mold Whiz are purchased trade additives to improve application properties. Flow control is important for those resins which are applied by spray chopper quns.

4.7 Nitrogen

Nitrogen is used to purge piping and reactors and to provide a reducing atmosphere.

4.8 Process Emissions

Vapour emissions from the tank farm tanks are controlled via open or vacuum/pressure vents. A high vapour pressure of 5.0 mm Hg requires that the styrene tanks be controlled by vacuum/pressure vents. Glycol vapour pressures are in the range of 0.01 mm Hg and the storage tanks are controlled with open vents.

Dust particulates which may contain diacids, organotins, phthalic acids and anhydrides are formed during the weighing of these products and loading of the reactors. The displaced reactor air and work area air is filtered through a baghouse or vented to an incineration furnace before discharge. Thinning of the resin involves the addition of styrene monomers. Displaced air and styrene fumes are vented to atmosphere.

During the reaction process, byproduct water vapour is condensed and then scrubbed with caustic to remove most vapours and neutralize the approximately 2% diacid content. Byproduct water is also drawn off the bottom of thinning and storage tanks and must be neutralized. The process water contains a variety of raw materials and is disposed of in two methods. One involves the discharge to a bio-oxidation process with

eventual discharge under GVRD permit to a sanitary sewer which receives secondary treatment and is discharged to the Fraser River at Annacis Island. The second involves the discharge under Provincial Permit to a remote lagoon in a gravel hillside near Winfield, B.C.

Water discharged to the lagoon is lost by evaporation and infiltration. A single groundwater test well at the evaporation lagoon has not detected the presence of water however the rate of loss of water suggests a significant seepage into the soil. The eventual fate and degree of treatment that this water receives is not known. There are no streams or lakes in the immediate area and it is approximately 4 km to the nearest body of water.

4.5 Organotin Compounds and Priority Chemicals

The organotin stabilizers used in the manufacture of polyester resins are on the Environmental Contaminants Act list of priority chemicals. This additive is handled as a dry white powder and is loaded to the reactor by dumping down a chute. The dusts generated are controlled by a bag house or vacuum system and the actual efficiencies of removal and the amount that is discharged to the environment is not known but expected to be small. Other priority and candidate chemicals include diethylaniline, dimethylaniline, and triethyl phosphate. (The paraffin waxes used are not expected to be chlorinated.)

4.6 Wastewater and Sludges

The condensed wastewater and sludges in the floor sewers are the other waste source from this operation. These sludges are likely to contain most of the raw materials, reacted products and priority chemicals handled in the reactor building. The sludge is scraped up and stored in metal barrels for transport to landfill. The fate of this waste upon discharge to landfill has not been determined. Approximately $0.400~\text{m}^3/\text{yr}$ is generated in the Winfield area and disposed at the Kelowna Landfill on Glenmore Rd. A maximum $7.5~\text{m}^3/\text{yr}$ is generated in the lower mainland (this also includes wastes from resins other than polyester).

5.0 PHENOL FORMALDEHYDE RESIN PRODUCERS

Phenol formaldehyde resins are produced in three plants in British Columbia. Two are located in metropolitan Vancouver and one in Kamloops. The resins are used as adhesives in bonding plywood, treated papers used for finished plywood and as coatings in glass fiber insulation. The feed stocks include methanol (for formaldehyde production), formaldehyde as 37 to 50% water solution, phenol, acidic or basic catalysts and water. Two of the facilities produce formaldehyde by the oxidation of methanol feed stock.

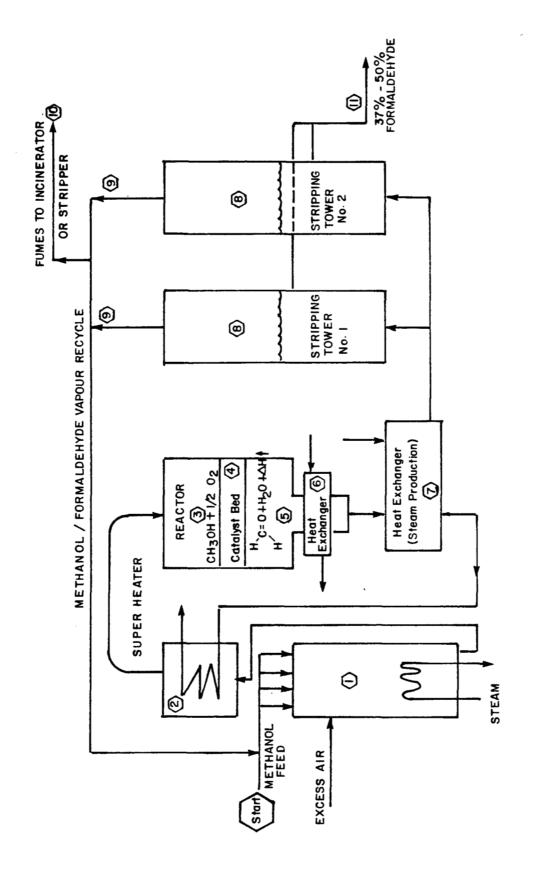
5.1 Formaldehyde Production

Formaldehyde is produced as a 37% to 52% solution with water in a continuous recycle reactor process as shown in Figure 5.1.

Liquid methanol is combined with a methanol/formaldehyde/air reflux (see Point 1) and aspirated into a steam heated vapourization chamber. Preheated compressed air is fed into the vapouriser to aid in volatilization and provide oxygen for the conversion to formaldehyde. The hot vapour is fed to a superheater (Point 2) prior to injection to the reactor (point 3). The vapour passes through a catalyst bed (Point 4) where the formaldehyde formation reaction occurs.

A)
$$H - \begin{matrix} H \\ C \\ H \end{matrix}$$
 - $OH + 1/2 O_2 \longrightarrow \begin{matrix} Cat \\ C \\ H \end{matrix}$ $C = 0 + H_2O + \triangle H$

Reactor temperatures reach 250°C to 600°C (Point 5) and vapours are cooled using a Dowthern heat exchanger (Point 6). Second stage cooling to 50°C-60°C (Point 7) is accomplished before the formaldehyde/water mixture is sent to tail gas stripping towers. Tail gas containing residual methyl alcohol, formaldehyde and air is vented at Point 9. The tail gas can be recirculated and/or vented for treatment (see Figure 5.1).



FORM ALDEHYDE PRODUCTION SCHEMATIC FIGURE 5.1

5.2 Phenol Formaldehyde Resin Production

Liquid phenol and formaldehyde is charged to a batch reactor and blended with basic or acidic catalysts to produce Resole or Novalak resins (see Figure 5.2). Resole resins are produced using a molar excess of formaldehyde and a basic catalyst (24). Catalysts include sodium, barium and calcium hydroxide, sodium carbonate or organic amines. Melamine formaldehyde is used as a catalyst and less than 15 000 kg/yr (E) is consumed for this purpose.

Novalaks use a lower than 1:1 formaldehyde/phenol ratio and acidic catalysts such as sulfuric, p-toluenesulfonic, hydrochloric, phosphoric and oxalic acids (24). Resole resins do not require curing agents and are thermosetting. Novalaks use a curing agent such as hexamethylenetetramine or a resole resin (24).

The basic reaction is

Pheno1

Formal dehyde

Dehydration

Catalysts which may be used are:

Acid Catalysts Sulphuric Acid p-toluene Sulphonic Acid Hydrochloric Acid

Base Catalysts
Sodium Hydroxide
Barium Hydroxide
Calcium Hydroxide

PRODUCTION PROCESS PHENOL FORMALDEHYDE 4 OF FLOWCHART 5.2

FIGURE

Acid Catylists
Oxalic Acid
Zinc Acetate
Sodium Acetate
Magnesium Acetate

Base Catylists
Sodium Carbonate
Amines

(24)

5.3 Process Waste Solids, Waste Water

Water vapour is drawn off, condensed and discharged to a main waste water sump. (This water is contaminated with reactants and catalyst.) The finished resin is pumped through a filter system before transfer to storage or packaging. Filtering removes any extraneous material including residual flaking from the reactor walls. The volume of waste produced is small (several kilograms/yr) and is disposed to landfill. The resin may be distilled to remove excess water and increase product viscosity. Distillate water is recycled into the reactor.

Process water is reused at all production facilities. The excess water discharged from the reactor or extracted as distillate (to increase the viscosity of the resin) is collected in a waste water sump. Solids are allowed to settle and the water is recycled into subsequent batches. The sumps are cleaned as required and the solids are dumped in an open area to drain and air dry. Two plants use a gravel based drying area where it evaporates or seeps into the ground and one uses a cement pit with a drainage collection system. Water which is drained from the cement pit is recycled back to the process. The air dried material which is primarily cured phenolic resin is disposed to secure landfill in the United States such as Oregon or Idaho.

Less than 3.0 m³/yr waste solids is produced and several years waste is stockpiled and shipped when volume is sufficient. In Kamloops solidified formaldehyde and waste resin from reactor cleaning and spills is stockpiled for several years in an open gravelled area. When sufficient volume has collected it is disposed to landfill in Kamloops. The landfill are located in Mission Flats along Mission Flats Road and at the end of Barnhart Bale Road.

Stormwater is treated differently at each facility. The Kamloops plant does not collect stormwater outside the tank farm and water within the tank farm is minimal due to the arid climate.

One plant in Vancouver collects stormwater, wash water and tanker washings and biologically treats the combined effluent before discharging to sanitary sewer for further processing at Annacis Island Sewage Treatment Plant. The other Vancouver Plant uses a central storm water collection system for paved driveways outside the production and tank farm areas. The water is collected in a sump and analysed for phenolics and formaldehyde before discharge to sanitary sewer and further treatment at the Iona Sewage Treatment Plant. If the storm water is contaminated it is pumped to a pollution water collection sump where it can be recycled into the process.

5.4 Air Emissions

Air emissions are controlled under GVRD permit numbers or provincial air permits and are monitored for the chemicals listed in Table 5.1.

TABLE 5.1 MAXIMUM LIMITS OF CHEMICALS DISCHARGED IN AIR PERMITS IN THE GVRD (19)

PARAMETER	RESTRICTION
Particulates	120 mg/m ³
Pheno1	100 mg/m ³
Formal dehyde	30 mg/m ³
Methyl ethyl ketone	900 mg/m ³
Methanol	2 600 mg/m ³
Isopropanol	10 000 mg/m ³

In Kamloops the vapours from the process reactors and tank farm are vented directly to the atmosphere. The odours were noticeable at the plant boundary. One plant in the GVRD incinerates all fumes from the formaldehyde process unit, reactors and reactor loading chutes. There were no noticeable fumes at this facility. The other plant in the GVRD vents all fumes from the reactor and weigh tanks through a countercurrent scrubbing tower using 20% sodium sulfite solution to remove vapours. Air is emitted to less than 26 ppm phenol and 20 ppm formaldehyde. No fumes were noticeable at this facility.

5.5 Cooling Water

All cooling water systems in the reactors are jacketed. In Kamloops the cooling water is discharged under permit to the North Thompson River and in the Lower Mainland it is discharged to Port Moody Harbour via Schoolhouse Creek and to the Fraser River by diffuser. All discharges are under the authority of a British Columbia Waste Management Branch Permit.

6.0 UREA FORMALDEHYDE RESIN PRODUCERS

Urea formaldehyde resins are produced at two facilities in the Pacific Region. Approximately 15 600 000 kg/yr are produced primarily for use as adhesives, coating and foam applications. The major use is in adhesives for the plywood and chip board industry. The adhesives are designed to remain in the glue line of the laminate and are highly viscous. Viscosity may be increased by the use of thickners and extenders such as powdered walnut and pecan shells, wheat flour, or blood albumen (25).

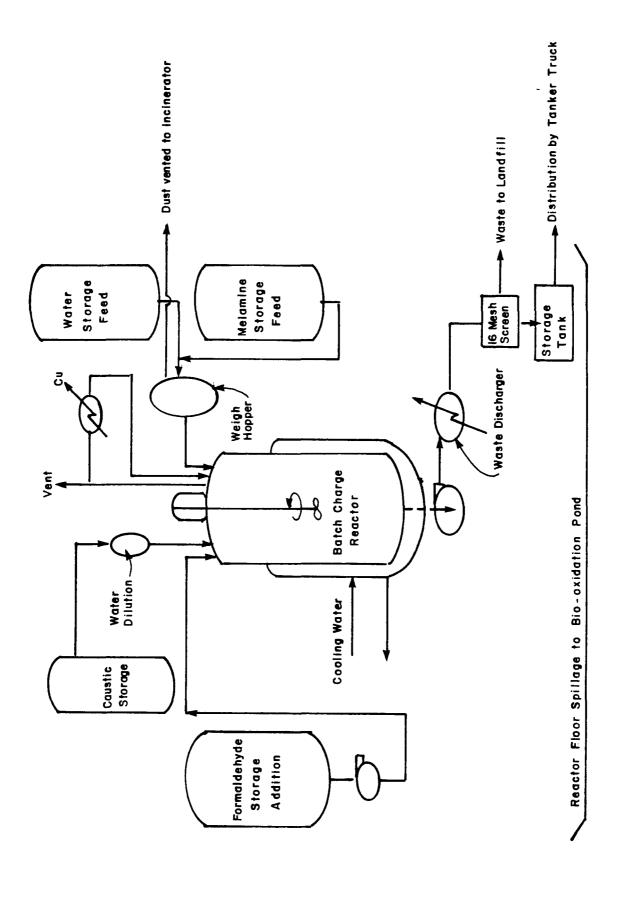
6.1 Urea Formaldehyde Reaction Mechanism

Solid urea and 37% formaldehyde solution are the two main raw materials for the production of urea formaldehyde resins. Solid urea and 37% formaldehyde/water solution is charged to a batch reactor and agitated (see Figure 6.1) (for formaldehyde production see Section 5.1). Caustic is added initially to control pH and promote hydroxymethylation of the urea. Reactions 1 and 2 describe the process.

(1) Hydroxymethylation

The second stage is polymerization by dehydration which is promoted by lower pH and higher temperature.

(2) Dehydration



RESIN PRODUCTION FIGURE 6.1 TYPICAL FLOWCHART FOR UREA-FORMALDEHYDE

The reaction is temperature controlled and can be stopped when the correct product viscosity is achieved. The viscosity will increase with an increase in the length of the polymer which grows by progressive condensation reactions.

(3) Polymerization

Catalysts used are acids or bases with the final polymerization catalysed by acids (3). The by-product water is condensed and discharged for treatment and may contain any of the raw materials.

6.2 Waste Urea Formaldehyde

Wastes produced from the production of urea formaldehyde resins are similar to those of phenol formaldehyde and are treated in the same systems. Dusts from reactor loading and fumes produced are either incinerated or scrubbed with sodium sulfite solution. Waste solids are included with those volumes given for phenol formaldehyde resins (see 5.3).

6.3 Polyvinyl Acetate Emulsions

Polyvinyl acetate and copolymer resins form the basis for a wide variety of surface coatings. Formulations with varying degrees of chemical resistance and fire retardancy can be blended using various co-monomers. The basic reaction involves the sharing of the vinyl paired electrons to form a polymer chain as shown below (20).

