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CHEMICAL HAZARDS IN THE PLASTICS INDUSTRY

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Since continuing technical development of new processes and products in the plastics industry must be expected in the years to come, it is increasingly essential to work toward the toxicity testing of new chemicals. The many untested and suspected chemicals used in the field of plastics and synthetic elastomers demonstrate the importance of control of both the occupational environment and the distribution of such chemicals from occupational sources. In the plastics processing industry it is necessary to evaluate possible health hazards of the fumes from plastics at high temperatures.

INTRODUCTION

The annual production of monomers and polymers in the plastics and elastomers industry over the past 30 yr has greatly increased (Fig. 1). In 1977, three countries—the United States, West Germany, and Japan—accounted for more than 60% of the total plastics production worldwide (Table 1). As far as the per capita use of plastics in different countries is concerned, Finland is first, using 92 kg per person in 1977 (Table 2).

Plastic materials have an extremely wide range of uses, and thus humans are very likely to be exposed to them both occupationally and through air, water, and food. Furthermore, there is close physical contact with manufactured products used in packaging, consumer products, construction materials, transport applications, textile fibers for clothing and furnishings, rubber goods, adhesives, insulation, electronic and electrical products, paints, etc. (Fishbein, 1979).

Polymeric materials were originally thought to be biologically inert. It must be borne in mind, however, that the biological effects of the plastic may include those of the monomer, of low-molecular-weight oligomers, or of additives such as plasticizers, stabilizers, curing agents, and catalysts. Thermal degradation of a polymer may take place when the material is placed or handled at high temperatures, producing additional risks of worker exposure to these chemicals.

PRODUCTION HAZARDS OF PLASTICS

The number of plastic materials is large and the list is growing. The large number of processes by which plastics can be produced is a further complication. However, nearly all plastics can be classified into two groups: thermosetting materials and thermoplastic materials. Thermosetting plastics are cured, set, or hardened into a permanent shape. This curing is an irreversible reaction and usually occurs under heat and pressure. Thermoplastics are not cured or set under heat; when heated, they soften to a fluid state. On cooling in a mold, thermoplastics harden and take the shape of the mold.

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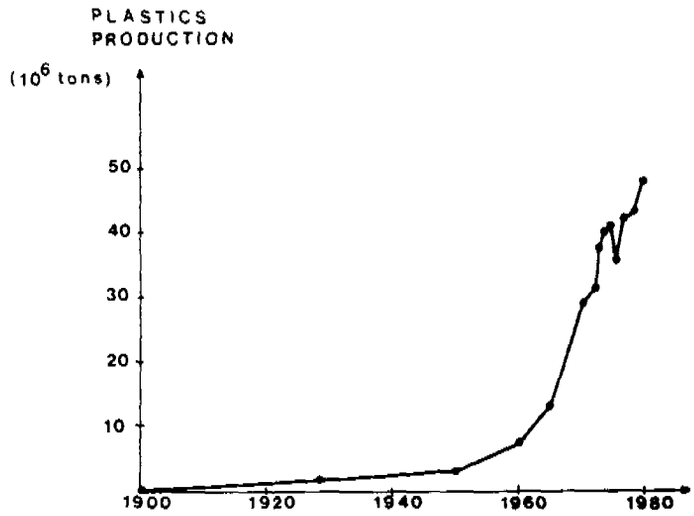

FIGURE 1. Plastics production worldwide.

In the three main chemical processes yielding polymers—polymerization, addition, and condensation—many additives and intermediates are physiologically active as irritants and sensitizers of the skin and the respiratory system (Table 3). Moreover, neurotoxic monomers such as methyl methacrylate and acrylamide have been identified. Neurotoxic organic phosphates are widely used as plasticizing additives.

Ever since vinyl chloride was recognized as a human carcinogen (Creech and Johnson, 1974), there has been increased concern about a number of the monomers used in the manufacture of synthetic polymers in the plastics and rubber industries. The common structural feature of these monomers involves either olefinic or aromatic double bonds, which can be metabolically oxidized to yield oxiranes or arene oxides. Because these are potentially reactive mutagenic or carcinogenic intermediates, long-term toxicity of the monomers from which they derive is suspected. Many of the monomers studied have proved

TABLE 1. Plastics Production in the World in 1977[a]

Country	Percentage of total production
United States	34.5
West Germany	14.6
Japan	13.6
U.S.S.R.	7.2
France	6.2
Italy	5.8
United Kingdom	5.6
Spain	2.3
Other	10.1
	99.9

[a] From NOWEA Presse-Informationen (1979).

