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The Nordic Expert Group for Criteria Documentation
of Health Risks from Chemicals

124. Thermal Degradation Products
of Polyethylene, Polypropylene, Polystyrene,
Polyvinylchloride and Polytetrafluoroethylene
in the Processing of Plastics

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Nordic Council of Ministers

ARBETE OCH HÄLSA VETENSKAPLIG SKRIFTSERIE

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National Institute for Working Life

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Preface

The Nordic Council is an intergovernmental collaborative body for the five countries, Denmark, Finland, Iceland, Norway and Sweden. One of the committees, the Nordic Senior Executive Committee for Occupational Environmental Matters, initiated a project in order to produce criteria documents to be used by the regulatory authorities in the Nordic countries as a scientific basis for the setting of national occupational exposure limits.

The management of the project is given to an expert group. At present the Nordic Expert Group consists of the following member:

Vidir Kristjansson	Administration of Occupational, Safety and Health, Iceland
Petter Kristensen	National Institute of Occupational Health, Norway
Per Lundberg (chairman)	National Institute for Working Life, Sweden
Vesa Riihimäki	Institute of Occupational Health, Finland
Leif Simonsen	National Institute of Occupational Health, Denmark

For each document an author is appointed by the Expert Group and the national member acts as a referent. The author searches for literature in different data bases such as Toxline, Medline, Cancerlit and Nioshtic. Information from other sources such as WHO, NIOSH and the Dutch Expert Committee is also used as are handbooks such as Patty's Industrial Hygiene and Toxicology. Evaluation is made of all relevant scientific original literature found. In exceptional cases information from documents difficult to access are used. The draft document is discussed within the Expert Group and is finally accepted as the Group's document.

Editorial work is performed by the Group's Scientific Secretary, Johan Montelius, and technical editing by Ms Karin Sundström both at the National Institute for Working Life in Sweden.

Only literature judged as reliable and relevant for the discussion is referred to in this document. Concentrations in air are given in mg/m^3 and in biological media in mol/l . In case they are otherwise given in the original papers they are if possible recalculated and the original values are given within brackets.

The documents aim at establishing a dose-response/dose-effect relationship and defining a critical effect based only on the scientific literature. The task is not to give a proposal for a numerical occupational exposure limit value.

The evaluation of the literature and the drafting of this document on Thermal Degradation Products of Polyethylene, Polypropylene, Polystyrene, Polyvinylchloride and Polytetrafluoroethylene in the Processing of Plastics was made by Dr Antti Zitting at the Finnish Institute of Occupational Health. The final version was accepted by the Nordic Expert Group November 20, 1997, as its document.

We acknowledge the Nordic Council for its financial support of this project.

Johan Montelius
Scientific Secretary

Per Lundberg
Chairman

Abbreviations

ABS	Poly(acrylonitrile-butadiene-styrene)
CP	Polypropylene-polyethylene copolymer
FEF ₅₀	Forced expiratory flow at 50% of vital capacity
FEV ₁	Forced expiratory volume in one second
FVC	Forced vital capacity
GC	Gas chromatography
GC/MS	Gas chromatography-mass spectrometry
OEL	Occupational exposure limit
OR	Odds ratio
PE	Polyethylene
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RD ₅₀	Decrease of respiration rate by 50%
SB	Styrene-butadiene

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Introduction

The thermal degradation of plastics is a complex process, which usually produces complex mixtures of individual products. This fact is reflected in the structure of this document, which differs from the standard documents of the Nordic Expert Group. The toxic properties of numerous emerging individual degradation products have not been examined. There exist a lot of publications on the analysis of degradation products, but only some examples that seemed to be representative and relevant for the occupational setting are presented.

The document also ignores the studies in combustion toxicology and is focused on degradation conditions, which typically occur in the processing of plastics. Polytetrafluoroethylene is somewhat of an exception – its typical occupational hazards originate from degradation at very high temperatures, for instance from smoking contaminated cigarettes.

Plastics are typically divided into two major groups: thermosets and thermoplastics. The former are polymerised or mechanically processed to the final form, while the latter are processed in molten state. This document deals with polyethylenes (PE), polypropylenes (PP), polystyrene (homopolymer) (PS) and polyvinylchloride (PVC), which all are thermoplastics. These polymers are the most used plastic materials. Polytetrafluoroethylene (PTFE) is included because its thermal degradation products are widely known to cause the so-called polymer fume fever.