6.4 Polymerization Process

Polyvinyl acetate can be polymerized by bulk solutions, suspension, and emulsion processes. In industry the emulsion process is the most common, and formulations contain an average of 55% polyvinyl acetate solids. The emulsion is formed by blending vinyl acetate monomer, water, surfactant, initiator, buffer and possibly a molecular weight regulator (i.e. a free radical absorber). The degree of emulsification and therefore micelle (small globule of polymer) size is dictated by the quantity of surfactant added. Emulsification is directly proportional to the quantity of surfactant.

Co-monomers used may include:

: ethylene

: dibutyl maleate

: bis (2-ethylhexyl) maleate

: ethyl, butyl or 2-ethylhexyl acrylates

: vinyl laureate (27)

Plasticisers other than co-monomers may be;

: dibutyl phthalate*

: tricresyl phosphate** (27)

Most common surfactants are;

: anionic sulfates and sulfonates (27)

Protective colloids are;

: Poly (vinyl alcohol)

: hydroxyethyl cellulose (27)

Initiators or catalysts are;

: hydrogen peroxide

: peroxysulfates

: benzoyl peroxide (27)

Reaction buffers include:

: phosphate

: acetate

: bicarbonate (27)

Chain transfer agents use such things as;

: aldehydes

: thiols

: carbon tetrachloride (27)

*Environmental Contaminants Act Priority Chemical

**Environmental Contaminants Act Candidate Chemical

Most reactions are carried out at atmospheric pressure in glass lined or stainless steel lined kettles.

6.5 Dust Control at the Resin Reactors

Dry reactants added to the resin processes are measured and poured under dust collection hoods. Dusts generated during the pouring of raw materials into the reactors are collected by the vacuum and incinerated before discharge to the atmosphere. The natural gas fired incinerator operates at 760°C (1400°F). The reactors are housed in a multilevel structure.

6.6 Priority and Candidate Chemicals

The two chemicals of concern in this process are di-n-butyl phthalate (DBP) and tricresyl phosphate (3). DBP is a water white oily liquid which is misible with most organic solvents, resins, oils and hydrocarbons. It is easily solubilized and dispersed and has high flexibility and low volatility when incorporated into the resin film. It is added to the resin blend during mixing and residual amounts would be lost in

reactor washings, tank washings, and during transfer and washing of transport tankers. The washings are collected in a sewer system and treated biologically prior to discharge to sanitary sewer. The percent reduction and amount discharged to sewer has not been determined.

It is not known if Tricresyl phosphate is used by resin manufacturers in B.C. It is a colourless, odourless liquid of low volatility that is miscible with linseed oils, castor oils, hydrocarbons and most solvents. Its use and path to the environment would be similar to DBP.

7.0 EXTRUDERS OF POLYVINYL CHLORIDE, ACRYLONITRILE BUTYL STYRENE, POLYETHYLENE/POLYBUTYLENE PIPES AND SIDING

Household siding, window frames, interior trim, conduit for telephone cables, plumbing, sewer and drainage pipes may be made from extruded polyvinyl chloride (PVC), acrylonitrile-butyl-styrene (ABS), Polybutylene (PB) or polyethylene resins. Additives are used in the manufacturing process, and such chemicals as organotin stabilizers and chlorinated paraffin lubricants are included in the Environmental Contaminants Act (ECA) list of priority chemicals. An examination of the pipe and vinyl siding extrusion industry was made to determine quantities and use patterns which would indicate potential routes to, and affects on the environment by these chemicals.

The annual consumption of chemicals in the plastic pipe and vinyl extrusion industry is based on replies to a questionnaire (see Appendix 1) and estimates based on typical formulations for plastic pipe and vinyl siding (4).

TABLE 7.1 ESTIMATED ANNUAL CONSUMPTION OF RAW MATERIALS IN THE PLASTIC PIPE AND VINYL SIDING INDUSTRY OF BRITISH COLUMBIA

CHEMICAL	CONSUMPTION (kg/y)
Polyvinyl chloride (PVC)	17 960 000
Acrylonitrile-Butyl-Styrene (ABS)	1 890 000
Polyethylene/Polybutylene	2 190 000
Organotin Stabilizers	115 900
Chlorinated Paraffin Wax	1 940 000
Pigments excluding TiO ₂ (5)	97 000
Titanium Dioxide	194 000
Carbon Black	5 600
Calcium Carbonate	582 000
Calcium Stearate	97 000
Oxidized Polyethylene	100 300

7.1 The Extrusion Process

Plastic piping and siding is extruded in a continuous process. usually 24 hours per day, five to seven days per week. Plastic material formulation depends on the end use of the final product and will contain the base resin of PVC, ABS, PB or PE and may contain the following additives (1).

Additive

- fire retardants
- colorants
- antimicrobials
- heat stabilizers
- blowing agents
- plasticizers
- ultraviolet stablizers
- impact modifiers/processing acids acrylics, elastomers
- lubricants
- antioxidants
- Antistatics
- *Priority Chemicals
- **Candidate Chemicals

Chemicals

- chlorinated paraffin waxes*
- metal oxides, organic pigments, dyes
- heavy metals, arsines, (1)
- organotins*, cadmiums, metal oxides
- azodicarbonamides, azo compounds
- phthalate acid esters*
- hindered amines (phenylformamidenes)
- heavy metal stearates
- organophosphites**, high molecular weight phenols

There are no producers of raw PVC, ABS, PB or PE resins in B.C. All resin is imported, usually from eastern provinces such as Alberta or Ontario. The resins may contain some or all of the additives listed above. Most additives are blended with the base resin just prior to extrusion

since the resins are taylored to the requirements of the end user and formulations are proprietory. Plastic pipe extrusion will be used as the process example as other products are made with minor variations to the extruder and resin formulation.

7.2 Transport, Blending and Extrusion of Resins

Pelletised PVC, ABS, PB and PE resins are shipped by rail car or tanker truck and unloaded via pneumatic piping to the appropriate resin storage silo. Storage silo's may be equipped with bleeder vents to allow displaced air to escape during filling. Dust control equipment such as bag filters or cyclone systems may be attached to bleeder vents to remove plastic fines which are collected and disposed to landfill.

The resin is transferred from the silos to a mixing system which consists of a weigh hopper (usually located on an interior mezzanine level), drum mixer and dust control system. Additives such as organotin stabilizers, chlorinated paraffin lubricants, fire retardants, pigments, calcium carbonate and calcium stearate fillers, acrylic impact modifiers are weighed and added to the blender drum before mixing. White is the natural color of PVC and PE and other colors required for pipe are green, (which are usually metal oxides) and grey and black (which are carbon based pigments). Several high visibility colors such as yellows and oranges have recently been specified for piping used in special construction applications for conduit, chemical and sewer piping. A variety of colors may be used for house siding and the pigments may be inorganic, organic or dyes. The rigid plastic applications use inorganic heavy metal colors such as titanium dioxide, iron oxide, manganese, antimony, lead, chrome, iron, zinc, cadmium and molybdate (1). Organic pigments include carbon black, phthalate blues, greens, reds, yellows or combinations (1). Polyvinyl chloride is never extruded as a pure resin and is sensitive to heat. Typical formulations for pipes and rigid products are given below.

TABLE 7.2 TYPICAL FORMULATIONS FOR RIGID PVC PIPE, BOTTLES AND SIDING

PVC PIPE (4)		BOTTLES, PIPE, SIDING (3)
PVC (K-65)*	100 parts	100 parts
TiO ₂	1.0 parts	7 0 20 "
CaCO3	3.0 "	0-30 "
Paraffin wax (165°F)	1.0 "	3.0 "
Calcium Stearate	0.5 "	n n
Oxidised Polyethylene	0.15 "	0-3.0 "
Organotin	0.4 "	2.0 "
Impact modifiers		0-15 "

*K = type of resin

**65 = molecular weight

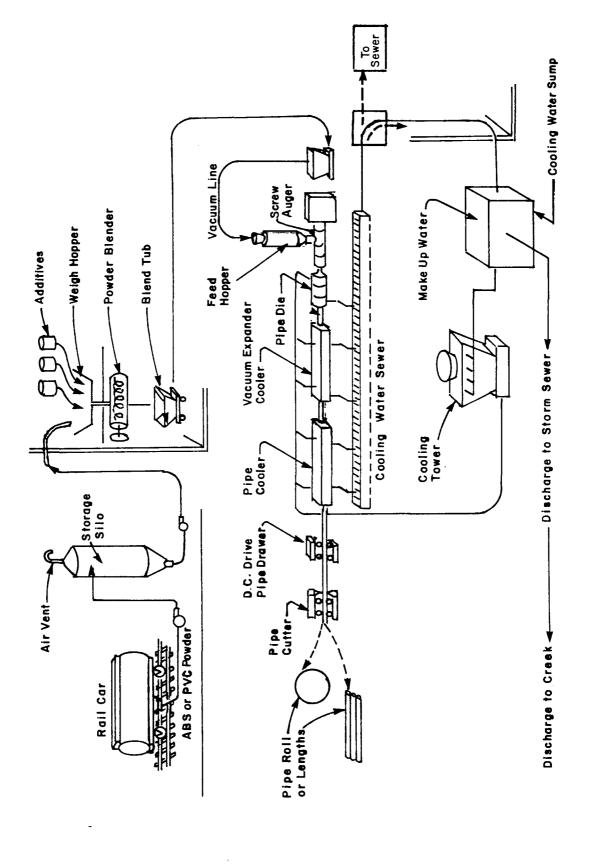
Flexible PVC compounds may use more than 25% plasticisers, calcium carbonate filler is added to reduce costs, and chlorinated paraffins are added as plasticisers and flame retardants (1). Piping, vinyl siding and construction products made from PVC require a rigid structure and therefore a lower percentage plasticiser (see Table 7.2). Highly plasticised products include flexible footwear and plastics used for clothing, shower curtains etc. which are not produced in large quantities in B.C. Pure PVC resin is 60% chlorine and highly fire retardant however this ratio decreases slightly when additives are included in the blend. Heat stabilizers are based on metallic salts of inorganic and organic acids, phenols, phosphates and epoxies (1). Several kinds may be blended for a particular application. In plastic pipe production organotin compounds are used (usually a butyltin complex). The heat stabilizer affects plating out on the equipment, melt rheology and finished product qualities such as surface finish, solubility, toxicity, heat and electrical characteristics.

The additives are usually handled as dry powders manually weighed and added to the blending drum. Some organotins may be added as an oily liquid (4). Dust control during loading and/or unloading of the blender is commonly via a baghouse or cyclone system. After all the components are added the blender is closed and mixing may take several hours. Excess heat may be generated by shear force in the blender, which requires cooling water to avoid overheating. The water is contained in a jacketed system

and is not subject to contamination. The homogenous blend is poured into a movable tub and stored to allow for cooling. When the blend is required for production the tub is moved to the extrusion line and connected to a pneumatic hose. The hose transfers the powder to a vertical feed hopper which may have a hot air intake for humidity control of the feed. (ABS is hygroscopic and may require several hours of drying at 85°C before extrusion (6)) (see Figure 7.1).

To produce hollow pipe the blend is fed into a heated screw auger which melts and compresses the resin. The fluid resin proceeds through a series of temperature controlled dies which shape the resin in an undersized bar. Two dies cut the bar into four strips which pass through a four bladed turbine shaped die. The four strips are flattened and fused back together into a tubular shape. The pipe is then drawn through a sizing die into a vacuum expander and cooling chamber. The vacuum forces the outside of the pipe against the die to ensure a standard size for fittings. The pipe is then rapidly cooled by continuous water spray or bath. A second cooling chamber at atmospheric pressure uses water spray or bath to bring the pipe temperature to below the glass transition temperature (tg). Uniform pipe dimensions are assured by continuous drawing of the entire line through a Direct Current (D.C.) drive system. D.C. current is required since Alternating Current (A.C.) would cause slight fluctuations in motor drive speed which affects the pipe wall thickness. The pipe is then marked, cut into lengths or rolls and sent to storage. Products such as vinyl siding, wall and corner moldings use different dyes to form the final product however the process is similar in design.

During startup, color changes, size changes or power fluctuations, off specification product is produced which in most cases can be recycled. Recycling consists of sorting clean material for regrinding and pulverising to the size required by the process equipment. The need for dimensional consistency of the finished product requires a uniform feed size for the extruder, therefore not all waste resin can be reused. If the pulverised resin is too fine it can cause surging in the feed system which



PLASTIC PIPE FLOW CHART OF A TYPICAL PVC, ABS, PE AND PB EXTRUSION PROCESS

FIGURE

affects uniformity. The unusable fines are separated in a cyclone system and are disposed to landfill.

7.3 Generation and Control of Dusts

Pure PVC, ABS, PE and PB resins have not been identified as being hazardous as solid piping is used for potable water supplies. PVC can be disposed of by landfill, incineration or recycle and pollution of water is minimal in landfill disposal (3). Certain additives such as organotin stabilizers and chlorinated paraffin lubricants/fire retardants have been identified as stable, persistant chemicals about which there is little environmental data regarding the concentrations of these chemicals in the environment or their toxicity (2). Several possible routes to the environment by PVC powder and additives have been identified at industrial operations in British Columbia. A sampling program (currently underway) will attempt to confirm the suspected routes and provide concentration data of priority chemicals.

Rail tank car or truck tanker unloading is achieved via pneumatic pipeline and there is the possibility of spillage when piping is connected or disconnected. The spillage of resin was observed at every facility and ranged from several kilograms to more than 1.0 tonne. The raw resin is usually pure PVC, ABS, PB, or PE and the concern is aesthetic pollution by resin dusts which are blown or washed from the plant yard down storm drains and eventually discharged to receiving waters. Application of conscientous plant hygiene procedures would eliminate this loss, improve aesthetics and reduce economic costs from the loss of raw materials.

In all cases the blending mezzanine areas were found to be major sources of fugitive dust. The resin and additives are measured by weight and added to the blender. Manual dumping of the powdered additives produces dust which is usually contained by a dust collection hood and filtered in a baghouse.

