

## PVC- AN ENVIRONMENTAL PERSPECTIVE

Paul Johnston, Simone Troendle [\*]

The definitive PVC conference



27-29 April 1993  
Brighton, UK

For further details  
contact The Institute  
of Materials

PVC '93  
THE FUTURE

Tel: 071-976 1339  
Fax: 071-839 3576

PVC production, use and disposal are associated with a number of environmental impacts identified at all phases of the life cycle. This paper briefly describes some of the identified problems in relation to the full life cycle analysis implied by clean production methods. It is concluded that given the problems inherent in the PVC life cycle this plastic is unlikely to be able to fulfil the requirements of such production methods.

### INTRODUCTION

Early applications of PVC included fibres, films and lacquers. Non-rigid applications followed improvements in plasticisers and heat stabilisation (Davidson & Gardner) (1). Steady growth of the market means that PVC now accounts for around one fifth of commodity plastics with global production of 18 million tonnes (Norsk Hydro) (2). Annual market growth of 5.8% was recorded between 1975 and 1989 and a single manufacturer may offer hundreds of individual formulations. After polyethylene, PVC is the largest volume thermoplastic accounting for around 30% of world chlorine production. This makes it the single largest end use for chlorine. The PVC industry is regarded as mature and much current research and development is focussed on the improvement of performance and economics of the existing wide range of applications and development of high value added grades.

Johnson (3) notes that developing countries have been generally identified as potential markets for PVC particularly in construction projects. This may result in considerable technology transfer in the future as manufacturers establish operations in developing countries. This allows forward integration with oil production, respond to environmental legislation directed at various phases of the PVC life cycle as well as development of new markets.

Investment reviews (Furnival) (4) (Shelley) (5) have identified trade in ethylene dichloride (EDC), vinyl chloride monomer (VCM) and PVC as crucial in balancing uneven market demands

[\*] Greenpeace Exeter Laboratory, Earth Resources Centre,  
University of Exeter, EX4 4QE

for co-produced chlorine and sodium hydroxide against a background of falling chlorine demand. Other market analyses consider that negative environmental impacts may result in increased restrictions on PVC use (3).

The environmental concerns surrounding PVC relate to the whole production, use and disposal cycle, including chlorine and additive production. A thorough examination of the societal need for this product is required since it is clear that "Best Available Technology" (BAT) particularly that "Not Entailing Excessive Cost" (NEEC) (2), is unable to holistically resolve the problems within a framework of Cleaner Production as endorsed by UNEP or the more rigorously defined Clean Production framework promoted by Greenpeace (Johnston & Stringer) (6).

## ENVIRONMENTAL ASPECTS OF PVC PRODUCTION

### Chlorine Manufacture

**Mercury Emissions** There is no doubt that emissions of mercury from chlor-alkali plants have created some serious and intractable environmental problems. Airey & Jones (7) state that a major UK chlorine plant was recorded as discharging up to 100kg/day of mercury at one stage. Levels in the sediment of the recipient canal were recently determined at up to 94.5 ppm wet weight (Johnston *et al.*) (8) The sediments of Liverpool Bay have become severely contaminated. (Norton *et al.*) (9). Despite reduction of inputs levels in fish are now only falling slowly after an initially more rapid loss. (Dickson) (10).

Environmental mercury problems due to the chlor-alkali industry have also been reported from Sweden. (Lindqvist *et al.*) (11). The most recent overview from Sweden (Lindqvist) (12), states that internationally, the major sources of Hg emissions to the atmosphere are chlor-alkali factories, waste incineration plants, coal (and peat) combustion units and metal smelter industries.

An extensive literature documents problems caused by mercury discharges from chlor-alkali production. Chlor-alkali emissions have dominated local mercury budgets and caused problems in areas of Finland, Portugal, Italy, Canada and Norway and India. These studies are indicative of a large problem. Overall 39% of global production and 76% European chlorine production is by mercury cell. The export of mercury cells to developing countries may increase as this production method is phased out in the North in response to regional legislation and international agreement. 3g of mercury lost per tonne of chlorine produced by mercury cells could represent up to 14% of the global mercury budget estimated by Nriagu & Pacyna (13). Certainly this is not the historical problem which industry considers it to be (2).

**Organic Contamination** Organic contamination arising from the decomposition of graphite electrodes has largely been eliminated in the US and Europe by the substitution of dimensionally stable titanium electrodes. Prior to this, electrode sludges (Leddy *et al.*) (14)

led to widespread environmental contamination with persistent organochlorines. (Kaminsky & Hites) (15); (Kjeller et al.) (16). The full extent of the problem is not known.