The toxic effects from synthetic polymers may arise from:

- Toxicity associated with the use of the final plastic products
- Toxicity that arises during the manufacture of the plastic materials
- Toxicity due to the thermal decomposition products of plastics
- Toxicity from compounds leaching from materials

The toxic properties of the monomers (e.g. vinyl chloride, butadiene) used to produce synthetic polymers have been the subject of extensive research. The investigations on the toxicity of thermal decomposition products have focused mainly on "combustion toxicology"; actual fires have been simulated to reveal the acute toxic hazards of smoke.

The polymeric organic materials are in general combustible and involve risk of fire when heated in air. In actual fires, most fatalities are due to smoke and toxic gases. The combustion products contain high quantities of acute inorganic toxicants (e.g., carbon monoxide, nitrogen oxides and hydrogen cyanide). This fact together with the short periods of exposure during fires explains combustion toxicologists' interest in studying the acute toxicity of thermal degradation products.

The toxicity of the combustion products is occupationally important to fire fighters, but during the processing and use of plastics the degradation tempera-

tures are typically much lower. Exceptionally high temperatures, however, are possible in work situations, especially during the incidental technical disturbances in the processing machinery.

The thermal decomposition of plastics at work occurs to some extent because the techniques used to process thermoplastics usually require raised temperatures that enable materials to be moulded and extruded. The process temperatures vary according to the applied technique and the type of plastics.

The thermal energy induces the degradation of the polymer and/or additives. Some of the decomposition products have molecular weights small enough to be volatilised. Degradation products also contain aerosols. Although the decomposition has to be minimised to keep the quality of the final products high, it cannot be totally eliminated. High temperatures may occur also in other uses of plastic materials. They are cut with heated tools, welded, used for shrink wrappings, etc.

The thermal decomposition of plastics is usually a sequence of complicated physical and chemical processes. Many parameters contribute to the quality and quantity of volatile degradation products – the temperature of the plastics, the quality and amount of additives, the access of the heated material to oxygen, and the processing technologies.

1. Polyethylene; PE

1.1 Composition of polyethylene

Polyethylene (PE) are produced by polymerisation of ethylene. Different polymerisation processes (high–pressure processes, Ziegler processes, the Phillips process and the Standard Oil (Indiana) process) give materials with differing molecular weights and degrees of chain branching. The technical properties differ accordingly:

- LDPE – low density polyethylene
- LLDPE – linear–low–density polyethylene
- MDPE – medium density polyethylene
- HDPE – high density polyethylene

The polymer can be cross–linked with radiation, peroxides or vinyl silanes to give it a network structure typical of a rubber material. Chlorinated polyethylene is used in blends with other polymers, especially PVC.

Polyethylene can be used for some applications without additives, but usually a number of these are blended with the resin for various technical reasons. The amount of additives in polyolefins is usually in the range of some percents – much lower than, e.g. in PVC. The additives can be classified as in Table 1 (1).

1.2 Processing of polyethylene

Brydson (1) has described the processing techniques of PE:

Compression moulding is used only occasionally with PE for the manufacture of large blocks and sheets. In the process, the material is heated in the mould, compressed to shape and cooled.

Melt processing is used almost exclusively with polyethylene. Many products are produced by *injection moulding*. In the process the material is melted and injected into a mould where it hardens.

There are many variations of *blow moulding* techniques. For example, a tube is extruded vertically downwards on to a spigot. The mould halves close on to the extrudate (‘parison’) and air is blown through the spigot so that the parison takes up the shape of the mould.

Most PE is formed into final products by *extrusion* processes. The process consists of metering polymer (usually granular) into a heated barrel in which a rotating screw moves up the granules, which are compacted and plasticised. The melt is then forced through an orifice to give a product of constant cross section.

Table 1. Additives in polyethylenes. Modified from Brydson (1)

Class of additive	Examples
Fillers	carbon black
Pigments	titanium dioxide, chromic oxide
Flame retardants	antimony trioxide, chlorinated compounds
Slip agents	fatty acid amines
Blowing agents	azodicarbonamide, 4,4'-oxybisbenzenesulphonohydrazide
Rubbers	polyisobutylene, butyl rubber
Cross-linking agents	peroxides
Antioxidants	phenols (like 4-methyl-2,6-tert-butylphenol)
Antistatics	polyethylene glycol alkyl esters

Table 2. Typical processing temperatures for polyethylene (12)

Processing method	Processing temperature (°C)
Extrusion (pipes)	140 – 170
Film and coatings	200 – 340
Injection moulding	150 – 370
Compression moulding	130 – 230

Typical processing temperatures for the different processing techniques are shown in Table 2 (12). Polyethylene is often exposed to elevated temperatures when materials are welded or thermocut. In these cases the temperatures may sometimes be significantly higher than in the above mentioned processing applications. Elevated temperatures appear also in the wrapping of PE films.