The manual handling of powders results in spillage to the floor which is spread by the movement of workers and machinery on the plant

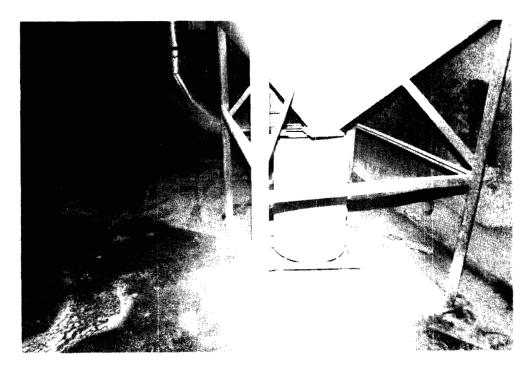


PLATE 7.1: SPILLED PVC DUST AT A BAGHOUSE

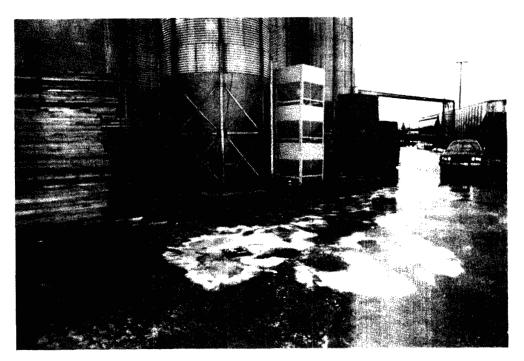


PLATE 7.2: SPILLED PVC RESIN WASHING DOWN A STORM SEWER

floor. These dusts are washed into floor sewers during cleanup operations. It is suspected that some of the priority chemicals can be discharged by suspension in overflow water to the storm and/or receiving water system. The amount of this loss is not known but is believed to be small. The dusts collected at baghouses are usually contained until the filtering system is cleaned. Improper handling results in resuspension of dust in the air which settles on the paved exterior work areas and is washed by the rain to the storm sewers or receiving waters.

Regrinding and/or pulverizing of off-specification resin for recycle is a major source of dust production and control is subject to the same problem as the mixing areas. The difference in the type of waste is the particle size and composition. A significant percentage (depending on the grinding method) of the regrind may be a fine powder which cannot be used in the forming process due to surging in the extruder. This regrind is disposed to landfill. The leachability and dust loss of priority chemicals from this powder has not been determined. The additives in the powder are expected to be fixed in the plastic matrix and not readily available to the environment.

Simple control measures such as cloth or plastic shrouds between the cleanout of the baghouse or cyclone dust resevoir and storage barrel would contain dusts created during cleaning (see Figure 7.2). In most instances the dust is allowed to fall into the waste barrels creating a cloud which settles on the surrounding area (see Plates 7.1 and 7.2). Routine enforcement of good work practices by management could prevent such losses and extrusion plants would be environmentally innocuous.

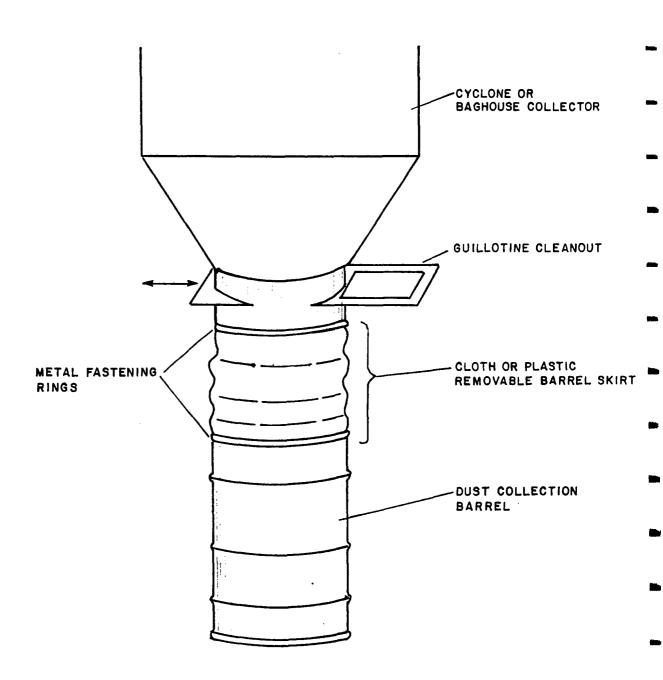


FIGURE 7.2 DUST CONTROL AT BAGHOUSE CLEANOUTS
USING A CLOTH OR PLASTIC BARREL SKIRT

8.0 POLYSTYRENE EXPANDER/MOLDERS

Custom designed insulation products, cups and eating utensils, egg cartons, packaging containers and fillers are some of the products produced from expanded polystyrene. Expanded polystyrene is easily molded and has a high insulating value making it suitable for the uses mentioned above. The two basic raw materials used are compressed polystyrene beads impregnated with pentane gas and steam. Pigments may be added but the majority of products are formed from the natural white polymer. Polystyrene is generally not considered hazardous although Sax (7) lists it as "an experimental carcinogen via an implantation route". Implantation is not a likely occurence under current handling and manufacturing conditions and therefore it is considered a relatively innocuous substance.

The estimated annual consumption of 1 650 000 kg polystyrene is based on replies to a questionnaire (see Appendix 1) sent to most of the companies involved in this industry.

8.1 Additives Used in Styrene Plastics

Polystyrene is used as a pure and co-polymer in a wide range of applications in laquer and binding agents to films, moldable plastics, electrical insulation, adhesives, transparent sheets and cases, machinable resins and improved chewing gum (8). It is subject to ultraviolet degradation, high flammability and is not recommended for exterior use. The expanded foam used in building applications is covered with other material or paint to protect against UV degradation. Upon ignition it burns with a thick black smoke and must be considered toxic (9). Halogenated alkyl compounds are used as fire retardants and are on the ECA priority chemicals list. Fire retardants added to Polystyrene used in the insulation/ construction materials are added as liquids, dry powders or incorporated directly in the resin.

Plasticisers are used in applications such as films, window and casing materials and include high boiling alkyd esters, halogenated aryl

compounds and phthalate esters which are also included on the ECA priority list. Flow agents such as powdered zinc stearate are used to prevent clogging in suction feed lines. (11) Other additives are listed in Table 8.1.

TABLE 8.1 ADDITIVES USED IN STYRENE PLASTICS

ADDITIVE	COMPOUNDS	SOURCE
Plasticisers	Lauric acid esters Highboiling alkyd esters* Semidrying, nondrying oils Soybean oil Alkyd halophthalates Halogenated aryl compounds* Phthalate esters* Adipate esters	(8) (8) (8) (8) (8) (8) (9)
Mold Release Agents	Stearic Acid Metal/organic stearates (zinc stearate)	(9) (9,11)
Antioxidants	Alkylated phenols organic phosphate thioesters**	(9) (9)
Antistatic Agents	Quarternary ammonium compounds	(9)
Ultraviolet Stabilizers	Benzotriazoles Benzophenones	(9) (9)
Fire Retardants	Hydrated aluminum oxide Antimony oxide Alkyd and aryl phosphates** Hexabromocyclododecane pentabromomonochlorocyclohexane	(9) (9) (9) (9) (9)

^{*}Environmental Contaminants Act priority chemical **Environmental Contaminants Act candidate chemical

8.2 Polystyrene Expanded Bead Process

The difference in the production process for insulation products and moulded products made from polystyrene is in the forming of the final product.

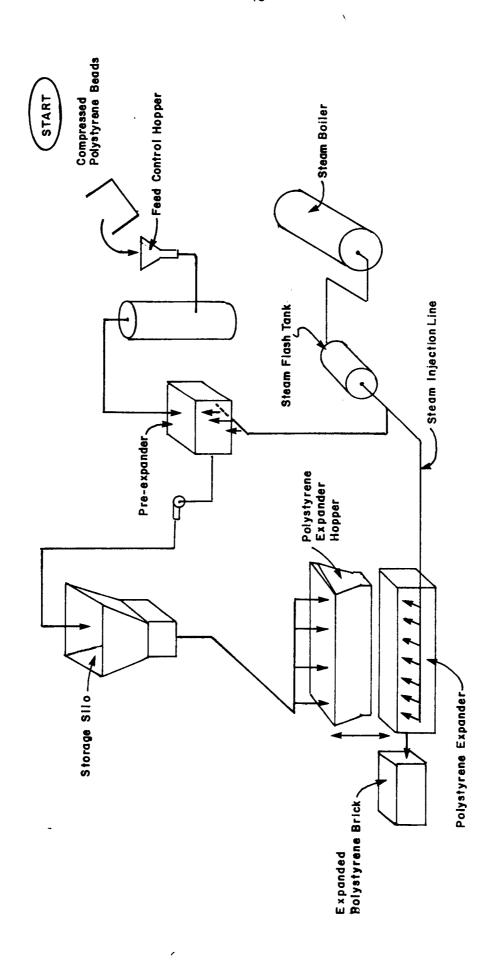
Insulation products are generally cut from a large block using a hot wire method which produces some styrene fumes while smaller articles are moulded into shape in an injection process. Both use steam to expand the compressed, pentane impregnated polystyrene beads. The product is formed in a two stage process. The compressed prepolymerised beads are shipped in 0.6 m³ plastic lined cardboard containers. They are fed by vacuum suction into a hopper and a pre-expander. In the pre-expander, heat from steam injection softens the polymer and allows the entrained pentane gas to expand the bead five to ten times the original size. The beads are then transferred via a vacuum line to canvas storage silos for aging. Aging allows cooling and bleeding of excess pentane gas. Final expansion must be done before a critical amount of pentane is lost. Second stage expansion involves pneumatic transfer of the bead to a feed hopper (see Figure 8.1). A hopper feeds the block molding machine for an expansion cycle. After the mold is filled it is sealed and steam is injected for a preset cycle. The secondary expansion increases the bead 25 to 50 times the original size depending on the block density required. The expanding beads push against each other and fuse together in the shape of the mold. The block is ejected from the machine on completion of the cycle and is ready for cutting.

8.3 Hot Wire Cutting of Expanded Polystyrene

Expanded polystyrene can easily be cut by hot electrical wires into blocks, sheets and complex shapes (See Figure 8.2). Depending on the design either the block or the grid moves to cut the piece.

8.4 Wastes Produced in the Polystyrene Expansion Process

There are some wastes produced in each stage of the expansion process. Pentane gas released by the first and second expansion process is



FLOW CHART OF A POLYSTYRENE EXPANSION PROCESS FIGURE 8.1

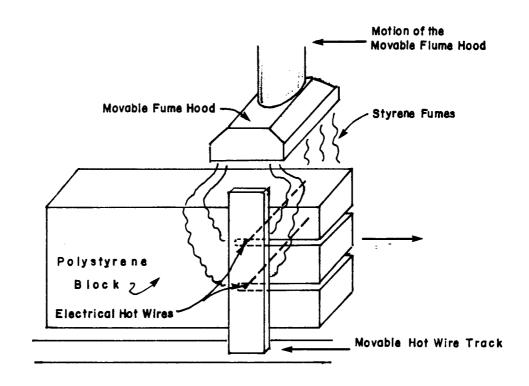


FIGURE 8-2 FORMATION OF STYRENE FUMES BY ELECTRICAL HOT WIRE CUTTING OF POLYSTYRENE BLOCKS INTO SLABS

vented to the plant air and then outside by the normal air exchange system. Pentane is extremely explosive however flammable concentrations would not be reached due to the low concentrations present in the raw material.

Handling the pre and post expanded beads results in spillage which is easily contained due to the clean dry nature of the product. It can easily be swept or vacuumed up and reused if clean, or disposed of if contaminated.

Polystyrene and incomplete combustion fumes are produced during the hot wire cutting of the polystyrene blocks. The vapours contain styrene which has a human detection limit of 5-10 ppm and a Threshhold Limit Value (TLV) of 100 ppm. (9) The fumes are collected by movable fume hoods which follow the wires along the block and are vented directly to the atmosphere. Solid polystyrene is a suspected carcinogen via an implanted route (1) but is not likely to pose a problem under normal usage.

Waste cuttings are reground and can be recycled as filler or packing material.

Cooling water and steam condensate is collected in a floor sump and discharged to sewer.

The concentrations of additives leached from the styrene beads during the expansion process has not been determined. Fire retardant resins used in construction applications are ECA priority chemicals and are used in two forms. A powdered or liquid retardant can be added to a resin and dispersed in a dry mixer. Retardants applied in this process may be leached from the resin during the steam expansion process. A second method incorporates a halogenated (usually chlorinated or brominated alkane) compound into the resin structure. This reduces contamination from dusting and fixes the retardant to the styrene molecule to reduce leaching during steam expansion.

The generation of solid sytrene waste is estimated at $19 \text{ m}^3/\text{d}^*$ or $142\ 500\ \text{kg/yr}$ which is disposed to landfill. Liquid waste is restricted to

^{*}d = operating days (approximately 250 days/year)

steam condensate and boiler blowdown, estimated at $10.8 \text{ m}^3/\text{d}$ which is discharged to sewer. Pentane gas released is estimated at 270 kg/d or $68 \ 000 \text{ kg/yr}$ (based on an average of 4.5% by weight in the resin) (9, 11).

Depending on the end use of the finished product 0.5% to 3.0% (by weight) fire retardants may be added to the polystyrene blend. Organochlorines or bromines are the most common ones used and are added as a powder or incorporated into the structure of the polystyrene. Molecular incorporation of the retardant into the resin is the most common form (12). Consumption would range from 7000 kg/yr to 42 000 kg/yr. The majority of products are produced in the lower range concentrations (12) and an estimate of 11 200 kg/yr is most likely. (Exact formulations are proprietory information.) Halogenated paraffins incorporated in solid waste would range from 700 kg/yr to 4280 kg/yr with the actual value estimated to be 1140 kg/yr. These wastes are sent to landfill. Under normal soil conditions certain grades of polystyrene degenerate within five years (11). It is not known how long construction grades of polystyrene remain stable in landfill conditions or the rate at which halogenated compounds are released from the degenerating polymer.

9.0 EXTRUDERS AND BLOW MOLDERS OF PLASTIC PARTS AND BOTTLES

Forty three firms were identified as being blow and/or injection molders of plastic parts and bottles. The size of the firms ranged from single to multiple machine operations with similar production techniques used at all the sites. The range of products produced by these firms is diverse, from component parts for manufacturing to varied liquid containers for use in the food, chemical and consumer industry. Table 9.1 identifies the major types of plastics used in the injection molding industry. These are the major classes and there are a broad range of variations in each class which can be altered by co-polymerization and addition of stabilizers, fillers, plasticisers, flow agents, pigments, antioxidants, fire retardants, blowing agents, antimicrobials, ultraviolet stabilizers, impact modifiers and antistatic agents.

TABLE 9.1 ESTIMATED CONSUMPTION OF PLASTIC RESINS USED IN THE INJECTION AND BLOW MOLDING INDUSTRY OF BRITISH COLUMBIA

COMPOUND	ESTIMATED CONSUMPTION* (kg/yr)
Acrylonitrile Butyl Styrene	294 000
Nylon 6 .	109 000
Nylon 66	N/D
Polyethylene (High density)	3 247 000
Polyethylene (Medium density)	104 000
Polyethylene (Low density)	1 580 000
Polyethylene terephthalate	402 000
Polystyrene	230 000
Polypropylene	1 025 000
Polyvinyl Chloride	827 000
Polycarbonate	76 000
Polyvinyl acetate	N/D
Polyurethane	38 000
Polychloroprene	200
Polymethyl methacrylate	2 000
Pigments	115 000
Plastic Waste	< 100 000

^{*}Consumption estimates based on 50% reply to questionnaire

9.1 Production Processes

All of the polymers identified in Table 9.1 are imported into B.C. There is no production of raw polymer and most additives used are also imported. Polyethylene (high, medium and low density) accounts for 46% of the polymer consumed and in most cases is used in the natural, white color. Polypropylene accounts for 25% of the polymer consumed and in both cases the pigments and additives used are premixed in a compatible carrier polymer.