**Energy Consumption** In 1973 the electrolytic energy requirement of the US chlor-alkali industry was just under 0.5% of the total utilisation of the continental US. Nisbet (27) notes that electricity consumption can represent over 70% of the variable costs of production while other estimates place this between 40% and 60%. Power consumption by the major UK producer is estimated at 1% of the national grid power output (4). Recently it has been reported that UK production is threatened by a removal of subsidies on electricity supplied to the chlor-alkali sector. Clearly, the energy efficiency of the plastic requires exhaustive evaluation before the resource efficiency claimed by industry (2) can be justified.

### **EDC and VCM Manufacture**

**EDC Production** The global production of EDC is around 17,500 Kt (EDC) per annum (CEC) (17). It has been estimated that 12.5 million people are exposed to EDC from manufacturing facilities in the US (Clement Associates) (18) at levels which may exceed 10ppb. Hydrolysis half life of EDC in water is estimated at 20 years and EDC is highly toxic in aquatic systems. Atmospheric half life is estimated at 3-4 months. EDC is regarded as a probable human carcinogen (Umweltbundesamt) (19).

EDC is separated from "light" and "heavy" ends and tarry residues by distillation. Process vents can be a major source of emissions from some plant designs. EDC production has been identified as a potential source of PCDDs and PCDFs (19). The heavy ends from EDC production can be used in the onward production of tri- and tetrachloroethene by oxychlorination or chlorinolysis. Final residues comprise highly chlorinated, hazardous, materials. The trading of EDC residues as a commodity will in future be influenced by falling market demand for CFCs and chlorinated solvents.

From the figures in Table 1, it can be calculated that 290 tonnes of lights and 230 tonnes of heavies are produced for every 100 kt of VCM production. Figures for a Belgian plant suggest that heavy end arisings were between 5450-6800 tonnes for a nameplate capacity of 200kt of VCM. 3600 tonnes of EDC were also reported as released annually. The production and fate of these residues by the industry as a whole awaits a detailed evaluation.

**VCM Production** The thermal cracking of EDC can lead to a substantial waste arisings of spent copper catalyst (2). Recent investigations of sediments from the Rhine River have shown increased concentrations of dioxins near a VCM plant in the Netherlands. It has been estimated that up to 80% of the dioxin content in these sediments is caused by VCM-production (Evers) (21); Evers et al.) (22). Researchers have since commented that information about possible waterborne dioxin emissions at other VCM plants is only sporadic and that the problem requires further study. (Christiansen et al.) (23).

**TABLE 1 - The unit ratios of organic contaminants for an integrated air based oxychlorination VCM plant. Figures are given in kg of material produced per Kg of VCM (20)**

Component	Plant Unit Ratio kg/kg VCM
<b>Raw Materials</b>	
Ethene	0.4656
Chlorine	0.5871
Air	0.7322
Water	0.0171
<b>By products</b>	
Lights	0.0029
Heavies	0.0023
Vents	0.6727 (0.5779 N <sub>2</sub> )
Aqueous streams	0.1218

Reliable estimates of vinyl chloride monomer releases from production facilities are not readily available. Maltoni (24) details research establishing the link between VCM and various cancers in laboratory animals. Angiosarcoma has been related to occupational exposure of VCM as have increased incidences of liver, lung and brain tumours in humans and animals. (Ware) (25), (Clement Associates) (26). Exposure to VCM is also associated with male reproductive disturbance including lowered androgen levels and impotence. Oedema during pregnancy (preeclampsia) has been reported in occupationally exposed women. Statistically significant elevation of congenital abnormalities has been reported in communities close to VCM/PVC plants (26).

### **PVC Manufacture**

Rigid or unplasticised PVC accounts for over 63% of PVC consumption on Western Europe and around 55% in Japan and the US. The finished product contains a variety of fillers, heat stabilisers, impact modifiers, pigments, flame retardants, biocides and lubricants. Plasticisers are added to produce flexible PVC (Wendland) (28).

**Fillers** Common mineral fillers for plastics including PVC are talc, barite, asbestos, dolomite, kaolinite calcium carbonate, mica and silicon dioxide. Non-mineral fillers include metals, metal oxides graphite, aluminium hydroxide, soot and organic fillers such as nutshells and corn husks (28). Such fillers can comprise up to 80 % of the final PVC product in, for example, flooring material. Fillers are not generally considered as problematic but there are obvious hazards in the use of known carcinogens such as asbestos and soot. Fillers such as kaolinite and dolomite exert environmental impact through mining and quarrying.