TABLE 2. Use of Plastics in 1977[a]

Country	Amount per capita (kg)
Finland	92
West Germany	89
Sweden	79
Austria	71
United States	64
Switzerland	60
France	48
United Kingdom	44
Japan	41

[a] From NOWEA Presse-Informationen (1979).

TABLE 3. Main Classes of Plastics, Basic Components, and Occupational Occurrence[a]

Polymer	Component	Occupational occurrence of active components
Polyvinyls[b]	Vinyl chloride	Mutagenic, carcinogenic
Polyurethane[c]	Diisocyanates and polyhydroxy compounds	Diisocyanates powerful respiratory irritants and sensitizers
Polyethylene[b] and propylene	Ethylene and propylene	Moderately narcotic, toxicity?
Polyacrylics[b]	Acrylic acid, methyl methacrylates, acrylonitrile, and acrylamide	Methyl methacrylate and acrylamide neurotoxic, acrylonitrile mutagenic and carcinogenic
Polyamides[b] (nylon 66)	Adipic acid and hexamethylenediamine or caprolactam (nylon 6)	Diphenyls used in heat transfer can be neurotoxic and carcinogenic
Polytetrafluoroethylene[b]	Tetrafluoroethylene	"Polymer fume fever"
Polystyrene[b]	Styrene (vinyl benzene)	Mutagenic
Polyesters (saturated[b])	Alkyls, MAA[d], and polyalcohols (glycerol)	MAA produced by oxidizing toxic solvent benzene
Polyesters (unsaturated[c])	MAA[d] or PAA[e] and ethylene glycol in styrene	Fiber production—dimethylterephthalate and a diol (ethylene glycol) dissolved in styrene
Phenoplasts[c] and aminoplasts[c]	Polycondensates of phenols and aldehydes, urea and aldehydes	Formaldehyde mutagenic, carcinogenic?
Acrylonitrile-butadiene-styrene[b]		All mutagenic
Epoxy resins[c]	Epichlorhydrin and polyhydroxy compounds, bisphenol A	Mutagenic, carcinogenic?

[a] Modified from Kay (1977).
[b] Thermoplastic.
[c] Thermosetting.
[d] Maleic acid anhydride.
[e] Phthalic acid anhydride.

to be mutagens and/or carcinogens, but considerably more research is needed to evaluate the final health significance of these data (Table 4).

In the production of plastics, closed processes are usually employed, since many of the components are gases or volatile liquids. The main occupational exposure to reactants and products probably occurs when reaction equipment is cleaned out. Since reactions of plastic components do not generally go to completion, residual components are present, either occluded or dissolved, in the final products. Hence production workers bagging the finished plastic are probably exposed not only to plastic dust but also to gaseous monomers. Table 3 lists the main classes of plastics and examples of occupational occurrence of reactive components. The data in Table 5 indicate that there are toxicologically active components even among the auxiliary substances used in the manufacture of plastics.

PROCESSING HAZARDS

Plastics are processed at temperatures high enough to produce a viscous product that permits the blending in of various auxiliary substances and allows for shaping, such as calendering to produce thin film and sheets. Thus there is a potential for exposure to gaseous and volatilized unreacted raw materials, auxiliary substances added before molding, and decomposition products.

Plastics partially degrade under the influence of agents such as ultraviolet light, oxygen, ozone, sulfur dioxide, nitrogen oxides, etc. They can also be broken down rapidly by high temperatures.

The processes, temperatures, machinery, and raw materials vary greatly in the plastics processing industry and the nature and amounts of different thermal decomposition products depend on all these parameters. The mechanisms of thermal degradation are often very complicated, leading to a wide variety of products that can be emitted to the workroom air. Some examples of thermal degradation products that can arise from plastics at temperatures of 150–500°C are given in Table 6. Among these are a number of known mutagens and/or carcinogens (e.g., benzene and styrene). Reports on exposure levels of thermal degradation products in the processing industry are, however, lacking, so that no definitive conclusions

TABLE 4. Mutagenicity and Carcinogenicity of Some Monomers and Plastics Chemicals[a,b]