Injection and blowmolding involves the reheating of thermoplastic polymers and extrusion into a preformed mold. The polymer retains the shape after it is cooled below its glass transition temperature and is ejected from the mold. Most pigments for plastics are rated as food grade. Any manufacturer wishing to use a new additive and have it approved by the Health Protection Branch must supply the data to justify its use. Pigments may be added as a dry powder or as a concentrate bonded in a resin carrier.

9.2 Blending of Plastic Concentrates

Precolored plastic concentrates are manufactured under strict quality control procedures. Cross contamination of blends is prevented by control of fugitive dust using bag and cyclone filters and water washes of the blending and pellet production equipment. Residual waste which is polyethylene based can be recycled by blending with a dark pigment for use in the production of polyethylene garbage bags.

Most injection molding is for custom parts used in other manufacturing and assembly processes. These parts often require custom colors which are not available as precolored plastics. The colors are custom formulated by pigment manfacturers and shipped to the molder in polyethylene lined cardboard containers. Pigments are added (usually at 1% to 2% by weight) to the polymer and blended before addition to the feed hopper. Dusts associated with blending are controlled by vacuum filtration systems.

9.3 The Injection Molding Process

In small production operations consisting of one or two machines the polymer feed pellets are manually loaded into the injection feed hopper (see Figure 9.1). In some cases the pigment is added as a dry powder to a mixer or feed hopper. This manual handling procedure increases the production of fugitive dust. The quantity of pigment handled is small and in several cases the dusts were discharged via a fume hood directly to the ambient air. Most facilities avoided this problem by premixing their own pigment or using a pigment concentrate impregnated in a dustless carrier resin. Larger production systems use a vacuum transfer line from the bulk storage to fill the feed hopper. The bulk plastic resin contains fines produced during manufacture of the plastic pellets and from grinding during movement through the transfer apparatus. The fines are removed by cyclone filters to maintain feed uniformity and can be recycled or are disposed to landfill. The percentage of fines produced is very low (no estimate is available). Forced air drying prior to, or during filling of the injector feed hopper is done to control humidity. The hopper feeds the pellets at a controlled rate to a screw auger. A single or double screw may be used. Heat generated by friction in the auger may be sufficient to produce a plastic melt, and can be supplimented by electrical heating coils. Heat control is critical to control rheological properties and prevent oxidation or polymer decomposition and fume generation. In all the injection/blow molding facilities inspected, the fume generation was negligible. Some production lines used fume hoods over the machines to aid in excess heat removal for worker comfort rather than fume control. Fumes which are produced are vented directly to the atmosphere. In some large facilities ceiling mounted electrostatic precipitators ("smoke eaters") are used to control fumes where polyvinyl chloride products are produced (see Plate 9.1). The augers also assist in producing a homogenous blend from a mix of pigmented and non pigmented polymer. The melt is injected into a hydraulically sealed mold which is usually a two piece unit. After several seconds of cooling and solidification the plastic piece is ejected to a storage container.

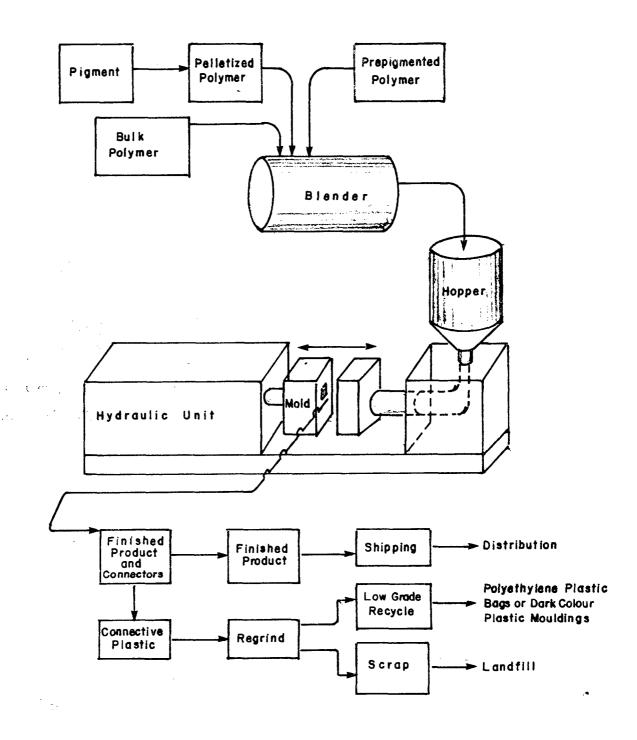
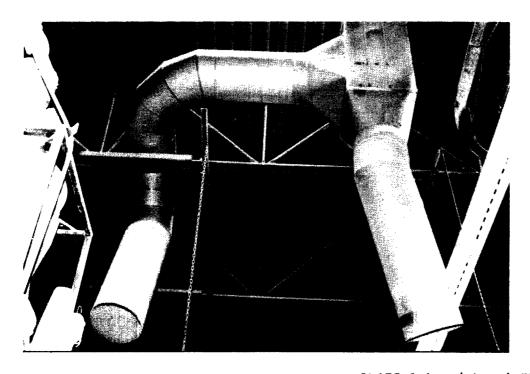


FIGURE 9.1 TYPICAL FLOW CHART FOR AN INJECTION MOULDING PROCESS



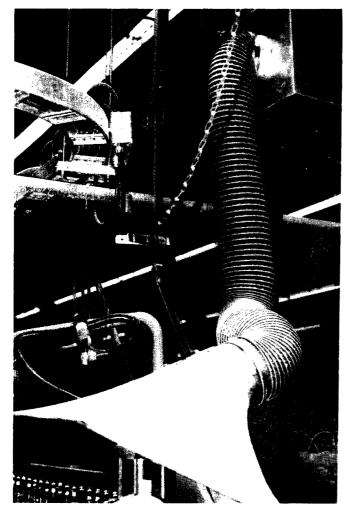


PLATE 9.1: (above) EXHAUST
PLENEM FOR PVC
FUMES

PLATE 9.2: (left)
ELECTROSTATIC

PRECIPITATOR
FOR PVC FUMES

The mold is designed so that the cooling water does not directly contact the plastic and is discharged to sewer as clean water. Some products are molded several units at once with connective runners (tabs) and injection port sprues still attached (see Figure 9.2). Flow interruptions may cause some parts to be defective and since injection molded plastics are thermoplastic they can be recycled. The pieces requiring assembly have the runners removed and combined with rejects of the same color and type of plastic. The waste is then reground into a flake or powder form and recycled. Dusts associated with the regrinding are controlled by bag or cyclone filters.

Plastics used for blow molding are handled the same as for injection molding except at the final extrusion and forming. Polyethylene, polyethylene terephthalate (PET) and polypropylene are the major raw materials for blow molding. Recent changes in additives are expected to increase the use of PVC resins in bottle and container manufacture (1). The heated plastic is extruded as a tube with air blown through the center. The mold is clamped around the tube, pinching the bottom and remaining open at the air injection port. The interior air pressure forces the tube against the wall of the mold and the plastic assumes its shape. A cutting tool pinches the formed bottle from the tube and the mold releases the finished piece. Excess trim is removed, and ground to a granular powder for recycle.

9.4 Disposal of Waste Plastic

Plastic resin is expensive and waste control was practised by all companies visited. Generally, wastes are less than 0.5% of raw materials, averaging 0.25% or less. Waste plastic is produced by contamination of parts with machine oils and dirt. Grindings which cannot be reused are powdered fines which would cause surging in the extruder. (Surging is mainly a problem where continuous extrusion occurs such as in piping.) All wastes are disposed to sanitary landfill. To reduce downtime during weekend shutdowns or for equipment servicing, a polymer blend using increased

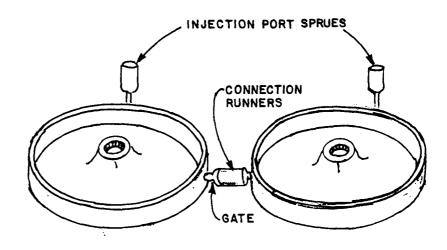


FIGURE 9.2 RECYCLABLE WASTE PLASTIC SPRUES AND RUNNERS ON AN INJECTION MOULDED PLASTIC PART

heat stabilizer may be fed into the extruder. This blend may contain organotin heat stabilizer compounds which will not decompose under the temperatures required for startup. This is used for continuous production runs, usually for polyvinyl chloride products. The volume of material is usually several kilograms which cannot be recycled and is disposed to landfill.

9.5 Disposal of Waste Fumes and Water

Plastic fumes are generated only when the materials become overheated. This is a rare occurrance with small volumes involved. These fumes are simply vented to the atmosphere and are not in sufficient quantity to be cause for concern. Cooling water is discharged to sewer and sanitary wastes are discharged to the sanitary system.

10.0 PLASTIC FILM EXTRUDERS

The survey of plastic production facilities identifed seven firms in the Lower Mainland/Vancouver Island region producing flexible film for sheeting, plastic bags, wrapping and assorted packaging. The materials used included linear low density, low density and high density polyethylene, polypropylene, and cellophane. Other additives used include pigments, slip and antiblock agents, printing inks and volatile solvents for labelling. The majority of the film is produced for the food packaging industry and is high quality food grade polymer. High polymer costs and plant efficiency produces low wasteage with an estimated 22,100 kg/yr of polymer disposed to various landfills. (Estimated based on replies to a questionnaire, see Appendix 1). Air emissions are produced from the volatilization of printing solvents such as short chain alcohols, napthas and spirits, and polymer fumes formed during extrusion, cutting or heat sealing on bag production lines. Table 10.1 outlining the estimated consumption of raw materials.

TABLE 10.1 ESTIMATED AMOUNTS OF RAW MATERIALS USED IN THE FLEXIBLE FILM INDUSTRY OF BRITISH COLUMBIA

MATERIAL	AMOUNT
High Density Polyethylene	2 478 000 kg/y
Medium Density Polyethylene	103 000 kg/y
Linear Low Density Polyethylene	10 395 000 kg/y
Low Density Polyethylene	150 000 kg/y
Polypropylene	18 120 kg/y
Cellophane	28 000 kg/y
Pigments	847 000 kg/y
Slip Agents	87 800 kg/y
Antiblock Agents	87 800 kg/y
Ink Solvents	603 713 1/y

10.1 Production Process

A typical plastic film extrusion plant consists of seven major areas (see Figure 10.1):

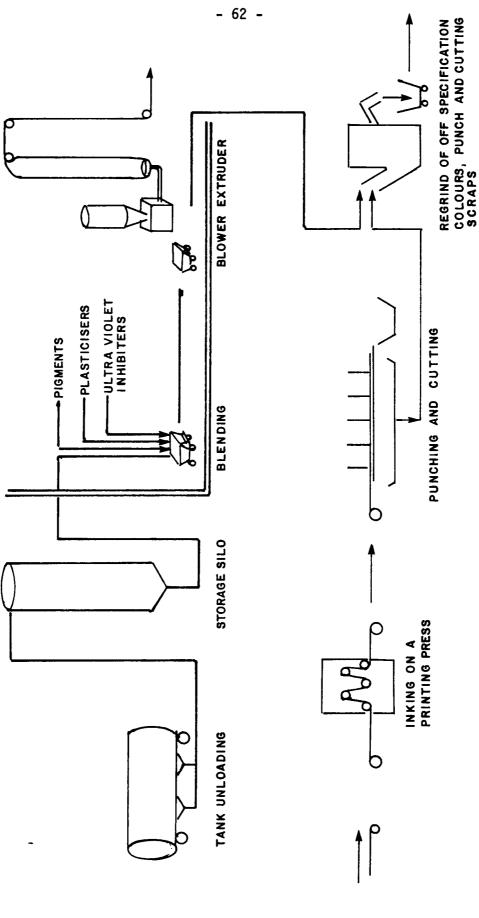
- 1) Outdoor resin storage silos
- 2) Extrusion room
- 3) Printing room
- 4) Cutting, punching and packaging lines
- 5) Waste regrind/recycle area
- 6) Warehouse
- 7) Exterior loading and waste storage area

10.2 Resin Handling and Storage

The prepolymerized resin is handled in a dry powder or pellet form and is transferred directly from tanker trucks or railcars into storage silo's. If clear nonpigmented film is made then the resin can be transferred directly from the silo to the extruder feed hopper. Specialty blends incorporating color require premixing with pigment or pigment impregnated carrier resin. Other additives such as slip and antiblock agents may be added to promote even flow of raw materials and prevent clinging of the plastic during processing.

10.3 Extruders

The polyethylene extruders use clear or colored resin fed from hoppers to the heater blower units (see Figure 10.2). The polyethylene is dustless and totally contained in the system. A pressure feed system forces the resin into a series of heating rings which produce a melt that is extruded into a blowing air stream. Some polyethylene fumes are released until the melt cools in a thin film. The fumes are vented to the atmosphere and the blown film is pulled in the form of a tube to the building ceiling to allow cooling before it is flattened and rolled onto a spindle. Extruders of varying diameters are used to produce different diameter tubes.



PLASTIC FILM EXTRUSION PROCESS FIGURE 10.1 FLOW CHART OF A

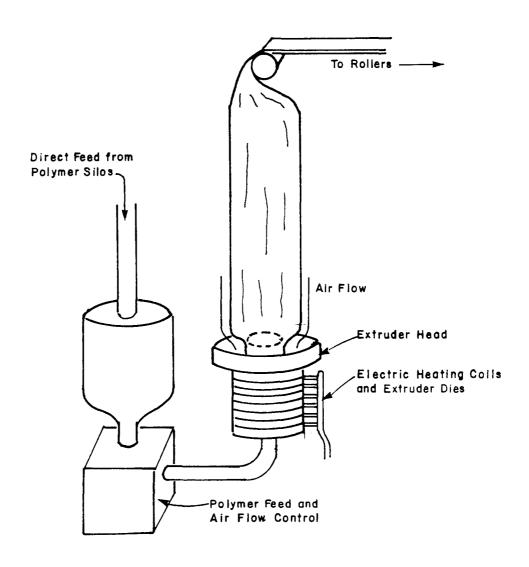


FIGURE 10.2 POLYETHYLENE TUBE FILM EXTRUDER

10.4 Inking and Printing of the Bags

Metal plates for the printing machines are manufactured in etching rooms. Acid baths are used to clean and etch the plates before use on the machines. Print machines apply the ink, and solvent vapors are vented to the atmosphere.

10.5 Cutting and Punching of Bags

Plastic bags are cut using a heat sealing knife edge which cuts the bags and seals one end. Some of the bags require the punching of holes for handles or air circulation. The punchouts are sent for regrind and recycle into dark colored garbage bags. The heat sealing produces polyethylene vapours which are allowed to rise and usually are not directly vented but escape to the atmosphere through building air circulations.