**TABLE 2 - Percentage composition of PVC products (28)**

PRODUCT	PVC	Filler	Plasticiser	Stabilisers
Cable coat	42	36	21	0.01
Films	32	51	16	0.02
Flooring	28	56	14	0.01
Pipes	93	0.05	--	0.02
Windows	78	12	--	0.04

**Plasticisers** 77% of the 1 million tonnes of plasticisers produced in Europe annually are used in PVC manufacture. The major group are the phthalates and fifteen of these are in common use (28). The most important is Di-2-ethylhexyl-adipate, commonly known as DEHP. Production estimates vary between 2.7 and 4 million tonnes globally (Wams) (29). DEHP comprises 50 % of the phthalate market in Germany (28). DoE (30) estimates global use as 2.7 million tonnes of which DEHP accounts for over 50%. Losses to the environment as a result of PVC production are a significant proportion of the total. Exposure to DEHP may result from the calendaring process (23).

**Stabilisers** The main groups of stabilisers used in PVC are organotin compounds, metal soaps, lead compounds, organic compounds and co-stabilisers. The major function of these compounds as additives is to render the finished plastic thermally stable at temperatures likely to be experienced in use (28).

**Lubricants** A variety of lubricants are used in PVC manufacture. stabilising additives. PVC production accounted for 58% of the use lubricants in the plastics industry in Western Europe in 1970 (28). The most common types are the fatty acids, paraffins, fatty acid esters and metal soaps. In 1985 approximately 20% of the 28,000 tonnes of lubricants used in Western European PVC processing contained metals such as lead and cadmium.

**Pigments** Concentrations of pigments in PVC range from 0.5% for the organic pigments to 2% for inorganic compounds (28). The organic pigments comprise a variety of azo-, nitro- and carbonyl dyes some of which are synthesised using chlorinated intermediates. These dyes are very likely to contain PCBs as a contamination. Contamination with PCDDs/PCDFs may occur since azo-pigments are synthesised from chloroaniline. Inorganic pigments are based around metal compounds including zinc, antimony, cadmium, lead, molybdenum, titanium and chromium. In addition, small quantities of optical brightener are often added, together with UV-stabilisers.

**Fire Retardants and Smoke Suppressors** The major fire retardants and smoke suppressors added to PVC include antimony trioxide, phosphate esters, chlorinated paraffins and aluminium hydroxide, boron compounds, molybdenum trioxide (28). Around a quarter of all flame retardants produced are used in the PVC industry.

**Foaming Agents** The most important blowing agents for PVC foam are air, CO<sub>2</sub> and N<sub>2</sub> (28). Other agents used include trichlorethylene and CFCs. These materials tend to escape fugitively from the end

product. Although data are scarce, azodicarbonamide appears to be an important agent at addition levels of between 0.3% to 1.0%. Gases given off by the foam include carbon dioxide and ammonia and a variety of nitrogenated solid residues remain in the PVC foam. The toxicological significance of these residues remains largely unknown.

**Biocides** Biocides are added to soft PVC to prevent the biodegradation of plasticisers by microorganisms (28). Landfill liners, carpets, cable covers and shower curtains are treated to prevent fungal degradation and insect attack.

Although additives can comprise 60% or 80% of the finished product the environmental effects of their production and use have not been addressed comprehensively to date. Life cycle analysis needs to take the high potential content of additives into account since they may significantly increase the potential environmental impact of plastic products made from PVC. Some toxic metal additives are no longer used in the production of PVC but items containing such additives will remain in use and enter the waste stream over a long period. Many PVC items are expected to remain in use for relatively long periods (2).

## **ENVIRONMENTAL ASPECTS OF PVC USE**

### **Additives**

PVC additives are mixed rather than chemically combined with the finished plastic and there is scope for environmental release of this after manufacture. Klassen *et al.* (31) note that DEHP is ubiquitously distributed in virtually all soil and water ecosystems. The consequences of distributing such synthetic compounds throughout the globe have not been fully assessed despite recognition as a potential problem some twenty years ago.

Estimates of processing losses of DEHP vary between 330 and 2460 tonnes per annum in the UK (30). Plasticisers do not form a stable chemical bond with PVC. They may be leached from the finished plastic, volatilised to the air or be degraded by microbes. Estimates of these losses vary from between 0.01%-0.35% over the lifetime of products (30).