	Mutagenicity		Chromosomal aberrations		Carcinogenicity	
Chemical compound	*Salmonella typhimurium*	*Drosophila*	Animals (bone marrow)	Humans (lymphocytes)	Animals	Humans
Acrylonitrile	+	ND[c]	ND	–	+	?
Aromatic epoxy resins	+	ND	ND	ND	?	ND
Chloroprene	+	+	+	+	?	?
Epichlorohydrin	+	+	ND	+	+	?
Styrene	+	+	+	+	?	?
Vinyl bromide	+	ND	ND	ND	+	ND
Vinylidene chloride	+	ND	ND	ND	+	ND
Vinyl chloride	+	+	ND	+	+	+

[a] From Hemminki et al. (1979), Bartsch et al. (1979), IARC (1979), Lee et al. (1978), NCI (1979).

[b] Sufficient evidence for mutagenicity or carcinogenicity in animals is indicated by a plus sign; limited evidence is indicated by a question mark.

[c] No data.

TABLE 5. Auxiliary Substances Used in Plastics Manufacture and Processing[a]

Type	Example	Occupational occurrence of active substances
Fillers and reinforcements	Fibers of asbestos, carbon black, and glass	As dust at addition; may run 10–15% in finished product; asbestos carcinogenic
Plasticizers	Dialkyl phthalates, alkyl or aryl phosphates	Low-volatility heavy solvents to increase moldability of plastics; content to 60%; some skin irritation, enzyme inhibitors, and neurotoxins
Colorants—dyes and pigments	Transparent organic dyes, opaque pigments—chrome yellow, titanium dioxide	Organic dyes added in volatile solvents that are narcotic and skin-defatting; pigment dust may occur on addition or mechanical stress
Solvents	Toluene, benzene, ethyl and amyl acetates, chlorinated hydrocarbons	Provide milieu for some polymerizations; volatile; fat-soluble; hepatotoxic or leukemogenic (benzene)
Stabilizers	Dialkyl tin esters; lead soaps and salts; Ba, Cd, Zn soaps	To prevent heat degradation of polyvinyl chloride; stabilizer content up to 10%; hazard undetermined
Antioxidant stabilizers	Butylated hydroxytoluene, dilauryldithiopropionate hydrazides, triazoles	To counteract atmospheric oxidation of unsaturated double bonds (e.g., in polyesters); occupational hazard undetermined
Ultraviolet-absorbing stabilizers	Benzophenones, triazoles, organonickel compounds	To protect against oxidation; hazard undetermined but organonickel exposure potentially dangerous
Biological preservatives	Copper quinolinolate, organomercurials, tributyltin oxide	No evidence that these preservatives constitute an occupational hazard in plastics, but they have demonstrated toxic potential
Foaming agents	Azoisobutyronitrile, chlorinated hydrocarbons, hydrogen peroxide	Release vapor during setting of plastics; in atmosphere during foaming; released from bubbles by mechanical stress; toxic
Lubricants and flow control agents	Ca, Zn, and Pb stearates and petroleum wax	Interpose between linear macromolecules; can be used only in small quantities; occupational hazard undetermined
Flame retardants	Organophosphates, organohalogens with antimony oxide synergist	Compounds of low volatility but high toxicity; hazard undetermined
Catalysts and accelerators	Organic peroxides, alkylaluminum compounds, cobalt naphthenate	All low-volatility compounds; peroxides present eye hazard (splashing); Al compounds explosive
Antistats	Quaternary ammonium compounds, organic phosphates, stannous chloride	Low-volatility compounds; occupational hazard undetermined

[a]Modified from Kay (1977).

about health hazards can be given. These evaluations are needed because of the increasing number of workers in the expanding processing industry. Below we will discuss in more detail the mechanisms of thermal degradation and the evolution of possible degradation products.