Cuttings from the extruder, bag lines and off specification film are sent to a regrind area for recycle. The reground material (see Plate 10.1) is pigmented with dark green or black pigments and used to make garbage bags or dark plastic film. If the scrap cannot be reused it is sold as scrap to recyclers at 20-30 ¢/kg. Only extremely dirty scrap is sent to landfill.

10.6 Disposal of Waste Products

The estimated wastage of 22 100 kg/y of polymer is expected to be a high value as recycle practices by the companies are extremely good. Components in the solid waste would include the following estimates.

TABLE 10.2 ESTIMATED AMOUNTS OF MATERIALS WASTED IN THE FLEXIBLE FILM INDUSTRY OF BRITISH COLUMBIA

- polymer - slip agents - antiblock agents - ink solids - pigments including carrier resin	22 100 kg/yr 3 110 kg/yr 110 kg/yr 466 kg/yr 1 105 kg/yr
--	--



PLATE 10.1: REGROUND POLYETHYLENE FOR RECYCLE TO GARBAGE BAG PRODUCTION

10.7 Consumption of Pigment

The estimated consumption of 847 000 kg of pigments is expected to be a high value and includes 80% to 85% carrier resin which is usually polyethylene. The active amount of pigmenting agent is $127\ 050\ kg/y$ to $169\ 400\ kg/y$. These pigments are rated as food grade and are color fast (see Chapter 14.0 re: pigmenting agents).

11.0 POLYESTER RESIN FABRICATORS

Fabricators of polyester resin products fit into two categories:

- 1) Filler based resin products
- 2) Fiber reinforced articles (glass, graphite, etc.)

Forty-one firms handling these materials were identified in British Columbia. The products produced include souveniers, games, aircraft warning devices, marine floats, truck body parts, truck canopies, bathroom fixtures, industrial tubs, tanks, and corrosion resistant piping, boats and display shelving, etc. The major consumers of resin were bathroom fixtures (tubs and hot tubs), corrosion resistant equipment for the pulp, paper and chemical industry and truck bodies.

11.1 Production of Filler Reinforced Polyester Resin Products

Filler reinforced products include articles that are designed to look like marble, or stone products. Some filler based products may use a solid colored gel coat surface.

Fabrication of a polyester unit begins in the gel coating area. The article (in this case a bath tub) is formed from a prepared mold which is first treated with a mold release agent such as a paraffinic wax or silicone spray. A polyester "gel coat" paint is spray applied to the mold if a solid color is required. Spraying is done in a negative pressure spray booth which filters the blow-by and discharges air to the atmosphere. When the gel coat is dry, a paste of polyester resin, curing catalyst and powdered calcium carbonate filler is mixed. Aluminum trihydrate may also be added as a filler. The paste is applied to the mold manually until a thickness of 1.75 to 3 cm is obtained. If a marble effect is to be achieved then a gel coat paint is not necessary and a first layer of resin streaked with pigment is applied to the prewaxed mold. The casting is allowed to cure for several hours, after which it is removed from the mold

TABLE 11.1 MATERIALS CONSUMED IN THE POLYESTER RESIN FABRICATION INDUSTRY OF BRITISH COLUMBIA

MATERIALS	ESTIMATED	CONSUMPTION*	
Polyester Resin (clear)	2 130	000 1/y	
Gel coat Resins (Pigmented resin)	176	000 1/y	
Silica based filler		230 kg/y	
Calcium Carbonate based filler	245	000 kg/y	
Hydrated Aluminum based filler	16	200 kg/y	
Titanium dioxide pigment	5	200 kg/y	
Iron oxide pigments		100 kg/y	
Miscellaneous pigments	1	225 kg/y	
Antimony oxide fire retardants		40 kg/y	
Acetone	114	000 1/y	
Styrene monomer	59	500 1/y	
Acrylic sheet	700	971 kg/y	
Polyurethane (expanded form)	50	400 kg/y	
Polyethylene	91	000 kg/y	
Methyl-ethyl ketone peroxide	17	250 1/y	
Dimethyl analine		820 kg/y	
Cobalt napthenate	3	260 kg/y	
Methylene chloride	17	860 1/y	
Solid Waste (including non polyester materials)	14	$000 \text{ m}^3/\text{y}$	

and prepared for fittings and attachments. This may involve cutting and grinding which is done in a booth with a filtered air recirculation system. A very fine polyester dust is produced and filtered from the air. The polyester used for domestic applications is based on an orthophthalic resin that is rated as a general purpose resin that provides only minimum corrosion resistance at moderate temperatures (21). (In other phthalic acid based resins the carboxylic acid group is only separated by one carbon).

11.2 Gel Coat Spray Area

Gel coat spray application is done in a spray booth which filters the exhaust air and discharges it to the atmosphere. The exhaust air is likely to be high in styrene monomers which have volatilized from the aspirated resin (see Plate 11.1).

11.3 Resin Mixing Area

Resin blending is done on a batch basis by adding measured amounts of raw materials to an open mixing tub. Styrene monomer fumes are released from the liquid styrene (used as a thinning agent in the polyester resin) which is poured into the tub. These fumes are vented directly to the atmosphere by vents and/or fans. Powdered calcium carbonate, silica or aluminum trihydrate is a major source of dust due to manual handling during the weighing and blending process. Handling practices result in spillage which can contaminate the workers clothes and escape the building by reintroduction into the air and traffic through the work area. The filler compounds are relatively innocuous and do not present a major environmental hazard. They are usually contained on plant property and none of the sites visited showed any signs of contamination of storm water runoff.

11.4 Molding Area

The polyester paste is applied by hand to the mold and allowed to cure. Waste produced in this area is spilled or excess resin, and styrene fumes evaporating from the curing paste. The waste produced is limited to several kilograms of unused resin per shift and is disposed with general refuse to landfill. After the resin is used the material is extremely hard and durable and not subject to leaching. The vulnerability to ultraviolet degradation has not been determined however as the material is sent to landfill it is expected to be covered and thus not subject to this form of decay. The amount of pigmenting agent is less than 0.01% and is fixed in the polymer.

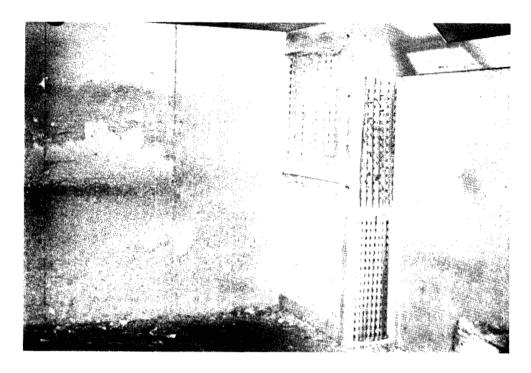


PLATE 11.1: GEL COAT SPRAY BOOTH WITH AIR CLEANER FILTERS

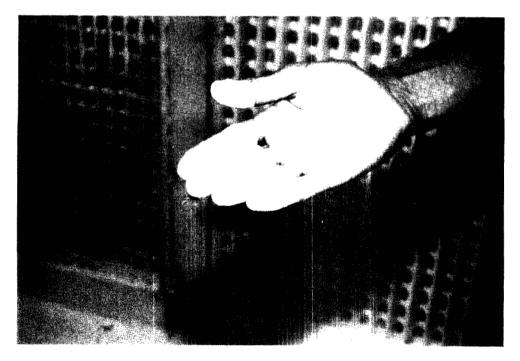


PLATE 7.2: DUST GENERATED AND COLLECTED IN A GEL COAT GRINDING ROOM

11.5 Grinding Booths

The cured product is sent to a finishing and grinding booth where edges are smoothed for appearance or attachment of fittings. Grinding produces a fine flour like dust which is filtered from the air by an air purity system (Plate 11.2). The end wall of the grinding room is a honeycomb grid filter system that traps the dust and recirculates the air to the front of the booth for reuse. Periodic cleaning of the dust traps and sweeping the floor is required to maintain filter room efficiency. The dusts are disposed to landfill.

11.6 Acetone Use and Storage

Mixing and material handling equipment is washed with acetone solvent which softens or dissolves the resin, often producing a sludge. The sludge is disposed to an outdoor area to allow the volatile acetone to escape and the sludge to solidify. Depending on the volume produced (which is usually only a few kilograms per day) the solids are disposed periodically to landfill.

11.7 Spill and Fire Hazards

Spills of several liters or kilograms of resins and dusts occur regularly and are easily contained and cleaned up. The styrene monomer in the polyester resin is highly flammible, kept from open flames and usually stored outdoors in a metal shed. Ventilation of the buildings prevents concentrations from reaching explosive limits.

Handling large amounts of powdered filler creates frequent spills of dust which contaminate the work area floor. The majority of this contamination is restricted to the paste blending area. Other than this dust formation, there is no great problem in dust control and most companies have installed filter systems in the grinding areas. No water is used in the plant area, there are no floor drains, and domestic consumption or leak testing are the only uses.

11.8 Fiber Reinforced Polyester Resin Products

The four forms of glass filament used for fiber reinforced polyester products are mat, woven, strand and chopped strand filaments. Depending on the structural integrity required by the finished product the fiber/resin ratio or combination of fibers and type of resin can vary. The two basic production techniques involve: a) overlay of fiber on a mold followed by saturation with resin; b) presaturation of the fiber followed by filament winding or chopping and spray application.

11.9 Overlay Resin Application Technique

Products such as air and marine warning devices, telephone cable protective cases, display tables, furniture, boats, automotive bodies, and certain tanks use overlay techniques. Some may require spray techniques in addition to overlay. In all cases the mold (eg. a boat) is pretreated with a mold release agent such as paraffin wax or silicone. A layer of pigmented polyester (gel coat) is brush or spray painted onto the mold. Gel coating is done in a negative pressure booth and fumes are vented to the ambient air. Some firms filter the air before discharge.

A glass fiber mat is applied with several centimeters of overlap over the edge of the mold. Polyester resin is poured, brushed or spray applied to saturate the mat. Spiked rollers are used to work the bubbles out of the resin to produce a solid film. Consecutive layers are applied until the appropriate thickness is achieved. Styrene monomer evaporates from the resin during the application and curing process and is vented directly to the atmosphere. Curing is usually achieved by addition of a free radical generating peroxide such as methyl ethyl ketone peroxide. The reaction is exothermic and drives off styrene monomer until curing is complete. The excess overlay is cut from the finished piece using saws and/or grinding disks. The cut edges are trimmed and polished using grinders, sandpaper or files. Cutting and grinding is generally done in an open building and frequently out of doors on the plant yard. This can generate a large amount of resin dust which spreads in the building, on the yards

and in a majority of cases beyond the plant property. The structural resins contain corrosion inhibiting formulations incorporating chlorinated acids or anhydrides and may use organotin initiators which are priority chemicals. The concentration of organotin is less than 0.02% by weight and would be released in trace quantities with the dust. The organotin is fixed in the resin matrix and environmental availability would be determined by leachability from the resin. The surface area/weight ratio for the dust particles is very high which would aid in the degeneration of the resin by ultraviolet radiation as it lies exposed on the ground. The rate of degeneration of the polymer and release of organotin is not known. Leaching from dust is expected to be the major source of organotin compounds released to the environment from the polyester resin industry. The amount released is expected to be trace quantities which would be determined by future sediment and storm water sampling techniques.

11.10 Filament Wound and Chopper Spray Applied Resin

Filament wound articles include large diameter corrosion resistant tanks and piping for sewer lines, chemical process, and the pulp and paper industries. There is little wastage of resin in this application method as feed rates are slower and depend on regular incremental layers of resin soaked filaments wound on a spindle. Edge finishing produces a small amount of dust and cuttings which are disposed to landfill. A small amount of resin is lost during startup and finish of the winding process and is limited to a few kilograms per application. Heat lamps are sometimes used to promote curing of the resin and drive off styrene which is vented directly to the atmosphere.

Spray applied resins involve the use of pressure feed or compressed air to force the resin into an inline manifold. The glass filament is fed into the resin stream and cut in lengths several centimeters long. The pressurized resin coats the filament and sprays it onto the mold. This technique produces the largest amount of waste due to overspray. Chopper spraying is done in negative pressure booths which filter

the air and exhaust it to the outside. A larger volume of styrene monomer is used to produce a proper viscosity in the resin for spray application. The aspirated resin volatilizes the monomer quicker and workers are required to wear breathing apparatus. One of the facilities visited in the Kelowna area had virtually no air circulation in the spray application area and the atmosphere was extremely difficult to breath. Spray application techniques produce equal or larger amounts of waste trim as those using matted glass. The floors in the chopper spray areas are covered in paper or cardboard sheets prior to a shift. The sheets are used to collect the oversprayed strands of resin soaked glass filament. Depending on the production activity the floor coverings are replaced daily or weekly. A layer of three to ten centimeters of resin filaments usually builds up before replacement. This resin is disposed along with general waste to landfill and is not subject to the exposure to ultraviolet light that grinding dust is.

The production of hot tubs, and other bathroom fixtures requires the use of polyurethane foam insulation. Hot tubs are formed from solid acrylic sheets which are imported from the United States. The sheets are electrically heated above the glass transition temperature and then vacuum formed to a precast mold. The acrylic sheet is brittle, and structural integrity is increased by spray application of polyester resin. Polyurethane foam is spray applied as an insulating layer. Overspray is the main source of waste.

12.0 RUBBER PRODUCT HANDLERS AND PRODUCERS

A wide range of articles can be classified as rubber, ranging from hard, highly crosslinked materials for bumpers to low sulphur elastomers capable of reversable extensions of over 700%. One hundred and seven firms handling or manufacturing with rubber products were identified in B.C. These were classified in eight categories as listed in Table 12.1. The materials and estimated volumes used are listed in Table 12.2.

TABLE 12.1 TYPES OF FIRMS HANDLING RUBBER MATERIALS IN BRITISH COLUMBIA

	TYPE OF FIRM	NUMBER OR FIRMS
_		
1	Warehouse distributors	23
2	Foam Rubber Upholsterers/Retailers	7
3	Cutting and Pressing rubber stamps	46
4	Cold bonding	8
5	Autoclaving and forming (tires)	3
6	Autoclaving and forming (machinery)	6
7	Forming rubber products	4
8	Rubber formulators	3

12.2 <u>Warehouse Distributors/Upholsterers/Rubber Stamp Manufacturers/</u> Cold Bonding

Warehouse distributors import and distribute raw, semi-finished and finished rubber products to industry and consumer outlets. The bulk rubber materials are shipped in polyethylene packaged containers and bags.