1.3 Products of thermooxidation at processing

The thermal degradation products of polyethylene have been widely studied. A wide variety of hydrocarbons and their oxygenated derivatives have been identified. The results naturally depend on the analytical methods that have been used. Many components escape identification, e.g. gas chromatograms show many unidentified peaks. To demonstrate the complexity, a list from the study of Hoff et al. (6) has been given in Table 3. The results are from laboratory simulations using degradation temperatures close to those in industrial processing. The identified compounds are listed in Table 3. Similar results have been obtained also in other studies, e.g. (8, 10).

The major thermal degradation products are formaldehyde, formic acid, acetaldehyde, and acetic acid.

A significant amount of aerosols is also formed. Their infrared spectroscopy showed that they closely resemble paraffin wax fumes (6). The thermal degradation of PE occurs by free radical mechanism, and free radicals have also been detected in the PE processing fumes (17).

Table 3. Identified compounds of polyethylene thermooxidation at processing temperatures (264 – 289°C) (6)

Carbon dioxide	Butanal
Water	Isobutanal
Ethene	Pentanal
Propene	Acetone
Propane	Methyl vinyl ketone
Cyclopropane	Methyl ethyl ketone
Butene	2-Pentanone
Butane	2-Hexanone
Pentene	2-Heptanone
Hexene	Formic acid
Hexane	Acetic acid
Heptene	Propionic acid
Heptane	Acrylic acid
Octene	Butyric acid
Octane	Isovaleric acid
Methanol	Hydroxyvaleric acid
Ethanol	Crotonic acid
Furan	Caproic acid
Tetrahydrofuran	Butyrolactone
Formaldehyde	Valerolactone
Acetaldehyde	Hydroperoxides
Propanol	Alkoxy radicals
Acrolein	

1.4 Occupational exposure data

When the workplace concentrations of individual decomposition products have been measured in normal operating conditions, the concentrations of major fume constituents have been very low when compared with occupational exposure limits (OEL) in the Nordic countries. The following examples are presented to indicate this.

Table 4 gives exposure information from measurements performed in the Finnish plastics processing industry (6).

In another Finnish study (16), air impurities in plastics processing industries were studied. The concentrations of measured compounds were very similar in different types of processes and also similar in the case of polyethylene and polypropylene (Table 5).

Health and Safety Executive (UK) has reported on formaldehyde emissions in wire cutting of polyethylene film (5). Transient formaldehyde levels of up to 11 mg/m³ (9 ppm) were measured during cleaning of wire (using elevated temperatures to remove residual material), and concentrations of 0.24 to 1 mg/m³ (0.2 to 0.8 ppm) were detectable immediately next to the cutting wire. However, despite these intermittent short-term peaks, the main conclusion of the study was that operator exposure to the major fume constituents is very low compared with occupational exposure limits in the Nordic countries.

Table 4. Oxidised thermal degradation products in the air during processing of polyethylene (6)

	Concentration (mg/m ³)		Number of processes studied	Number of measure- ments	Highest con- centration (mg/m ³)
	Mean	SEM ^a			
Aldehydes					
Total conc ^b	2.2	0.6	11	74	18.1
Formaldehyde	0.10	0.02	10	60	0.2
Acetaldehyde	0.16	0.05	2	8	0.4
Acrolein	< 0.02		10	60	–
Ketones					
Acetone	0.78	0.12	2	8	1.5
Organic acids					
Total conc ^c	15.4	1.4	11	41	46.7
Formic acid	0.83	0.13	13	41	2.1
Acetic acid	0.86	0.39	12	52	4.9

^aSEM = standard error of the mean of the number of processes.

^bTotal concentration of aldehydes calculated as CHO groups

^cTotal concentration of acids calculated as COOH groups

The exposures to the measured decomposition products in polyethylene lamination work in Sweden were low (volatile organic compounds 2.94 mg/m³ (TWA 8h), range of short term samples 0.16–11.10 mg/m³; formaldehyde 0.018 (< 0.005–0.036) mg/m³) (9).

1.5 Effects in animal and in vitro studies

The cellular levels of nonprotein sulfhydryl groups (mainly glutathione) were markedly decreased in isolated hepatocyte suspensions when exposed to thermooxidative degradation products of polyethylene (6). The effect was seen at all the degradation temperatures studied (200, 250 and 300°C). The exposure atmospheres were analysed for acrolein only (concentrations were 0.0023 mg/m³ (0.01 ppm), 0.015 mg/m³ (0.05 ppm) and 0.041 mg/m³ (0.18 ppm), respectively) because acrolein alone was also observed to have a similar effect. At the highest degradation temperature, the viability of the cells was decreased.