The migration of DEHP and DOA (dioctyladipate, a similar phthalate plasticiser) from cling film into fatty foods has led many manufacturers to offer non-PVC film, or to reduce the content of DEHP (MAFF) (32; 33). In Switzerland the use of DEHP for the manufacture of toys for children aged less than three years was banned in 1986 and in Germany its use in teething rings is "not recommended". In the Netherlands the potential ecotoxicological consequences appear better recognised - it is on the priority list of environmentally toxic substances. DEHP is also a priority pollutant in the USA (SRSU) (34).

### **Accidental Fires**

In fires involving PVC, corrosive hydrogen chloride (HCl) is readily formed (Plehn & Lohrer) (35). Thermal decomposition

processes begin at temperatures around 100 degrees Celsius, and high concentrations of HCl may be generated long before the presence of visible fire (Wallace) (36). Additionally, the HCl given off during fires reacts with the many additives present, creating further toxic fumes. Heavy metals contained in PVC stabilisers will be released in fires (35).

The formation of PCDD's and PCDF's has been linked to PVC use and decomposition for some time (Theisen) (37). Dangerous compounds may additionally be formed from the brominated flame retardants which are often added to plasticised PVC. These additives, including polybrominated aromatic compounds, may form polybrominated dibenzodioxins and -furans (PBDD's and PBDF's) (37). The German Ministry of Health (BGA) and the German Federal Office of the Environment (UBA) have recommended that chlorine and bromine containing plastics are excluded from areas susceptible to fire (Lukassowitz) (38). The German Ministry of Health recommends that fires involving even small amounts of PVC in flats schools offices and shops, should be cleaned up by specialists.

### ENVIRONMENTAL ASPECTS OF PVC DISPOSAL

Currently, as with most plastics post-consumer recycling of PVC is at a very low level (2). Recycling is considerably hindered by the wide range of additives producing a complex waste from multiple-sources. PVC additives also have to be considered in the context of other disposal routes. In landfill, (28) additives such as plasticisers may leach in the presence of organic solvents. Incineration may also release toxic compounds as a result of mobilisation of the metal content. PVC is estimated to comprise some 50%-75% of the total chlorine in domestic landfill. (VKE) (39). Hydrogen chloride evolution from a burning landfill cannot be predicted easily but heavy metals from additives can form soluble metal chlorides. PVC is a significant environmental vector of metals. Almost half of processed PVC contains lead-based stabilisers (approximately 20,000 tonnes lead/annum in Germany alone); organo-tin stabilisers are prevalent in PVC food packaging. Barium/cadmium stabilisers are common in PVC for outside and construction uses.

The incineration of PVC will mobilise metals and contribute to dioxin formation. PVC present as part of the scrap charge to steel mills may contribute to the emissions of chloroorganics reported by Oberg & Allhammar (40) and Tysklind (41) including dioxins. The evolution of PCDDs/PCDFs from the recycling of PVC coated wire has been described by Marklund *et al.* (42) from a copper smelter in Sweden. The reprocessing of copper scrap often involves the precleaning of the material by combustion or pyrolysis, followed by smelting (Christmann) (42). The pyrolysis of PVC cable coatings has been shown by these workers to produce PCDDs and PCDFs in significant quantities.

### CONCLUSION

This limited overview of the potential environmental impacts

of PVC manufacture use and disposal indicates that environmental impacts can result at any phase of the life cycle. In many cases the full impacts are unknown but clearly need to be factored into life cycle analysis in a more meaningful way than has been attempted to date. Given the nature of the product and its additives, it is unlikely that PVC can conform to the requirements of a clean technology framework. Accordingly, uses of PVC need to be evaluated comprehensively with a view to their substitution with environmentally sound alternatives.

#### REFERENCES

- (1) Davidson, J.A. & Gardner K.L. (1982). Kirk-Othmer Encyclopedia of Chemical Technology 3rd Edition, Volume 23. Publ. Wiley Interscience, New York. 886.
- (2) Norsk-Hydro (1992) PVC and the Environment. Oslo, Norway
- (3) Johnson D. (1990) The Future of Plastics. Financial Times Business Information.
- (4) Furnivall, I. (1989) (Ed) Investing in a Green Europe. Publ. UBS, Phillips and Drew, London
- (5) Shelley (1990) European Chemical News 55, 20
- (6) Johnston, P.A. & Stringer R.L. (1993). Proc. 1st Irish Conference on Air Pollution, February 11-12, Dublin.
- (7) Airey, D. & Jones, P.D. (1982). Wat. Res. 16, 565
- (8) Johnston, P.A., Stringer, R.L. & French, M.C. (1991) Sci. Tot. Environ. 106, 55
- (9) Norton, M.G., Franklin, A., Rowlatt, S.M., Nunny, R.S. & Rolfe, M.S. (1984). MAFF Direct. Fish. Res., Lowestoft, 76, 1
- (10) Dickson, R.R. (Ed). Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft, 17
- (11) Lindqvist, O., Jernelov, A., Johansson, K. & Rhode, H. (1984). Nat. Swed. Environ. Protect. Bd. Report SNV PM-1816.
- (12) Lindqvist, O. (Ed) (1991). Wat. Air Soil Poll. 55, 262
- (13) Nriagu & Pacyna (1989) Nature 333, 134
- (14) Leddy, K.K., et al. (1978). The Kirk-Othmer Encyclopedia of Chemical Technology. Volume 1, Wiley-Interscience.
- (15) Kaminsky, R. & Hites, R.A. (1984). Environ. Sci. Technol. 18, 275
- (16) Kjeller, L.-O. et al. (1991). Proc. Dioxin '91, September 23-27 Research Triangle Park, N. Carolina.



