

EMISSION CONTROL:

Control Methods for Vinyl Chloride

Some tips on how PPG handles sample collection and analyses of VCM, and on how it handles the tricky aspects of loading operations.

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Vinyl chloride monomer (VCM) is hazardous not only because it is highly flammable, but also because of its toxicological effect on human beings. Consequently, the design and operating procedures of our vinyl chloride facilities at Lake Charles, La., and Caribe, P.R., provide that the release and exposure of VCM to personnel be minimal. This article describes two procedures that we have adopted, which have contributed to improved VCM confinement and employee exposure control.

Sample collection and analyses

The first of these techniques involves sample collection and analyses. In our process, quality control sample collection is achieved from different points in the system by attaching the sample cylinder or bomb to a small fitting in a closed loop system, Figure 1. The sample bomb is installed vertically in the system with its stand leg fitting in the top position to prevent overfilling and bomb overpressurization. The bomb is equipped with a safety relief valve as further protection. To assure that the bomb is inserted properly, its fittings are of different sizes. The sample collection lines are small diameter stainless steel tubing. Valves are located as close as possible to the sample bomb connections to minimize the quantity of vinyl chloride in the tubing. Before the bomb is removed, the small amount of vinyl chloride trapped between the valves is released to a remote location, and the tubing between the valves is purged with nitrogen.

The storage of sample bombs within the main or plant laboratories is prohibited, and although these sample bombs were capped between use, a storage rack or cabinet similar to a gun rack is provided, Figure 2. All vinyl chloride bombs must be stored in the cabinet while not in use, and all analyses of samples must be accomplished within a laboratory hood. A flexible line is installed on the gas chromatograph back into the laboratory hood.

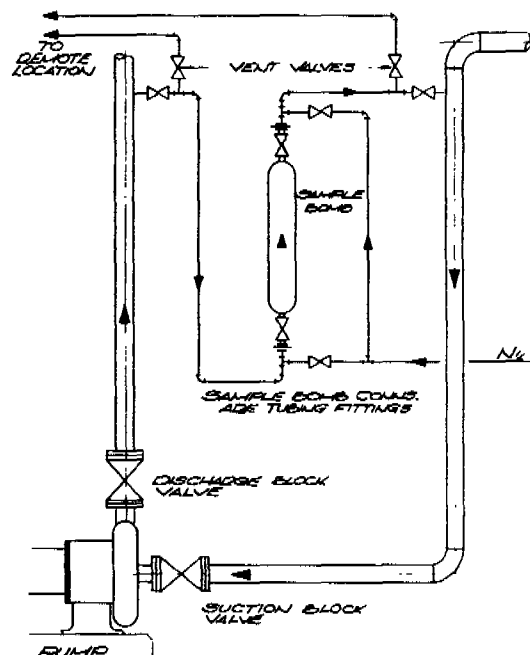


Figure 1. Sampling system.

After the analysis, there is from 600 to 700 ml. of vinyl chloride remaining in the bomb. The sample bombs are capped and returned to the plant where the bomb and its residual contents are inserted during the next sample collection round, returning the unused vinyl chloride to the process.

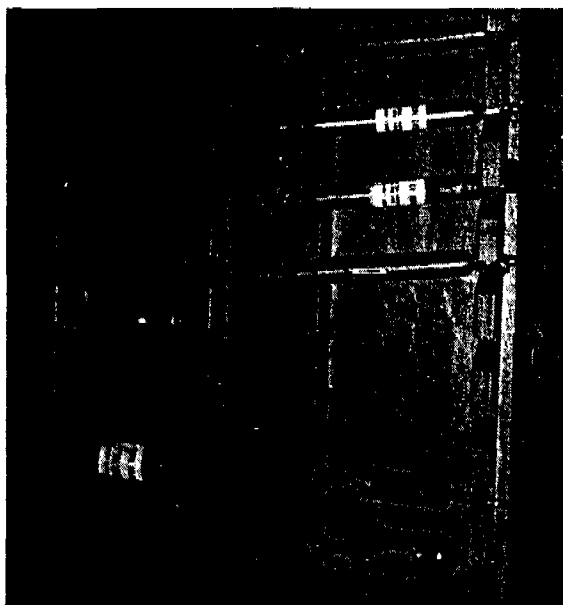


Figure 2. Storage rack for sample bombs.