Rats were exposed to thermooxidative decomposition (325°C) products of polyethylene (6). The exposures (a single 6-h exposure, and a three-week exposure – 6 h/day, 5 days/week) slightly affected the glutathione status and xenobiotic metabolism in the liver and kidney. The concentrations of measured acrolein were 1.24 mg/m³ (0.54 ppm), formaldehyde 1.7 mg/m³ (1.4 ppm), total aldehydes (as formaldehyde) 23.2 mg/m³ (19.3 ppm) and the mean particulate concentration 9.8 mg/m³.

Table 5. Air impurities from processing of polyolefins (modified from ref. 16)

Agent	Injection moulding, blow moulding		Packaging, cutting, shrink wrapping		Film extrusion, extrusion coating		Joint sealing, welding					
	x±SEM (mg/m ³)	N (n)	median (mg/m ³)	x±SEM (mg/m ³)	N (n)	median (mg/m ³)	x±SEM (mg/m ³)	N (n)	median (mg/m ³)			
aerosols	0.4±0.2	2 (5)	0.4	0.8±0.4	5 (19)	0.9	0.6±0.4	4 (25)	0.4	1.0±0.5	4 (7)	0.9
dust	0.2±0.1	5 (9)	0.1	0.2±0.1	1 (7)	0.2	0.2±0.03	3 (9)	0.2	0.8	1 (2)	0.8
total carbonyl compounds ^a	0.5±0.3	5 (18)	0.4	0.4±0.2	5 (16)	0.1	0.5±0.2	5 (27)	0.4	0.7±0.3	4 (7)	0.7
formaldehyde	0.08±0.02	5 (24)	0.09	0.03±0.01	6 (27)	0.04	0.04±0.01	6 (40)	0.05	0.09±0.02	5 (9)	0.12
acetaldehyde	0.11±0.05	5 (15)	0.11	0.07±0.04	6 (14)	0.07	0.06±0.03	4 (17)	0.05	0.02	1 (2)	0.02
total acids ^b	11.2±3.4	5 (20)					0.9±0.07	2 (8)				
formic acid	0.43±0.15	6 (23)	0.35	0.20±0.10	4 (17)	0.13	0.29±0.16	5 (26)	0.09	0.17±0.08	5 (12)	0.13
acetic acid	0.20±0.07	6 (23)	0.10	0.08±0.04	5 (19)	0.07	0.12±0.03	5 (26)	0.10	0.08±0.04	5 (12)	0.07

N = number of workplaces

n = number of samples

x = arithmetic mean

SEM = standard error of mean

^aas CHO groups

^bas COOH groups

Zitting and Savolainen (18) exposed rats for 2, 3 and 5 weeks, 6 h/day, 5 day/week, to oxidative thermal degradation products (325°C) of polyethylene. To evaluate the exposure atmospheres carbon monoxide ($< 23 \text{ mg/m}^3 \approx 20 \text{ ppm}$), formaldehyde ($1.7 \text{ mg/m}^3 \approx 1.4 \text{ ppm}$), acrolein ($1.2 \text{ mg/m}^3 \approx 0.5 \text{ ppm}$) and total aldehydes ($22 \text{ mg/m}^3 \approx 18 \text{ ppm}$ expressed as formaldehyde) were measured. The total particulate fraction amounted to 8 mg/m^3 . The neurochemical effects associated with the exposure included a significant increase in the cerebral RNA concentration as well as initial significant increase in the glycosylation of cerebral protein *in vitro*. NADPH-diaphorase activity was below the control range throughout the exposure while the superoxide dismutase activity displayed a significantly increasing trend five weeks after the beginning of the experiment. The authors speculated that the latter effects were taken as a response to potentially harmful oxidative stress in the brain whereas the effects on the RNA and glycosylation might have resulted from the sensory irritation.

The respiratory irritation of polyethylene fumes has so far only been studied using temperatures, which are relevant in fire situations, not occupationally. The studies of Schaper et al. (13) and Detwiler–Okabayashi and Schaper (2) were carried out using relevant temperatures, but they did not study "pure" polyethylene; instead polypropylene–polyethylene copolymer was used. The studies are described in the polypropylene part of this document.