TABLE 12.2 MATERIALS CONSUMED IN THE RUBBER INDUSTRY OF BRITISH COLUMBIA

MATERIALS	ESTIMATED ANNUAL CONSUMPTION
Rubbers Natural Rubber Styrene Butadiene Rubber Polychloro Butadiene Rubber Acryolitrile Butadiene Rubber Poly Butadiene Rubber Polyurethane Rubber Urethane Resins Poly Ethylene Poly Propylene Miscellaneous Rubber mixtures	< 760 000 kg/y < 2 060 000 kg/y < 10 000 kg/y < 15 000 kg/y < 5 000 kg/y < 350 000 kg/y < 22 000 kg/y < 2 000 kg/y
Plasticisers Di-n-Butyl-Phthalate* Di-Octyl-Phthalate* Acrylamino Diaryl Disulfide Butyraldehyde Napthenic Oil Aliphatic Hydrocarbon Rape Seed Oil (Vulcanised) Vulcanised Vegetable Oil Petroleum Wax Stearic Acid	< 800 kg/y < 1 500 kg/y < 100 kg/y < 100 kg/y < 2 800 kg/y < 100 kg/y < 100 kg/y < 100 kg/y < 300 kg/y < 1 200 kg/y < 1 500 kg/y
Vulcanisers Sulfur Benzothiazyl Mono or di-Pentaerythritol N-N'm-Phenylene Dimaleimide 1,2-Dihydro-2,2,4-Trimethyl Quinoline Di-8-Napthyl-P-Phenylene Diamine	< 16 000 kg/y < 100 kg/y < 100 kg/y < 100 kg/y < 120 kg/y < 120 kg/y < 270 kg/y
Reaction Catalysts Stannous Octoate Dicumyl Peroxide Amine Catalysts 2,4 or 2,6 Toluene Diisocyanate	< 400 l/y < 500 kg/y < 650 l/y < 175 000 l/y

TABLE 12.2 MATERIALS CONSUMED IN THE RUBBER INDUSTRY OF BRITISH COLUMBIA (Continued)

MATERIALS	ANNUAL CONSUMPTION
Solvents Methylene Chloride* Toluene Naptha Propylene Glycol	< 3 500 1/y < 8 700 1/y 500 1/y < 500 000 1/y
Metallic Soaps Lead Surfactants (Napthenates)	< 6 000 1/y
Resins Phenolic Resin Miscellaneous Hydrocarbon Resin	< 500 kg/y < 1 200 kg/y
Bonding Agents 1,3-Butylene-Glycol-Dimethacrylate Tri-methylol-Propane-Trimethacrylate Tetrahydro Furfuryl-Methacrycate Acryclic Monomer Epoxy	< 100 kg/y < 2 000 kg/y < 1 000 kg/y 300 kg/y 300 kg/y
Pigments Carbon Black Iron Oxide (red) (Fe ₂ O ₃) Magnesium Oxide (tan) (MgO Fe ₂ O ₃) Titanium Dioxide	< 1 000 kg/y < 1 000 kg/y < 500 kg/y 1 600 kg/y
Fillers Barytes (Clay) Clay Silica SiO ₂ Alumina Clay (AL ₂ O ₃ SiO ₂) Glass Shot	< 1 200 kg/y < 6 000 kg/y < 20 000 kg/y < 5 000 kg/y < 4 000 kg/y

⁽E) = Estimated maximum value, actual value is expected to be lower
* = Environmental Contaminants Act priority chemical

Upholsterers and retailers of foam rubber (generally polyurethane based) produce such things as cushions, pillows, furniture and upholstered items. Waste foam is cut and recycled as fill for pillows, toys, and soft articles. A negligible amount of waste rubber is produced and included with miscellaneous waste sent to landfill.

Rubber stamp manufacturers for business stamps, letterhead and printing rollers and labels may use vulcanizing processes, however the majority cut prefabricated, finished polymer and imprint the required designs using a hot press method. The average rubber stamp manufacturer wastes less than 100 kg/yr, usually 20 to 30 kg.

Cold bonding manufacturers cut and glue prefabricated rubber sheets into useful articles such as clothing, scuba diving/survival equipment and miscellaneous consumer goods.

All of these firms are small and recycle as much as possible due to the high costs of the polymer.

12.3 Forming and Autoclaving Rubber (Tires)

Tire recycling is one of the largest consumers of raw rubber in the region. In excess of 1 600 000 kg of Styrene Butadiene Rubber (SBR) and Natural Latex Rubbers (NLR) are consumed annually. Used tires are separated into three categories, those suitable for retreading, those for recycle into bumper materials for use at marine docks and low-grade tires used for burning and landfill.

Remanufacturing of tires requires that the old tread be cut or ground off to produce a new clean surface suitable for bonding (Plates 12.1 and 12.2). The grindings can be recycled and approximately 1 500 000 kg/yr are produced and sold for recycle into other products. The SBR rubber retread may require steam heating to complete vulcanization after it is bonded to the tire. Some plants mill their own rubber to produce the required blend however most facilities use preblended polymers.

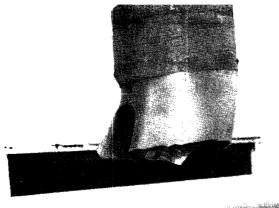


PLATE 12.1: (left)
RUBBER
GRINDINGS
FROM TIRE
TREADS

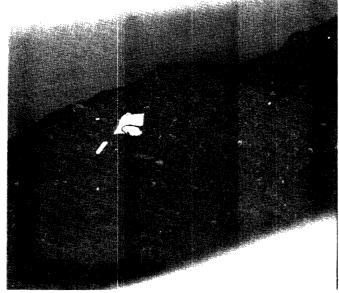


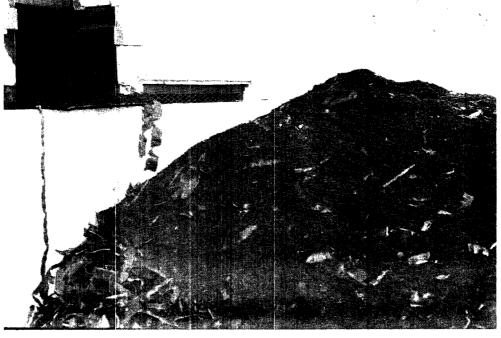
PLATE 12.2: (below)

RUBBER

GRINDINGS

FOR

RECYCLE



12.4 Forming and Autoclaving Rubber (to Machinery)

Pulp and paper machine rollers, mining equipment and machinery that handles slurries, conveys rock and gangue materials, require pumps, piping and conveyor systems that are rubber lined. The replacing of rubber linings and production of new equipment consumes approximately 800 000 kg of SBR and natural rubber combined. Some manufacturers also produce polyurethane pump parts such as impellers and housings.

- Metal Cleaning. Metal parts must be cleaned to white metal before refinishing (ie. free of any oxides, rubber, paint or scale). Sand or metal spheres (micro ball bearings) are used as abrasives in compressed air blasting of the metal part. If metal spheres are used these can be recycled by separation in a cyclone with abraded dusts removed in a secondary cyclone/filter unit. The residues which are comprised of rubber dust, paint, oxides and dirt are disposed to landfill. An estimated 572 000 kg (72%) of the rubber consumed is eventually disposed to landfill while 228 000 kg (28%) is lost through wear during the service life of the machinery.
- 12.4.2 <u>Rubber Formulation</u>. Raw natural rubber is shipped in slabs wrapped in polyethylene. (Rubber which is partially preformulated ie. milled with the addition of sulfur and carbon black is coated in talc to prevent sticking of the prevulcanised polymer.) The rubber slabs are cleaned, weighed and then fed into a blending mill. The mills consist of two steel rollers which press and tear the slabs between them.

A blend of additives is dry mixed and poured into the mill. A dust collection hood vents dusts to the outside. The end use of the rubber determines the degree of crosslinking required and the agent used. (Usually sulfur based (14).) Tables 12.3 and 12.4 list typical formulations which may be used.

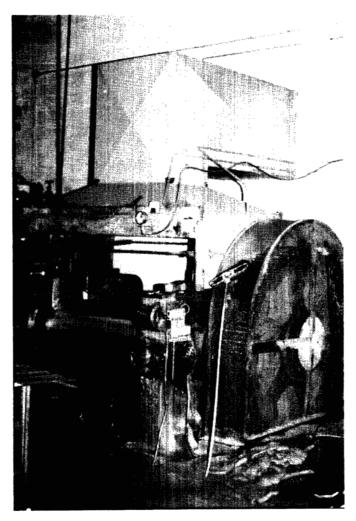


PLATE 12.3: RUBBER BLENDING MILL

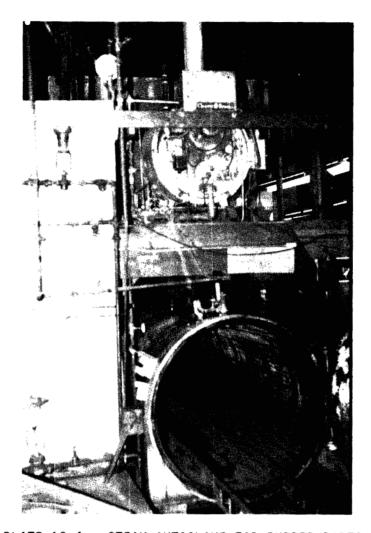


PLATE 12.4: STEAM AUTOCLAVE FOR RUBBER PARTS

TABLE 12.3 NATURAL RUBBER VULCANIZATION AGENTS

USE	PARTS/100	VULCANIZATION AGENT
Tire Treads	0.5-0.7	N-cyclohexyl-2-benzothiazole-sulfenamide (C.B.S.) (14)
	0.5-0.7	N-tertbutyl-benzothiozole-sulfenamide (NBBS) (14)
	1.75-2.75	Sulfur (14)
Foot Wear i.e. shoe heal	0.5 or 1.0 3.0	benzothianzyl disulfide (MBTS) (14) diphenylguanidine (DPG) (14, 16) sulfur
Black Mechanical Parts	0.2	Tetramethylthiuran disulfide (TMTD) (14)
i.e. gaskets,	or 0.2	zinc dimethyldithiocarbonate (ZMDC) (14)
rollers, linings,	or 0.2	tetraethylthiuron disulfide (TETD) (14)
seals	or	DPG (16)

TABLE 9.4 STYRENE BUTADIENE RUBBER ACCELERATORS AND VULCANIZING AGENTS (14)

USE	PARTS/100	ACTIVE AGENT	
Tire Treads	1.20	N-tertbutyl-benzothiozole-sulfenamide	
		(TBBS)	
	and 1.75	Sulfur	
	or		
	0.90	CBS	
	and 0.15	TMTD	
	and 0.30	BIK	
Retreads	1.00	TBBS	
	and 0.20	tetramethylthiuram monosulfide (TMTM)	
	and 2.0	sulfur	
Mechanicals	1.5	MBTS	
	0.3	DPG	
	2.0	Sulfur	
	or		
	0.5	MBTS	
	0.3	Copper - dimethyldithiocarbonate (CuMDC)	
	2.0	Sulfur	
	or		
	0.2	tetramethylthiurian monosulfide	
	3.0	sulfur	
Hard Rubber Compounds	2.0	butyraldehyde and aniline (B.A.)	
	45	sulfur	

In some cases the rubber is preblended and requires the addition of sulfur prior to the bonding and heating process. Many preblended rubber materials which are shipped to B.C. are proprietory and the manufacturer using the polymer does not know the contents but purchases the material based on performance criteria produced by the supplier.

Adhesives used to bond the rubber to the metal contain toluene, xylene, methyl-isobutyl-ketone, naptha, varsols and/or other petroleum based solvents.

If the parts are required to be fuel and oil resistant they may contain the following plasticisers, dioctyl phthalate, tricrysl phosphate (liquid esters), coumerone-indene (coal tar resins), or polymeric esters (14).

12.5 Polyurethane Foam Rubber Production

Polyurethane foam (sponge) rubber is produced by reacting 2,4 or 2,6-toluene diisocyanate with a polyol such as propylene glycol and a blowing agent such as trichloromonofluromethane. Other additives may include stannous octoate and amine catalysts, and various pigments.

In polyurethane foam production the high reactivity and accessibility of the cyanate groups accounts for its use in rapid polymer formation foams. The cyanate group is believed to have an oscillating structure as given below.

R = carbon chain or benzene structure

N = nitrogen atom

C = carbon atom

0 = oxygen atom

The unsymmetrical nature of the 2,4-isomer allows the isocyanate group in the 4 position to be statistically prone to reaction. The second

stage involves reaction with water and evolution of CO_2 gas. The exact mechanism has not been defined but is believed to be as follows (1).

(1)
$$H-C-H$$
 $N=C=0 + B:$
 $N=C=0$
 $N=C=0$

Stannous octoate is used as the catalyst to promote polymerization. Other metal catalysts and ethylamines will promote the reactions however organotins are the most highly reactive

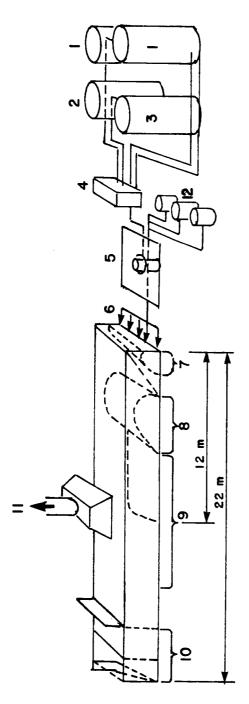
Propylene glycol and liquid toluene-diisocyanate are usually stored in tanks on site. Tank size may exceed 20 000 l and both materials have low vapour pressures and can be stored in pressure controlled vessels. The isocyanates can create toxic fumes if ignited so that adequate fire protection is required.

9.5.1 Foaming Process. Tin and amine catalysts are blended in exact proportions to promote foam production. The tin promotes the gel formation which will trap the $\rm CO_2$ gas produced by a water reaction which is catalyzed by the amine. A specific gel density is required so that the foam will not collapse on itself due to lack of gelling (caused by too low

a tin concentration). High gel density is caused by excess tin creating a rigid foam that does not allow expansion by the gas before the mixture is fully polymerized. Fluorocarbon blowing agents are combined with CO2 gas produced in the amine catalyzed water reaction to increase vapour pressure for foam bubble expansion. Lead soaps (surfactants) are used to control surface tension during bubble formation. This provides a uniform bubble size which can be controlled to suit the end use of the foam. amounts of pigment (an average of 0.01% by volume) are added prior to mixing to produce colored foams. The mixture is blended in a multi-component header and injected onto the paper lined slope of an expansion channel (see Figure 12.2). The foam rises as it slides down the channel into the shape of a large loaf or bun. The injection rate is usually greater than 45 kg/min (15). The foam will expand as long as the polymer is plastic against the pressure of the entrained gas. Typical foam densities are 0.024 g/cm^3 to 0.045 g/cm^3 (15). The foam loaves expand to approximately 1.5 m by 1.5 m in a continuous flow (see Figures 12.1 and 12.2).

The blocks are then cut by bandsaws into useful shapes with a trim excess of up to 20% of the block (15). This trim is cut into small pieces for use as pillow and upholstery filler or blended with urethane binder and formed into carpet underlay.

- 12.5.2 Aging and Cutting of the Foam. The foaming reaction is exothermic and contains residual isocyanate fumes. The fumes are vented using high volume blower fans (up to $1400 \text{ m}^3/\text{min.}$) and it is estimated that less than 1.5 kg/yr of isocyanate is discharged. Concentrations of isocyanate greater than 0.02 ppm have not been detected (18).
- 12.5.3 Environmental Concerns (Fire Hazard). Polyurethane foams are used in a wide variety of areas from bathroom sponges, car, bed, and upholstery cushions to insulation. They are flammable and cannot be used as building insulation unless they are coated with fire retardant material. When fully cured they are considered non toxic, insoluble in water and most solvents (15).