The bomb valve integrity is checked periodically using a Century organic vapor analyzer. All laboratory hoods where vinyl chloride is used or analyzed have been checked for adequate capture velocity. A baffle has been installed across the front lip of the hood to prevent any vinyl chloride vapors, which are heavier than air, from exiting the hood. The levels of vinyl chloride are routinely monitored.

Loading operations

The second procedure involves loading operations for tank cars, tank trucks, barges, and ships. The potential problem areas are sampling, vehicle emissions, vehicle gauging, and loading line clearing. The oxygen content of empty transportation vehicles is determined prior to loading, and the oxygen analyzer is vented remotely so that personnel exposure is avoided. There are equalizing lines so that vehicle vapor content may be displaced during loading. See Figure 3 for tank car loading. The vapor space material is equalized with the storage tank from which the vehicle is being loaded.

There are a number of ways to determine when a tank car or tank truck is full. The vinyl chloride may be scale loaded (for trucks and cars), or a flow meter may be used. A magnetic level indicator is used by some producers. Special procedures are required so that personnel exposure may be avoided. Exposure may be prevented by using a flexible hose to connect the gauge rod to a bull's eye. Liquid can be observed in the bull's eye when the car is filled. The bull's eye must be vented remotely to an incinerator or tall stack, as shown in Figure 3.

The final problem of loading operations is the clearing of the loading hose so that the hose may be disconnected without allowing exposure. The liquid in the loading hose

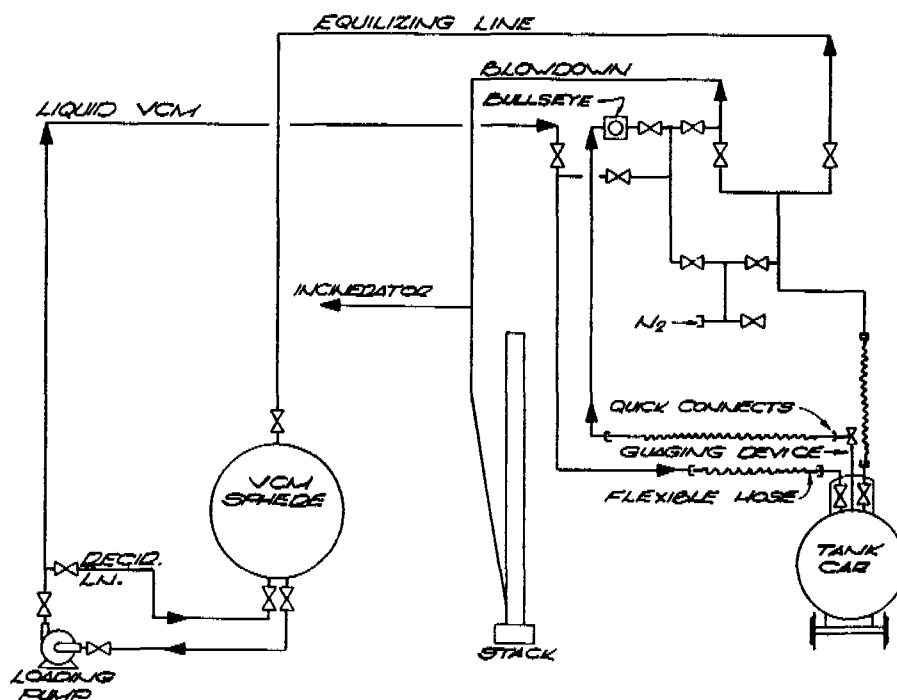


Figure 3. Piping diagram for tank car loading.