1.6 Observations in man

Høvdning (7) reported that the fumes from hot polyethylene caused mild dermatitis in four female workers in thermocutting and sealing. The workers presented similar subjective complaints: burning sensation in the eyes, a feeling of dryness and irritation in the nose and throat, itching and irritation of the skin of the face and neck and partly of the forearms. The workers had been engaged in thermocutting from one half to one and a half years. These women and a fellow worker working next to the cutting machine also gave positive skin patch test reactions to formaldehyde. The degradation temperature was not estimated and no hygienic measurements were performed, but seemingly the hygienic conditions were poor: "During heavy smoke exposure, itching eruptions developed on the uncovered parts of the skin, especially in the ocular regions." In addition, a certain feeling of drowsiness and headache was noted at the end of the working day. All symptoms disappeared during absences (duration not specified in the article) from the workplace, but recurred on resumption of the work.

Skerfving et al. (14) described asthma in a woman working in polyethylene film wrapping. The plastic was cut at 200°C and heated in an oven at 220°C. The heating wires (700°C) of the oven probably also contributed to the quality of the decomposition products. Carbon monoxide levels were less than $1,2 \text{ mg/m}^3$ (1 ppm) and carbonyl compounds less than 0.6 mg/m^3 (0.5 ppm). In the same article, the authors state that they have seen two further cases of bronchospasm

caused by polyethylene fumes and one by polypropylene fumes. All three, however, were patients with a pre-existing bronchospastic disease.

Rasmussen et al. (11) described that workers who were thermocutting plastic films complained of irritative symptoms in the eyes and upper respiratory tract, neurological symptoms and an itching skin eruptions on their hands, arms, neck and face. The clinical skin allergy tests were negative. The workers were using intermittently polyethylene and polyvinyl chloride. No industrial hygiene measurements were conducted.

Stenton et al. (15) reported a case of occupational asthma associated with repair work of polyethylene-coated electrical cables. In the process, a PE repair tape incorporating dicumyl peroxide as a cross-linking agent was heated to 140°C. The composition of the emitted fume was unknown. Because of fairly low temperature, the authors speculated that the causative agent(s) is/are probably unknown degradation products of reactive dicumyl peroxide rather than the degradation products of the polymer.

Michel (9) observed a decrease in FEV₁ in male paper mill workers (n = 73). Polyethylene was used for lamination. The reference group (n = 185) consisted of workers from mills where PE-lamination was not used. The exposures to the measured decomposition products and some other agents were low (volatile organic compounds 2.94 mg/m³ (TWA 8h), range of short term samples 0.16–11.10 mg/m³; formaldehyde 0.018 (< 0.005–0.036) mg/m³).

Gannon et al. (4) described a case of asthma from polyethylene used for shrink wrapping of paper goods. The temperature for wrapping was 166°C. No exposure measurement data was given. The patient was atopic and had a pre-existing asthma. The bronchial challenge test with polyethylene heated to 76°C gave a bronchoconstrictor response. The value of the observation is reduced by the fact that no placebo was used in the test. Moreover, at 76°C, there is no significant degradation of polyethylene.

1.7 Conclusions for polyethylene

1.7.1 Critical exposing agents

The major degradation products of PE in the occupationally relevant temperatures are formaldehyde, formic acid, acetaldehyde and acetic acid and other aldehydes and acids. Their most obvious effect is probably the irritation. The aerosols (which resemble paraffin wax fumes) are formed also in a significant amount, and may contain biologically active oxidised compounds. The detected reactive alkoxy radicals may be also a health hazard if they contact eyes and respiratory tract. The workplace measurements have revealed concentrations of the individual degradation products, which are much lower than their occupational exposure limits in the Nordic countries; only the aerosol fraction concentrations have been close to the limits.

1.7.2 Critical effects

In the limited animal studies, the exposure conditions have been much more severe than in workplaces. Thus extrapolation from the observed effects on the xenobiotic metabolism, protective glutathione levels, and neurochemistry in animals is questionable.

The studies on the respiratory irritation in mice (13) suggest that irritation might be used as a critical effect with polyethylene and polypropylene fumes, although the researchers used polypropylene–polyethylene copolymer and polypropylene.

The observed effects of the thermal degradation products of polyolefins in man are mainly case reports of bronchoconstriction. In most cases, the exposure conditions are poorly described and some reports suffer from shortcomings of methodology.

In heavy exposures to PE fumes CNS effects (feeling of drowsiness and headache) have been noted (7).

An epidemiological study suggests that polyethylene fumes can cause a decrease in FEV₁. No other epidemiological evidence on the health effects of polyethylene was found.