Monomers

The appearance of monomers among thermal degradation products of plastics depends on the degradation mechanism of the plastic. Thermal degradation of polymers can be

TABLE 6. Thermal Degradation Products of Some Polymers in Air at 150–500°C[a,b]

Polymer	Monomer	Aliphatic hydrocarbons, C_1–C_6 . . . C_n (alkanes, alkenes, alkadienes)	Aromatic hydrocarbons, C_6–C_8 . . . C_{10}	Oxidized aliphatic compounds, C_1–C_4	Oxidized aromatic compounds, C_6–C_8	Aliphatic nitriles	Aromatic nitriles	Halogenated hydrocarbons	Gases	Aerosols
Polyolefins	(+)[c]	+++	(+)	++	–	–	–	–	+++ (CO)	+++
Polyethylene										
Polypropylene										
Polystyrene	++++	+	++	+	++	–	–	–	(+) (CO)	++++
Copolymers										
ABS, SAN[d]	++++	+	++	+	++	+	+	–	(+) (CO) + (HCN)	+++
SB[e]	++++	++	+	++	+	–	–	–	+ (CO)	+++
Polyacrylonitrile	++					++	(+)		+ (CO) + (HCN)	
Polyvinyl chloride	(+)	+	+++ (benzene)	+	(+)	–	–	(+)	+++ (CO) ++++ (HCl)	++
Polyurethanes	+	++	+	++		(+)	(+)		+++ (CO) ++ (HCN) + (NH_3)	++

[a] From Boettner et al. (1973) and Hoff (1977).
[b] The proportional concentration among the decomposition products is indicated, with + denoting the lowest and ++++ the highest.
[c] (+) denotes probable occurrence of trace amounts.
[d] ABS, copolymer of styrene with acrylonitrile and butadiene; SAN, copolymer of styrene with acrylonitrile.
[e] SB, copolymer of styrene with butadiene (high-impact polystyrene).

divided into two general categories: random chain scission and depolymerization (Conley, 1970).

The scission occurs at random points along the chain, leaving fragments of different molecular weights. It can be assumed that practically no or only small amounts of the monomer are liberated in this type of thermal degradation. This is the case with, for example, polyolefins and polyvinyl chloride.

The second type of degradation is depolymerization, where monomer units are released (e.g., polystyrene, polymethyl methacrylate). Depending on the composition of the polymer, both of these mechanisms may also occur simultaneously.

Aliphatic and Aromatic Hydrocarbons

Aliphatic and aromatic hydrocarbons are released from plastics by the random scission mechanism. The aliphatic hydrocarbons appearing in the gaseous phase are relatively low-molecular-weight compounds, having 0–2 double bonds. The aromatic hydrocarbons are alkyl benzenes. The alkyl group can also contain double bonds. Even benzene (C_6H_6) is reported to develop (e.g., from polyvinyl chloride) in significant amounts (Boettner et al., 1973; Hoff, 1977).

Oxidized Aliphatic and Aromatic Compounds

The action of oxygen during thermal degradation causes the most important group of secondary reaction products. The reaction is oxidation of free hydrocarbon radicals, with peroxy radicals, hydroperoxides, and peroxides acting as intermediates (Conley, 1970). The end products of oxidation are acids, ketones, and aldehydes. After oxidation of low-molecular-weight aliphatic hydrocarbons, formic acid, acetic acid, propionic acid, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde, and acrolein are generated. Aromatic hydrocarbons produce similar compounds, including benzoic acid, cinnamic acid, acetophenone, benzaldehyde, and cinnamaldehyde. Other oxygen-containing compounds (e.g., alcohols) can appear among thermal degradation products if the plastic exposed to heat is based on polyols or polyethers.

Nitriles

Both aliphatic and aromatic nitriles come from plastics that contain nitrogen, and especially nitrile groups.

Halogenated Hydrocarbons

Halogenated hydrocarbons are generated from halogen-containing plastics, such as polyvinyl chloride and polytetrafluoroethane (Teflon).

Gases

Carbon monoxide and carbon dioxide are common oxidation products. The amounts seem to be highest when plenty of low-molecular-weight hydrocarbons are produced.

Hydrogen chloride is released from polyvinyl chloride at moderately low temperatures before the beginning of hydrocarbon chain scission. Nitrogen-containing plastics produce hydrogen cyanide and, at high temperatures, nitrogen oxides.

Aerosols

The aerosol phase contains dimers, trimers, and other oligomers, as well as other fragments of polymer chains having the same elementary composition as the plastic itself. New double bonds and oxidized functional groups joined to molecules may also appear.

Free Radicals

When oxidation reactions go through radical formation, the thermal degradation products may contain free radicals, hydroperoxides, and peroxides. Free alkoxy radicals, which exist long enough to reach the breathing zone of workers, have been detected among the thermal degradation products of polyethylene and polystyrene (P. Pfäffli et al., in preparation).

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