- 1) Propylene Glycol Tanks
- 2-6, Toluene Diisocyanate
- 2-4, Toluene Diisocyanate 4

Control Panel and Header

- Blender/Pump 2

- 6) Foam Dispersion Header 7)-10) Foam Expansion Channel 8) Foam continues to expand
- High Volume Fan is mounted at the point of Maximum Foam Production
- A Band Saw cuts the Foam into Large Blocks for handling purposes <u>⊙</u>
 - II) High Volume Fan
- 12) Pigment Tanks

FOAM EXPANSION EQUIPMENT DIAGRAM OF THE FIGURE 12.1

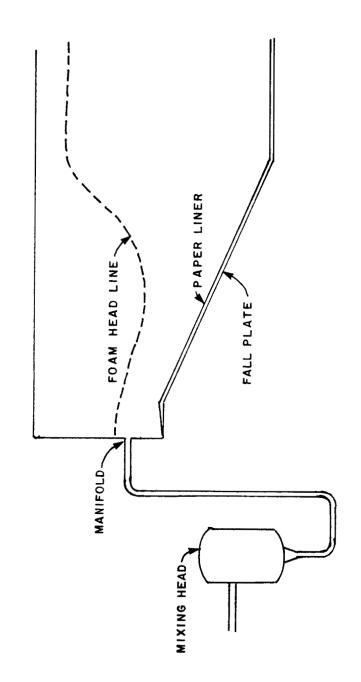


DIAGRAM OF THE FOAM EXPANSION FIGURE 12.2

Spill containment of the TDI would be complicated if a fire were to occur. TDI is highly reactive at elevated temperatures and emits toxic fumes on combustion. Polyurethane foams are combustible and emit carbon monoxide and hydrogen cyanide fumes when burning. There is a danger of spontaneous combustion of the molded foam if an excess of unreacted TDI is present.

- 12.5.4 <u>Foam Additives</u>. Specific precautions should be noted for the handling of the chemicals used because of their potential detrimental qualities.
- 12.5.5 <u>Tertiary Amine Catalysts</u>. The amine catalysts used to react with the water in the prefoamed mixture are also reactive with mucus membranes in the eyes, nose, throat and lungs. The eyes are particularly susceptible and protective goggles and respirators are required during handling. Protective clothing and gloves should also be worn to prevent contact dermatitis.
- 12.5.6 Organotin Catalysts. Little information exists however these are ECA priority chemicals.
- 12.5.7 <u>Isocyanates</u>. TDI is reactive and will produce CO_2 gas if contaminated with water. Gas pressure buildup in a closed system must be monitored to prevent explosion. Thermal degradation will occur at temperatures above $100-120^{\circ}C$ and an uncontrolable reaction can occur above $175^{\circ}C$. Isocyanate spills may be counteracted by the addition of basic solutions such as aqueous ammonia or sodium carbonate (15).

Polyurethanes are combustible (15) and a large quantity in the form of expanded blocks, cuttings and packaged foams are present in production facilities. The foam blocks are cut by bandsaw and some small chips and dusts are produced. This dust is periodically swept up and disposed in containers for landfill. Reasonable care is taken to prevent exposure of the foam to heat sources. Once the product is in the foam form there is

little risk of environmental impact except in the case of fire. All facilities visited in British Columbia collected and reused all the trim cuttings.

12.6 Wastes Produced

Wastes in the rubber industry include:

- a) rubber grindings from custom shaping of SBR and NLR to fit tires,
 machine parts and piping;
- b) rubber grindings from old tires;
- c) grindings and sand blasting dusts which contain sand, paint, metal oxides, rubber;
- d) steam condensate which may contact the rubber directly;
- e) hydraulic oils which are used in pistons of compression molding machines;
- f) trimming of polurethane foams and solids;
- g) fumes during the exhausting of plant areas, steam autoclave;
- h) cuttings of other waste rubbers.
- 12.6.1 <u>Disposal of Waste Rubber Grindings</u>. The rubber dusts produced from the custom shaping of SBR and NLR are recycled, disposed to landfill, or incinerated. Table 12.5 identifies the methods of waste disposal.

TABLE 12.5 DISPOSAL OF WASTE RUBBER PRODUCTS*

DISPOSAL METHOD	AMOUNT DISPOSED (kg/yr)
Landfill disposal	190 000
Recycled rubber	1 500 000**
Incinerated	115 200

^{*}Estimated value based on replies to a questionnaire (See Appendix I) **An estimated 3 000 000 kg of waste rubber is imported for recycle

TABLE 12.6 CHEMICAL OXYGEN DEMAND AND TOTAL METALS SCAN OF WATER FROM THE SUMP OF A HYDRAULIC RUBBER PRESS

ELEMENT	TOTAL (ug/ml)	ELEMENT	TOTAL (ug/ml)	ELEMENT	TOTAL (ug/ml)
As	.08	Mo	< .005	V 7-	.02
B	.016	Ni	< .02	Zn	5.86
Ba		P	16.4	Al	.2
Be	< .001	Pb	1.5	Fe	3.27
Cd	.082	Sb	1.3	Si	7.8
Co	< .005	Se	< .05	Ca	26.6
Cr	13.1	Sn	1.77	Mg	3.7
Cu	3.51	Sr	.142	Na	149.
Hg		Ti	.037	COD	10560.0
Mn	.141				

Burners used for incineration of waste rubber are equipped with a primary furnace and a natural gas afterburner designed for complete combustion.

12.6.2 <u>Disposal of Waste Water</u>. Water is used for domestic, boiler and cooling purposes. In most facilities water is recycled in an internal cooling system or discharged directly to sewer. The 13 firms identified as actively processing rubber consumed approximatly $15 \, \text{m}^3/\text{day}$ for sanitary (16) and $58 \, \text{m}^3/\text{day}$ as steam and cooling water. Steam condensate which contacts the rubber material is discharged to sanitary sewer. Cooling water is used in jacketed systems and discharged to storm sewer systems as clean water.

There is no data available regarding the possible leaching from rubber materials which are in direct contact with autoclaving steam. The

amount of effluent subject to contact with rubber materials is extremely small in comparison to the overall waste water flow in any of the regions where these facilities are located.

Several facilities use large hydraulic presses to compression mold the rubber. Oils used as hydraulic fluids leak from the pistons and are collected in floor sumps or contained by absorbant powders. Solid absorbants are disposed to landfill and oil that is collected in sumps is sold for recycle. The oil/water mixture is separated by the recycler. A sample of water from a waste oil sump was analysed for Chemical Oxygen Demand (COD), and total metals scan. The results are listed in Table 12.6.

13.0 RUBBER RECYCLERS

Rubber recycling in British Columbia focuses on reusing automatic tires. The two types of products produced are marine bumper guards and floor mats.

The marine bumpers are made by cutting and splicing tires together in chainlink fashion. The links are then mounted to the edges of docks by metal fasteners or chains. The amount of rubber recycled is less than 1 000 000 kg/y.

In excess of 4 000 000 kg of rubber is recycled in the production of floor coverings for agricultural, industrial and transportation uses.

A network has been developed to collect the waste rubber from automotive tire retreaders. The waste rubber is screened for debris which includes miscellaneous solids and metal tire strengthening cords. The screened rubber shavings are then ground and mixed with sulfur and a small amount of oil. The oil softens the rubber by partial solvation and the sulfur acts as the vulcanization agent and binder. The mixture is poured into steam heated trays which are compressed, heated and autoclaved. The mats are then cut to the desired shapes with the trimmings being reground and recycled back into the process.

14.0 POLYESTER RESIN, PIGMENT AND ADDITIVE DISTRIBUTERS

Seven major and several minor distributers of polyester resin, pigments and additive suppliers were identified in the Pacific Region. The major distributers are involved in mixing and repackaging of specialty resins and gel coats while the minor ones may be involved in repackaging. The inventory handled includes safety equipment, machinery, hand and power tools, and the chemicals required to produce custom made polyester products. Table 14.1 lists the chemicals handled.

14.1 Blending of Gel Coat Resins

Bulk gel coat resins are blended at five facilities using techniques similar to the paint industries but on a smaller scale. Multihorsepower blenders are used to mix the additives and viscous resins. Clear resins are pigmented with a base color which is usually titanium dioxide. The base color is then tinted with several grams of pigment per barrel of resin. Pigments may be in the powder, paste or liquid form and are not manufactured in the region. Paste and concentrates are blended using imported pigments. Some powdered pigments require blending in ball mills before use. The mills may use cooling water in a jacketed system before discharge to a storm sewer. Resin mixing is done in well ventilated, explosion proof rooms which are equipped with fans to remove the styrene monomer vapours that volatilize from the resin diluent. Mixing is done directly in the 200 1 barrels or in vats for smaller orders. Most distributers repackage the resins and gelcoats in 0.5 1 to 45 1 containers for retail and industrial sales. Exceptional care is taken to recover all of the resin from the large drums by scraping as polyester resin costs are as high as \$800.00/drum (28). The empty drums are recycled to the bulk suppliers.

Epoxy resins are blended at one location. The extremely high cost of \$700.00 to over \$1000.00/drum ensures that there is essentially no wastage. The epoxy resins are blended using similar techniques to

polyester resin with almost negligible fume production. They are then repackaged and distributed in 0.250 l to 4.0 l packages for consumer and specialty industrial use.

Polyurethane resins are also repackaged and distributed with negligible wastage.

Acetone is distributed and used as a solvent to clean mixing equipment as a base for sundeck coatings.

The spent acetone is grey in color and has a high polyester concentration which makes it suitable as a solvent in exterior polyester based coatings. Some waste acetone can also be sold for redistillation. Other products handled include:

- mold release agents
- promoters/catalysts
- inorganic pigments
- organic pigments
- fillers and thickeners
- solvents
- putties
- adhesives
- plasticisers

14.2 Distribution of Priority and Candidate Chemicals

Polyester resins which are fire retardant and chemical resistant are halogen based. They may be formulated from HET (hexaclorocyclopentadiene) acid or chlorendic anhydride. (These are not ECA chemicals).

ECA chemicals which are used include di-methyl aniline and Di-n-butyl phthalate.

Promotors based on di-methyl aniline or polyamides are repackaged in small quantities for redistribution. Wastage would occur at the fabrication of FRP products and is expected to be negligible.

Di-n-butyl phthalate is used at less than 4000 kg/yr in the production of coatings used for waterproofing. There is virtually no wastage.

Environmental availability of these compounds in the unsolidified resin has not been determined and would only occur during the fabrication of FRP products.

TABLE 14.1 CHEMICALS HANDLED BY RESIN SUPPLIERS AND DISTRIBUTERS

	MATERIAL	ESTIMATED	AMOUNT DI	STRIBUTED
A)	Resins Orthophthalic Polyester Isophthalic Polyester Chlorendic Polyester Bisphenol A fumerates Vinyl esters	1 500	000 kg/y	(E)
	Furon Acrylic based Epoxy based Polyurethane resins Polyurethane Spray foam	55	000 kg/y 000 kg/y 000 kg/y	(E)
В)	Mold Release Agents Silicons Parting Wax Honey Wax Mold Whiz			
C)	Promoters Cobalt Napthenate Antimony Trioxide Ethyl Acetate Methyl ethyl ketone peroxide Dimethyl aniline Polyamides	12	750 1/y 000 1/y	
ם)	Isophthalic Based Gel Coat Resins Pigments Titanium dioxide Antimony dioxide		000 kg 500 kg**	(E) (E)

TABLE 14.1 CHEMICALS HANDLED BY RESIN SUPPLIERS AND DISTRIBUTERS (Continued)

	MATERIAL	ESTIMATED AMOUNT DISTRIBUTED	D
D)	Isophthalic Based Gel Coat Resins Pigments Chrome yellow Chrome green Carbon black Cadmium red Ferrous brown Iron blues Molybdates Phthalo greens Phthalo blues Others	12 000 kg*** (E)	
E)	Fillers and Thickeners Glass bubbles Aerosil/Cabosil (SiO ₅) Talc Hedmonite (SiO ₂ , MgO based filler) Milled Fibers Aluminum flake Aluminum Oxide Aluminum Hydroxide Asbestos Walnut Shells Other		
F)	Solvents Acetone Ethylene glycol Methanol Methylene Chloride Styrene	130 000 1 (E) 62 000 1 (E)	
G)	Toluene Putties Polyester based body putties Asbestos based body putties	4 600 kg (E)	

₩Over one hundred variations of proprietory formulations exist.

**Total inorganic pigments other than TiO₂

***Maximum total organic pigments CON

TABLE 14.1 CHEMICALS HANDLED BY RESIN SUPPLIERS AND DISTRIBUTERS (Continued)

	MATERIAL	AMOUNT CONSUMED
н)	Adhesives Contact Cement Poly vinyl acetate based Cosein based Chlorothen NU	36 000 kg (E) 5 500 kg** (E)
I)	Plasticisers di-n-butyl phthalate*	< 2 500 kg (E)
J)	Solvent based paint	

(E) = Estimated maximum value based on questionnaire, see Appendix I

^{* =} Environmental Contaminants Act Priority Chemical

BIBLIOGRAPHY

- "Plastic Additives", Modern Plastics, McGraw Hill, Sept. 84, Vol. 61, Number 9, September 1984, pgs. 61-68.
- "Priority and Candidate Chemicals", Environmental Contaminants Act, Dept. of Environment and Department of National Health and Welfare, June 1984.
- 3. Kirk-Othmer, "Vinyl Polymers", Encyclopedia of Chemical Technology, John Wiley & Sons, Toronto, 1983, pgs. 886-936.
- 4. "Safety Data Sheet Thermolite 175-C, Butyl tin"
- 5. Plastics Industry, personal contact.
- 6. Kirk-Othmer, "Acrylonitrile Polymers, ABS", Encyclopedia of Chemical Technology, John Wiley and Sons, Toronto, 1978, pg. 442-455.
- 7. Sax, N.I., "Dangerous Properties of Industrial Materials", 5th Edition, Van Nostrand Reinhold, Toronto, 1979.
- 8. Mellan I., "Industrial Plasticisers" The MacMillan Company, New York, 1963, pgs. 64-69.
- 9. Kirk Othmer, "Styrene Plastics", Encyclopedia of Chemical Technology, John Wiley & Sons, Toronto 1983, pgs. 801-847.
- 10. Crystal, B., Personal Communication, Canada Cup. Ltd.