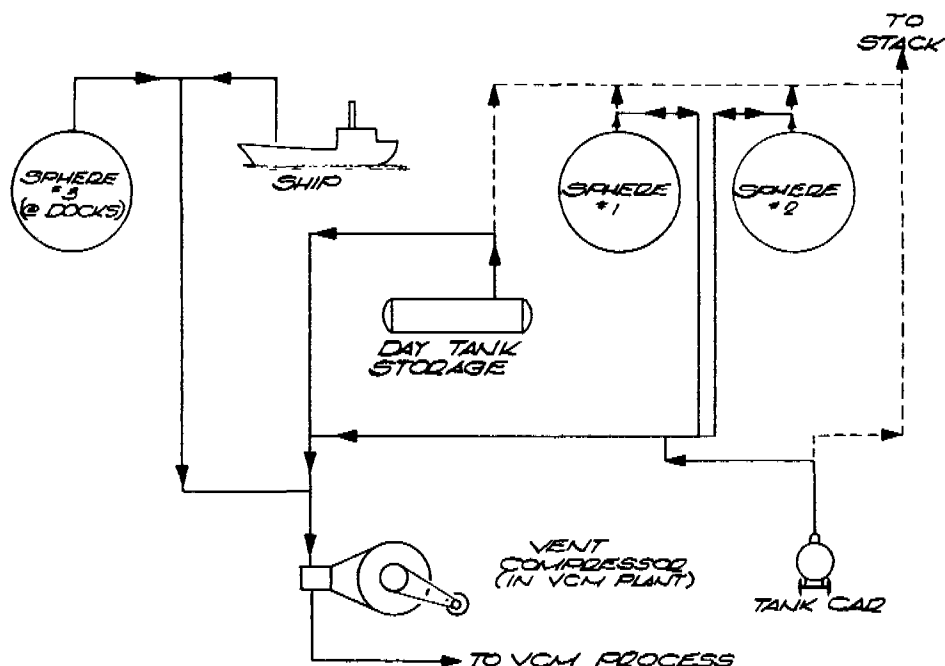


Figure 4. VCM storage vent recovery.

must be pushed (with nitrogen) into the transportation vehicle. The loading line is then nitrogen-purged to an incinerator or tall stack so that vinyl chloride vapors are removed before the hose is disconnected.

The displacement of inerts to the storage tank from transportation vehicles during loading operations will cause the storage tank pressure to be excessive as the tank is refilled unless a recovery system is provided. If a refrigerated vent recovery system is used, some vinyl chloride must be vented to the atmosphere or to an incinerator. A viable alternative is to compress this stream and feed it to the plant process where the VCM is recovered and the inerts, normally nitrogen, accompany the byproduct HCl stream, Figure 4.

Clearing a filter

There are other procedures that may be followed so that equipment can be cleared for maintenance work, or made ready for service without exposing personnel to VCM. In order to do this, some high pressure nitrogen must be used and a sufficient amount of nitrogen must be available for purging. The procedure for clearing a filter for element replacement will provide an example of how most process equipment and piping may be cleared, Figure 5.

The first step is to push the filter liquid into the process piping with high pressure nitrogen. The filter is then blocked and the filter depressurized through a hose to a vent system. The final step is to continue a small nitrogen purge through the filter until VCM is removed. After the elements are removed and replaced, the filter is nitrogen purged to remove air and a leak check is made. The filter is then depressurized and filled with vinyl chloride. When the filter is completely filled, a nitrogen purge is used to clear all hoses to the vent system prior to disconnecting. #

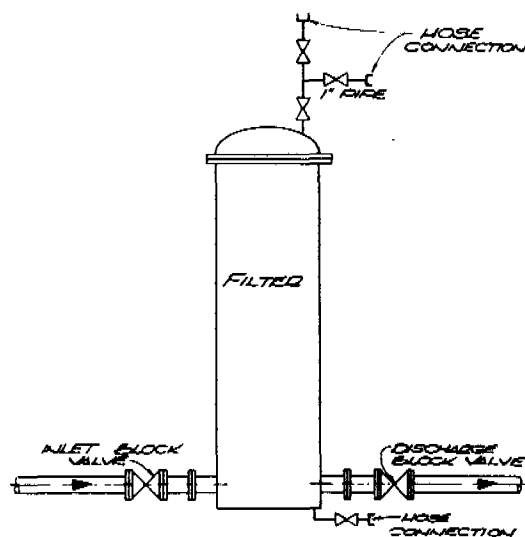


Figure 5. Connections for clearing filter.



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PHARMACOKINETICS OF VINYL CHLORIDE IN THE RHESUS MONKEY

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SUMMARY

The metabolic elimination of vinyl chloride in Rhesus monkeys is a dose-dependent, saturable process, as in rats. Below 200-300 ppm of vinyl chloride (VC) in atmosphere, elimination obeys a first-order law; the clearance rate is much closer to that found in man than the values for rats, mice and gerbils. The maximal velocity of metabolic elimination of VC at high concentrations in Rhesus monkeys is only about half that of rats when related to kg body weight. It is suggested that Rhesus monkeys mimic the quantitative aspects of VC metabolism better than rats or mice.