1.7.3 Approaches to workplace monitoring

The evaluation of the exposures necessitates the use of marker substances. The amounts of total aldehydes, formaldehyde, acetaldehyde have been analysed nowadays mainly after collection into chemisorption tubes as 2,4–dinitrophenylhydrazones derivatives. The individual aldehydes and ketones are determined by liquid chromatography. Ion chromatography is nowadays the preferred method for organic acids.

Some hygienists stress the importance to measure aerosol concentrations, (3, 6). The analysis can be done gravimetrically after collecting the material on filters. The drawback of this method is that it is not specific. Infrared spectroscopy is rather specific and has also been used (3, 6) but the problem is that there exist no good reference substances.

1.7.4 Recommended basis for an occupational exposure limit

The data concerning dose–effect relationships for the plastic fumes are currently very poor and therefore scientific basis for an OEL is not pertinent.

The case reports of subjective symptoms, notably bronchoconstriction caused by the processing of polyolefins suggest, however, that proper hygienic practices need to be followed to keep the exposures as low as possible.

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2. Polypropylene; PP

2.1 Composition of polypropylene

Polypropylene is produced from the C₃ fraction after cracking petroleum products (5). The catalytic polymerisation process produces two types of polypropylenes which are separated at the end of the process: atactic and isotactic polymer. In the isotactic form, the methyl groups are all positioned on one side of the molecule. The crystalline isotactic form is used in the plastics processing industry, and almost amorphous atactic material is compatible with mineral fillers, bitumen and many resins.

Commercial grades of polypropylene are blended with a number of similar additives that are used in polyethylene (see section 1.1).

2.2 Processing of polypropylene

Polypropylene is processed by methods very similar to those for polyethylenes (see section 1.2). Most processing operations use melt temperatures in the range 210–250°C, and because polypropylene is easily oxidised, the heating is kept down to a minimum (5).

2.3 Products of thermooxidation at processing

Thermooxidative degradation of polypropylene (PP) was studied in laboratory simulations close to the industrial processing temperatures (220 – 280°C) (8). Gas chromatography–mass spectrometry allowed identification of 46 volatile degradation products (Table 1). Antioxidants markedly slowed down the degradation of polypropylene and the evolution of the degradation compounds. The relative amounts of the oxidised products were mostly independent of the degradation temperature or the type of antioxidant.

The major products were acetaldehyde, formaldehyde, acetone, acetic acid, and α -methylacrolein. A significant amount of aerosols is also formed, and they resemble paraffin wax fumes (8).

2.4 Occupational exposure data

Measurements in the Finnish PP processing industry revealed low airborne concentrations of individual volatile products (Table 2) (8). The exact composition of the materials was unknown, but they all contained antioxidants. The

Table 1. Identified compounds of polypropylene thermooxidation at processing temperatures (8)

<i>Hydrocarbons</i>	
Ethene	Ethane
Propene	Propane
Isobutene	Butane
Pentadiene	2-Methyl-1-pentene
2,4-Dimethyl-1-pentene	5-Methyl-1-heptene
Dimethylbenzene	
<i>Alcohols</i>	
Methanol	Ethanol
2-Methyl-2-propen-1-ol	
<i>Ethers</i>	
2-Methylfuran	2,5-Dimethylfuran
<i>Aldehydes</i>	
Formaldehyde	Acetaldehyde
Acrolein	Propanal
Methacrolein	2-Methylpropanal
Butanal	2-Vinylcrotonaldehyde
3-Methylpentanal	3-Methylhexanal
Octanal	Nonanal
Decanal	
<i>Ketones</i>	
Ethenone	Acetone
3-Buten-2-one	2-Butanone
1-Hydroxy-2-propenone	1-Cyclopropylethanone
3-Methyl-3-buten-2-one	3-Penten-2-one
2-Pentanone	2,3-Butanedione
1-Cyclopropyl-2-propanone	2,4-Pentanedione
4-Methyl-2-pentanone	4-Methyl-2-heptanone
<i>Acids</i>	
Formic acid	Acetic acid
Propionic acid	

processing temperatures ranged from 200 to 240°C. The concentration of aerosols, which infrared analysis showed to resemble paraffin fumes, was significant and the authors considered this as probably the most important hygienic hazard.

2.5 Effects in animal and in vitro studies

Rats were exposed to the thermooxidation (260 and 300°C) products of PP (8). The exposure concentrations of some degradation products are reproduced in Table 3 to allow the comparison with occupational concentrations (Table 2). The exposures decreased the concentrations of nonprotein sulfhydryl groups (mainly

glutathione) in the liver, lungs, and brain. The microsomal monooxygenase activities were slightly but significantly increased in kidney but decreased in lung. The authors stated that the results show polypropylene fumes to be biologically active, and comparable to the results from polyethylene exposures (11, 23). They noted that although the concentrations of the measured degradation products were higher, the effects were milder with polypropylene.