- 11. Industry Contact.
- 12. Jamkouski, J., Personal Contact, BASF Canada Ltd., Montreal, Quebec.
- 13. Lukey, B., Personal Contact, Food Inspector, Health Protection Branch, 601-1001 West Pender, Vancouver, B.C.
- 14. Kirk-Othmer, "Rubber Compounding", Encyclopedia of Chemical Technology, John Wiley and Sons, Toronto, 1983, pgs. 265-465.
- 15. Kirk-Othmer, "Vinyl Polymers", Vol. 23, Encyclopedia of Chemical Technology, John Wiley and Sons, Toronto 1983, pg. 576-607.
- 16. Metcalf and eddy, "Wastewater Engineering, Treatment, Disposal, Resins", McGraw Hill Book Company, 1979.
- 17. Personal Contact, Industry source.
- Industry source report based on Workers Compensation measurements.
- 19. Greater Vancouver Regional District Air Emission Permit, 1985.
- 20. Morrison, Boyd, "Organic Chemistry", 3rd Edition Allyn and Bucon, 470 Atlantic Ave. Boston, 1977.
- 21. Talbot, R.C., "Using Fiber Reinforced Plastics", Chemical Engineering Magazine, McGraw Hill, Vol. 91, No. 22, Oct. 1984, pg. 76-82.
- 22. Brown, K., Personal contact, Fiberplast Products Ltd., Kelowna, B.C.
- 23. Merck Index, Merck and Co. Inc., Rahway, New Jersey, USA, 1976.

- 24. Kirk-Othmer, "Phenolic Resins", Encyclopedia of Chemical Technology, John Wiley and Sons, Toronto, 1983, pgs. 384-416.
- 25. Kirk-Othmer, "Amino Resins and Plastics", Encyclopedia of Chemical Technology, John Wiley and Sons, Toronto 1983, pgs. 440-469.
- 26. Boxal, Von Frauenhoffer. "Concise Paint Technology", Paul Elek (Scientific Books) Ltd., 1977. Great Britian.
- 27. Kirk-Othmer, "Vinyl Polymers (Acetate)", Encyclopedia of Chemical Technology, John Wiley & Sons, Toronto 1983, pgs. 817-843.
- 28. Chapman, W., "King Fiberglass Company", Personal contact.
- 29. Krahn, P., "Characterization and Chemical Use Patterns of the Paints and Coatings Industry In British Columbia; EPS Regional Program Report 85, Unpublished.

Environmental Contaminants Act

PRIORITY AND CANDIDATE CHEMICALS

June 9, 1984

This fifth review of the List of Priority and Candidate Chemicals is published as an indication of the substances that are of particular interest to the two Departments for the gathering and analysis of information. The mere mention of chemicals in this List does not mean that they will be proposed for regulation. Rather, this List is intended as information for the public, industry, academia, provincial governments and other federal government departments so that they may be aware of the information gathering activities which are being carried out by the Department of the Environment and the Department of National Health and Welfare. Interested parties who have information which may be of assistance in evaluating the potential of a chemical to adversely affect the environment or human health are invited to communicate this information to either of the officials identified at the end of this notice.

The priority and candidate chemicals lists comprise, principally, chemical substances that are imported into Canada or manufactured or processed in this country. Chemicals that are used solely as drugs, food additives or pest control products may not be included in this List if they are already scrutinized or controlled under other federal legislation. Chemicals that have been included in the List may subsequently be removed by adding the substance to the Schedule to the act for regulation, or by a decision that the substance does not pose a threat to human health or the environment and, therefore, does not warrant regulation under the Environment Contaminants Act. In the latter case, for some substances, the two departments may still have a continuing concern under other federal mandates. Those substances that appeared on the previous (1982) version of the List and that are not included in this version are mentioned in a separate section of this notice with a brief explanation of why they have been removed from the List.

The same three criteria announced in the December 1, 1979, Canada Gazette notice that pertain to the hazards posed by a chemical substance to human health or the environment were applied to the selection of chemicals for this version of the List. These criteria encompass the several properties of a chemical substance, e.g., carcinogenicity, mutagenicity, reproductive and other forms of toxicity, volatility, solubility, routes of entry into the environment, dispersion and distribution throughout the environment, nature of transformation products, impurities, persistence, accumulation in tissues and amounts imported, manufactured or processed. The three criteria are:

- (1) Toxic effects criterion. Evaluation of scientific data leads to the conclusion that the chemical substance could cause or causes adverse effects on human health or the environment.
- (2) Persistence criterion. Evaluation of scientific data leads to the conclusion that the chemical substance accumulates or could accumulate to significant concentrations in air, water, soil, sediment or tissue.
- (3) Quantity and use criterion. Evaluation of available data on the importation, manufacture, processing or use of a chemical substance leads to the conclusion that the substance is in commerce and could enter or has entered the environment in significant quantities.

LIST OF PRIORITY CHEMICALS

The current List of Priority Chemicals, which supercedes previous lists, is presented below with a description of each category.

Category I: Those substances for which regulations or specific control strategies are being developed under the Environmental Contaminants Act.

Polychlorinated Biphenyls (PCBs)

Chlorobiphenyl Regulations No. 1 under the Environmental Contaminants Act came into effect in 1977, restricting use of PCBs in new non-electrical equipment. An amendment which extended the prohibition to new electrical equipment and which further restricted the use of PCBs in existing equipment came into effect in July 1980. Two further regulations on PCBs were proposed in the Canada Gazette Part I on January 21, 1984. Proposed Chlorobiphenyl Regulations No. 2 (Product) will control commercial activities involving products designed to use PCBs that contain more than 50 parts per million of PCBs. Proposed Chlorobiphenyl Regulations No. 3 (Release) will establish limits on quantities and concentrations of PCBs that may be wilfully released into the environment. Also, a strategy is being developed to achieve an orderly and accelerated phase-out of PCBs currently in use.

Chlorofluorocarbons (CFCs)

A regulation under the Environmental Contaminants Act, restricting the use of chlorofluorocarbons as aerosol propellants in hair sprays, underarm deodorants and antiperspirants came into effect on May 1, 1980. An amendment to this regulation, extending the restriction to all deodorants, came into effect on May 7, 1981. The need for controls on the non-aerosol uses of CFCs is being reviewed.

Category II: Those substances which are being investigated to determine the nature and the extent of the danger to human health or the environment and the appropriate means to alleviate that danger.

Chlorobenzenes

Many of the chlorinated benzenes have been identified in the tissue of fish or herring gulls from the Great Lakes, indicating the presence of these chemicals in the environment and their persistence and accumulation. The use of mixtures of tri- and tetrachlorobenzene as replacements for PCBs could lead to an increase in their consumption and thus an increase in environmental exposure. Hexachlorobenzene (HCB), a waste-product of several industrial processes, is persistent and can be bioaccumulated. Review of the national situation shows that HCB occurs throughout the environment. There is recent evidence that some chlorobenzenes are toxic, especially HCB, and while environmental levels are not of immediate concern, there is a need to investigate the pathways of exposure through the environment and the potential effects on health and environmental biota.

Phthalic Acid Esters

Large quantities of phthalic acid esters are used in Canada and are released into the environment during processing and as a result of the use and disposal of products containing them. Their greatest use is as plasticizers although they have numerous other uses such as replacement for polychlorinated biphenyls. Several, including diethyl phthalate, dibutyl phthalate (DBP), and di-(2-ethylhexyl) phthalate (DEHP), have been studied in detail. Residues of DEHP and DBP in air, sediment, water, fish, and herring gull eggs have been detected, indicating their presence in the environment. DEHP has been reported to be carcinogenic in the rat and the significance of this with respect to human health has yet to be determined. A number of phthalates are currently undergoing long-term toxicological testing. Sublethal toxicity testing and environmental measurements for the aquatic medium are needed.

Category III: Those substances which may pose a significant danger to health or the environment and about which further detailed study or information (for example toxicology, amounts used or concentrations in the environment) is necessary.

Chlorinated Paraffins (CAS No. 63449-39-8)

For the purposes of this List, chlorinated paraffins are defined as complex mixtures of compounds having more than 10 carbon atoms and 35-70% chlorine by weight. These chemicals are produced in large quantities and are used as lubricants and cutting oil additives, plasticizers and, in particular, as flame retardants. They are considered to be stable and to have a high potential to contaminate the environment. There is a paucity of data concerning the concentrations of these chemicals in environmental media and their toxicity, although some of these substances are currently undergoing tests for mammalian and aquatic toxicity.

Chloroethanes

1,2-Dichloroethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane are produced and used in high volume; their loss into the environment and their potential toxic and environmental effects are cause for concern. Information is being collected on the use patterns of these three chemicals. Data are needed on environmental levels and the possible resultant effects on humans and other organisms.

Chioroethylenes

Trichloroethylene and tetrachloroethylene exhibit a variety of toxic effects and are employed in large quantities for essentially dispersive uses such as cleaning solvents. Information is being collected on the use patterns of these chemicals. Data are needed on environmental levels and the possible resultant effects on humans and other organisms.

Chloromethanes

Carbon tetrachloride, chloroform and dichloromethane are used in high volume and have high potential for release to the environment. They have been observed in Great Lakes waters and some have been found in finished drinking water as a result of environmental contamination and the use of chlorine as a disinfection agent. There is concern over the chronic toxicity of these compounds, and the triand tetrachloromethanes have been reported to be carcinogenic based on animal studies. Information is being collected on the use patterns of these chemicals. Data are needed on environmental levels and the possible resultant effects on humans and other organisms.

Organotins

Organotin compounds are incorporated (as antioxidants, stabilizers, biocides, etc.) into a variety of synthetic materials. The widespread use of these substances, coupled with their stable chemical nature suggests that organotins may be widely distributed and persistent; these aspects are under investigation. A brief review of these chemicals ("Organotins in the Canadian Environment – A Synopsis", Environment Canada Report EPS 3-EC-82-1, 1982) has been published which identified the lack of data on environmental concentrations and ecotoxicity.

LIST OF CANDIDATE CHEMICALS

The List of Candidate Chemicals includes chemicals which may pose environmental contamination problems and for which the concern is insufficient to warrant placement in the List of Priority Chemicals. For some Candidate Chemicals the available data are inadequate and must be supplemented where appropriate by information on commercial use-patterns, biological effects, other properties, or environmental occurrences. This information will be sought, but at a lower level of effort that for Priority Chemicals. As the information is accumulated, some of the substances may warrant more detailed study and be placed on the List of Priority Chemicals or may not warrant continued investigation and be deleted from the List of Candidate Chemicals.

Aromatic Amines

For the purpose of this List, aromatic amines comprise:

(a) diphenylamine and derivatives

(b) aminobiphenyls and derivatives

(c) aniline, its methyl or ethyl derivatives whether these groups are substituents on carbon or nitrogen, and those derivatives of all these compounds that carry chloro, bromo or nitro substituents in the ring.

Some of these chemicals are produced in large quantities and are put to a variety of uses including dyes, antioxidants, explosives, plastics, stabilizers, and precursors for the manufacture of herbicides and fungicides. Some have been detected in the Great Lakes and some are believed to be carcinogenic or otherwise toxic.

Ethylenethiourea (2-imidazolidinethione)

This chemical is used in the rubber, dyestuff and pharmaceutical industries. It also occurs as a degradation product of ethylene bis-dithiocarbamate fungicides which are used in agriculture. Literature reports indicate this chemical is mutagenic and has produced tumorigenic and teratological effects in laboratory animals.

Halogenated Diphenyl Ethers

These compounds are used principally as flame retardants. Some are persistent and in laboratory studies have been found to accumulate in fish. Chlorodiphenyl ethers have been detected in sediments.

Halogenated Toluenes

Almost all the chemicals in this class are used as intermediates; some are used as solvents. Specialized product uses include frothing agents, gasoline gum inhibitors and flame retardants. Tetra- and pentachlorotoluene have been found in fish from the Great Lakes.

Nitrophenols

For the purpose of this List, nitrophenols comprise those chemicals which contain one or more nitro substituents on the aromatic ring of a mono- or polyhydroxybenzene. These compounds are widely used as intermediates in the chemical industry. They are moderately persistent in the environment and are reported to be toxic.

Organophosphorus Compounds

For the purpose of this List, organophosphorus compounds comprise:

(a) phosphines

- (b) phosphine oxides and derivatives
- (c) phosphinic acids and derivatives
- (d) phosphonic acids and derivatives
- (e) phosphites and derivatives
- (f) phosphates and derivatives
- (g) phosphoranes and derivatives

Some of these compounds are used as plasticizers, flame retardants, lubricants and fuel additives. Many are very stable and may persist in the environment. The triarylphosphates were included in the preceding List of Candidate Chemicals and have been retained on this List as part of this group of chemicals.

DELETIONS FROM THE LIST OF PRIORITY CHEMICALS

The following chemicals were on the previous (1982) List and do not appear on this version for the reasons indicated below.

Cadmium

Investigation by the two Departments has shown that at the present time there is insufficient evidence to warrrant the addition of cadmium to the Schedule to the Act for regulation. Cadmium and its compounds continue to be of concern to other high-priority programs of both Departments which are designed to control specific contamination problems.

Details of the investigation which served as the basis for deleting cadmium from the List of Priority Chemicals are contained in the publication entitled "Environmental Contaminants Act: Hazard Assessment Report on Cadmium" (December 1983); copies of this report may be obtained by contacting either of the officials identified at the end of this notice.

Chlorophenols

Commercial formulations of these compounds have been of concern because of their widespread use, toxicity and the presence of various impurities such as chlorodibenzodioxins and chlorodibenzofurans. These compounds have been under review for some time now and have been the subject of three reports ("Chlorophenols and Their Impurities in the Canadian Environment", Environment Canada Report EPS 3-EC-81-2, 1981; "Chlorophenols and Their Impurities in the Canadian Environment; 1983 Supplement", Environment Canada Report EPS 3-EP-84-3; "Chlorophenols and Their Impurities: A Health Hazard Evaluation" Health and Welfare Canada Report 84-EHD-110 (in press)).

Chlorodibenzodioxins have been the subject of two separate reports released in December 1983 and entitled "Report of the Ministers' Expert Advisory Committee on Dioxins" and "Dioxins in Canada: The Federal Approach". Both documents provide an overview of the potential problems posed by chlorodibenzodioxins and enumerate actions to be taken by the federal government, often in collaboration with provincial agencies, to reduce the exposure of Canadians to dioxins.

Some of the major uses of chlorophenols are controlled by the Pest Control Products Act administered by Agriculture Canada, and recent changes in the permitted uses will reduce the potential for releases into the environment. Another change has set lower limits for the dioxin

content of some chlorophenols. Furthermore, measures have been initiated to implement a code of good practice for the use of chlorophenols in wood treatment and preservation which should further assist in reducing human exposure and releases to the environment.

With the measures which have been taken and are proposed, the two Departments have concluded that there is not sufficient cause to warrant the addition of chlorophenols to the Schedule to the Act for regulation at the present time. Chlorophenols and their contaminants will continue to be of concern to other high priority programs of both Departments.

Dodecachloropentacyclooctadecadiene (CAS No. 13560-89-9) and Hexachlorobutadiene (HCBD)

Evaluation of the commercial use patterns and data on environmental concentrations led to the conclusion that the potential exposure of humans and the ecosystem was not sufficient to merit further in-depth investigation at this time.

Anyone who has comments or seeks clarification regarding the present document, or has pertinent information on these chemical substances, should contact either of the following officials.

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