INTRODUCTION

From experimental research on the mechanism of action of VC it has been inferred that this compound is transformed by the liver to reactive metabolite(s) capable of binding irreversibly to nucleic acids and thereby initiating malignancy [1-3]. It has been postulated that any resolution of dose-response toxicity data for VC must be based on the amounts of VC actually metabolized rather than on exposure concentrations [4]. Attempts to calculate the risk of angiosarcoma in man after exposure to VC must consider possible species differences in the rate of VC metabolism [5]. Some knowledge of the rates of VC metabolism in man is required and in a previous report [6] data for low exposure concentrations were presented. However, it is well known from animal experiments that saturation of metabolic pathways of VC occurs at higher exposure concentrations [4, 5, 7].

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Abbreviation: VC, vinyl chloride.

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As ethical considerations do not allow human experimentation with VC at higher concentrations, the present report evaluates the usefulness of Rhesus monkeys.

MATERIALS AND METHODS

The pharmacokinetics of VC were assessed by methods previously described [7]. The animals were placed in a closed exposure system [8] into which VC was injected and air samples taken for gas-chromatographic analysis. From the decline of VC in the gas phase of the system the processes both of equilibration of the organism with the atmospheric VC and of metabolic elimination were determined [7].

Rhesus monkeys were exposed in a similar system; for a 4 kg animal a system of 200 l was used. This relatively large volume was necessary to introduce the animal's transport cage easily into the closed exposure system and facilitated handling of the animals. In some experiments, metabolism of VC was inhibited by disulfiram; a 4 kg animal received a 0.1 g Antabus® tablet 1 h prior to exposure.

VC was purchased from Linde, Munich, not < 99% pure as checked by gas chromatography. The gas-chromatographic method of determination of VC in air samples taken from the exposure cage and the basic pharmacokinetic analysis of results have already been described [7].

RESULTS

When Rhesus monkeys were exposed to VC at concentrations up to 200 ppm in the closed exposure system, VC disappeared from the atmosphere according to a first-order law. The clearance was 3.55 l/h/kg body weight, but could be decreased by 90% after administration of a metabolic inhibitor,

TABLE I

FIRST ORDER METABOLIC CLEARANCE RATES FOR VINYL CHLORIDE IN RHESUS MONKEY AS COMPARED WITH OTHER SPECIES

	Clearance (l/h/kg body wt.)	Ref.
Rhesus monkey	3.55	
Rhesus monkey, pretreated with disulfiram	0.35	
Rat (Wistar)	11.0	7
Mouse	25.6	6
Gerbil	12.5	6
Rabbit	2.74	6
Man	2.02	6

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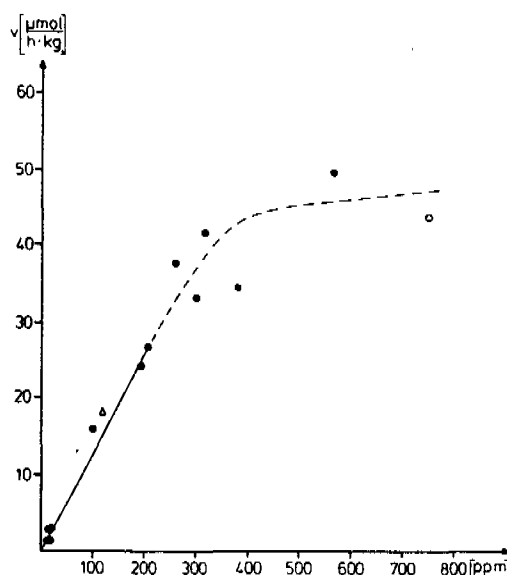


Fig. 1. Metabolic elimination of vinyl chloride in the Rhesus monkey at different concentrations of atmospheric exposure. Different symbols represent different sets of experiments with different animals.

disulfiram (Table I). A comparison of the metabolic clearance of VC in the Rhesus monkey with appropriate values for other species is given in Table I.