Schaper et al. (17) studied respiratory responses in Swiss–Webster mice that were exposed to thermal decomposition products from poly(acrylonitrile–butadiene–styrene) (ABS), polypropylene–polyethylene copolymer (CP), PP, or plasticised polyvinyl chloride (PVC). At processing temperatures between 200–300°C RD₅₀ (decrease of respiration rate by 50%) values (based on particulate concentrations) were 21.1, 3.51, 2.60, and 11.51 mg/m³ for ABS, CP, PP, and PVC, respectively. The authors recommended exposure limits 0.63, 0.11, 0.08, and 0.35 mg/m³ of particulates for degradation products of ABS, CP, PP, and PVC, respectively, to protect workers from their irritating properties. Guinea pigs

Table 2. Concentrations of degradation products in the industrial processing of polypropylene. Modified from (8).

Product	Average concentration (mg/m ³)		Highest concentration (mg/m ³)		No of samples/plant
	Mean	SEM	Mean	SD	
	Aerosol	0.9	0.7	2.2	
Total carbonyl compounds*	0.8	0.02	1.2	1.2	4
Formaldehyde	0.05	0.01	0.1	0.1	4
Acetaldehyde	0.02	0.01	0.1	0.1	4
Acetone	0.3	0.3	0.6	0.1	4
Total acids**	0.2	0.1	0.3	0.2	2
Formic acid	0.1	0.03	0.1	0.04	4
Acetic acid	0.05	0.03	0.1	0.05	4

Concentrations in mg/m³

* Calculated as carbonyl compounds

** Calculated as carboxylic groups

Table 3. Concentrations of degradation products of PP in animal exposures (8)

Product	Degradation temperature			
	260°C		300°C	
	(mg/m ³)	(ppm)	(mg/m ³)	(ppm)
Carbon monoxide	3.6	2	90	50
Formaldehyde	1.2	0.9	10	7.6
Acrolein	0.02	0.01	1.2	0.5
Acetaldehyde	2	1.1	21	11.9
Total carbonyl compounds	5	4.3	60	52
Acetone	0.5	0.2	12.3	5.2
Formic acid	3.6	1.9	9.7	5.1
Acetic acid	3.7	1.5	15.7	6.4
Aerosols	21		400	

were exposed in the same way (7). In single 50-min exposures to the fumes, guinea pigs exhibited sensory irritation, coughing, and airway constriction. RD_{50} particulate concentrations of 1757, 502, 176 and 228 mg/m^3 were obtained for ABS, CP, PP, and PVC, respectively. Thus, the relative potencies were $PP \approx PVC > CP \gg ABS$. Mice seem to be 20–500 times more sensitive than guinea pigs; the relative potencies in the mice were $PP > CP > PVC > ABS$. Thus, there was no complete agreement with the potency ranking between the two species. Using the RD_{50} concentrations of each resin, guinea pigs were exposed for 50 min/day on 5 consecutive days. These repeated exposures also resulted in sensory irritation, coughing, and airway constriction. Deaths occurred during exposures except with ABS.

2.6 Observations in man

Skerfving et al. (19) briefly stated in their case report on polyethylene fume asthma that they have also seen a case of bronchospasm caused by polypropylene fumes; but the patient had a pre-existing bronchospastic disease.

An asthma case in the production of polypropylene bags has been reported (16). The exposure levels of the degradation products were not measured. The patient reacted in the challenge test where polypropylene was heated at 250°C. No exposure data was given. When the patient was exposed to formaldehyde, no bronchospastic reaction was elicited.

Epidemiological studies of polypropylene production workers and carpet manufacturing employees who used polypropylene showed a significant excess of colorectal cancer (1, 2, 20-22). These studies were based on clusters of colorectal cancer. In one study, 5 of the 7 cases were diagnosed within a 5-month period and in the other study 5 cases were diagnosed within an 18-month period. The exposure data were very poor in these studies, and it is not even possible to state if there had been any significant exposure to the thermal degradation products of polypropylene. Recent updates of these two original study populations have found no continuation of the excess of colorectal cancer, thereby indicating the chance nature of the clusters (9, 10, 14, 15). Other investigations of polypropylene production workers in Canada (18), Germany (12), Australia (3, 6) and the United Kingdom (4) found no link with colorectal cancer. Lagast et al. (13) pooled the results of the above studies and calculated an aggregate number of 20 observed cases and of 14.65 expected cases. The difference is not statistically significant. As a whole, the combined weight of epidemiological evidence does not support an association between the work at polypropylene production and colorectal cancer.