- (17) CEC (1990) Organo-chlorine solvents. Commission of European Communities/Royal Society of Chemistry, London
- (18) Clement Associates (1989) U.S. Public Health Service. Contract Report No: 205-88-0608.
- (19) Nolte, R.F. & Joas, R.F. (1992) Handbuch Chlorchemie I. Umweltbundesamt Texte 55/91.
- (20) Rossberg, M., et al. (1986). Chlorinated Hydrocarbons. Ullmann's Encyclopedia of Industrial Chemistry 5th Edn. Publ. VCH Publishers NY. Vol A6, 233
- (21) Evers, E.H.G., Ree, K.C.M. & Olie, K. (1988) Chemosphere 17, 2271-2288
- (22) Evers, E.H.G. (1989) University of Amsterdam MTC Publication No: MTC89EE.
- (23) Christiansen, K., Grove, A., Hansen, L.E., Hoffmann, L., Jensen, A.A., Pommer, K. & Schmidt, A. (1990) Danish Ministry of the Environment Project No: 131, Summary 28pp.
- (24) Maltoni, C. (1986) Vinyl chloride carcinogenicity: Available scientific evidence and control measures. Association of Plastics Manufacturers in Europe 36pp.
- (25) Ware, G.W. (1989) Rev. Environ. Contam. Toxicol. 107, 166
- (26) Clement International Associates (1991). US. Department of Health and Human Services, Washington DC Contract Report No: 205-88-0608
- (27) Nisbet, A. (1989) Chemical Business December 1989, 24
- (28) Wendland F. (1988) Kernforschungsanlage Juelich GmbH. Interener Bericht: KFA-STE-1B-8/88.
- (29) Wams, T.J. (1987) Sci. Tot. Env. 66, 1
- (30) DoE (1991) Report No: TSD/2. Department of the Environment
- (31) Klaassen, C.D., Amdur, M.O. & Doull, J. (1986) Casarett & Doull's Toxicology. Macmillan, New York.
- (32) MAFF (1987) Ministry of Agriculture Fisheries and Food, UK. Food Surveillance Paper No: 21, Publ HMSO, London.
- (33) MAFF (1990) Ministry of Agriculture Fisheries and Food, UK. Food Surveillance Paper No: 30. Publ HMSO London.
- (34) SRSU (1990) Sondergutachten des Rates von Sachverständigen für Umweltfragen. Abfallwirtschaft.
- (35) Plehn, W. & Lohrer, W. (1987) Rheinhalt. Luft 47, 7
- (36) Wallace, D.N. (1981) Dangers of polyvinyl chloride wire insulation decomposition. J. Combust. Toxicol. 8, 10

- (37) Theisen, J. (1991) Report No: UBA-FB 104-09-222  
UmweltBundesamt, Berlin. 25pp.
- (38) Lukassowitz, I. (1990) Bundesgesundheitsblatt 8/90 pp350-354
- (39) VKE (1986): Informationsschrift. PVC- Ursache fuer Dioxin-  
Bildung. -Frankfurt/M. Karlstr.
- (40) Oberg, T. & Allhammar, G. (1989) Chemosphere 19, 711.
- (41) Tysklind, M., Soderstrom, G., Rappe, C., Hagerstedt, L.-E. &  
Burstrom, E. (1989). Chemosphere 19, 705.
- (42) Marklund, S., et al. (1986). In: Chlorinated dioxins and  
dibenzofurans in perspective. Lewis Publishers MI.
- (43) Christmann, W., Kasiske, D., Kloppel, K.D., Partsch, H. &  
Rotard, W. (1989) Chemosphere 19, 387.