In further experiments determinations of the rates of metabolic elimination of VC have been carried out at multiple ranges of atmospheric concentration of VC. In Fig. 1 the absolute rates of metabolism are plotted against the exposure concentrations. First-order kinetics apply in the lower concentration range, up to 200–300 ppm (solid line). At higher concentrations (broken line) the curve is non-linear and shows saturation characteristics, in agreement with findings in other species [4, 5, 7].

DISCUSSION

Available data on rates of (first-order) metabolism of VC in different species (Table I) have demonstrated that rats, mice and gerbils metabolize VC 5–12 times faster than humans. From this point of view these laboratory animals represent models of only limited validity for man. Rhesus monkeys are closer to man, as indicated by (first-order) metabolic rates of VC.

Gehring et al. [5], on the basis of rat experiments, calculated a risk of angiosarcoma in man after a 35-year exposure to 1 ppm VC (8 h/day; 5 days/week) of $1.5 \cdot 10^{-8}$. This calculation did not take into account the differences in metabolism of VC between rat and man. Such calculations may overemphasize the risk of low levels of VC in human population.

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The present data (Fig. 1) show that the inference from rat experiments [4, 5, 7] that metabolism of VC is a dose-dependent and saturable process, is valid also for the Rhesus monkey. The relative similarity of the pharmacokinetic behavior of VC in the lower concentration range between the Rhesus monkey and man (Table I) might indicate that a similar saturation phenomenon might occur in humans at higher exposures to VC. Compared with the maximal velocity of VC metabolism in the rat [7] of 110 $\mu\text{mol/h/kg}$ body weight, the maximal velocity is about 50 $\mu\text{mol/h/kg}$ body weight in the Rhesus monkey (Fig. 1).

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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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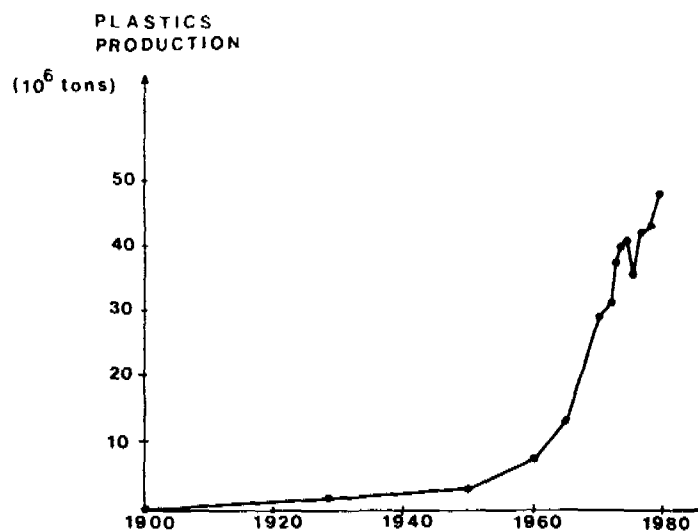


FIGURE 1. Plastics production worldwide.

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
	<u>99.9</u>

^aFrom 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

^aFrom 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 hexamethylene-diamine 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—dimethyl-terephthalate 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?

^aModified from Kay (1977).^bThermoplastic.^cThermosetting.^dMaleic acid anhydride.^ePhthalic acid anhydride.

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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 calendaring 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}

Chemical compound	Mutagenicity		Chromosomal aberrations		Carcinogenicity	
	<i>Salmonella</i>		Animals (bone marrow)	Humans (lymphocytes)	Animals	Humans
	<i>typhimurium</i>	<i>Drosophila</i>				
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	+	+	+

^aFrom Hemminki et al. (1979), Bartsch et al. (1979), IARC (1979), Lee et al. (1978), NCI (1979).

^bSufficient evidence for mutagenicity or carcinogenicity in animals is indicated by a plus sign; limited evidence is indicated by a question mark.

^cNo data.

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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, alkyl-aluminum 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

^aModified 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 ₈ ... 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)	++

^aFrom Boettner et al. (1973) and Hoff (1977).^bThe proportional concentration among the decomposition products is indicated, with + denoting the lowest and ++++ the highest.^c(+) denotes probable occurrence of trace amounts.^dABS, copolymer of styrene with acrylonitrile and butadiene; SAN, copolymer of styrene with acrylonitrile.^eSB, 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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