2.7 Conclusions for polypropylene

2.7.1 Critical exposing agents

The major degradation products of PP in the occupationally relevant temperatures are similar to those of PE: formaldehyde, formic acid, acetaldehyde, and acetic acid and other aldehydes and acids. Their most obvious effect is probably the irritation. The aerosols (which resemble paraffin wax fumes) are formed also in a significant amount, and may contain biologically active oxidised compounds. The detected reactive alkoxy radicals may be also a health hazard if they contact eyes and respiratory tract. The workplace measurements have revealed concentrations of the individual degradation products, which are much lower than their occupational exposure limits in the Nordic countries; only the aerosol fraction concentrations have been close to the limits.

2.7.2 Critical effects

The studies on the respiratory irritation in mice (17) suggest that the irritation might be used as a critical effect for polypropylene fumes.

2.7.3 Approaches to workplace monitoring

The evaluation of the exposures necessitates the use of marker substances. The amounts of total aldehydes, formaldehyde, and acetaldehyde have been analysed nowadays mainly after collection into chemisorption tubes as 2,4-dinitrophenylhydrazones derivatives. The individual aldehydes and ketones are determined by liquid chromatography. Ion chromatography is nowadays the preferred method for organic acids.

Some hygienists stress the importance to measure aerosol concentrations, (8, 11). The analysis can be done gravimetrically after collecting the material on filters. The drawback of this method is that it is not specific. Infrared spectroscopy is rather specific and has also been used (8, 11) but the problem is that there exist no good reference substances.

2.7.4 Recommended basis for an occupational exposure limits

The data concerning dose-effect relationships for the plastic fumes are currently very poor and therefore a scientific basis for an OEL is not pertinent.

Some case reports concerning workers have linked the symptoms of bronchoconstriction and processing of polyolefins show, thus it would be advisable to follow proper hygienic practices and keep the exposures as low as possible.

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3. Polystyrene; PS

3.1 Composition of polystyrene

Polystyrene is produced from styrene by mass, solution, suspension, or emulsion polymerisation processes. Because of its low cost, good mouldability, low moisture absorption, good dimensional stability, good electric insulation properties, colourability, and reasonable chemical resistance, it is widely used as an injection moulding and vacuum forming material. Polystyrene foam is widely used for thermal insulation. The principal limitations are brittleness, inability to withstand temperature of boiling water, and poor oil resistance. For these reasons the material is often modified, e.g. by copolymerisation with acrylonitrile and/or butadiene — most common copolymers are poly(acrylonitrile–butadiene–styrene) (ABS) and styrene–butadiene (SB)(1).

3.2 Processing of polystyrene

Polystyrene is processed by such techniques as injection moulding, extrusion and blow moulding. Typical processing temperatures are 170 – 250°C.

3.3 Products of thermooxidation

The compositions of thermal degradation products of polystyrene have been widely studied in the laboratory. The results of Shapi and Hesso (4) serve as an example. The volatile products were analysed by GC and GC/MS. Varying proportions of chiefly phenyl–substituted saturated or unsaturated aliphatic compounds of up to 12 carbon atoms in chain length and molecular weight in the range 92–430 were found. The products also included a number of oxygen–containing compounds, e.g. alcohols, aldehydes, and ketones. The decomposition in air or nitrogen produced at least 190 compounds, and at least 45 of these in both atmospheres. Most of the compounds occurred in small relative yields. By far the most abundant product was styrene.

Similar results have been reported in several studies, e.g. a significant amount of aerosols is present in PS fumes (2). Free radicals have also been found in PS processing fumes (6).

Table 1. Thermal degradation products in Finnish factories processing styrene polymers. Modified from Vainiotalo and Pfäffli (5)

	Concentration mean \pm SEM (mg/m ³)	Number of workplaces
Styrene	0.13 \pm 0.02	4
Aerosols	0.4 \pm 0.2	4
Total carbonyls (as -CO group)	0.5 \pm 0.1	7
Formaldehyde	0.05 \pm 0.01	7
Acetaldehyde	0.04 \pm 0.01	4
Acetone	0.20 \pm 0.09	4
Benzaldehyde	0.13 \pm 0.01	1
Formic acid	0.38 \pm 0.28	6
Acetic acid	0.10 \pm 0.02	7

3.4 Occupational exposure data

The reported degradation product levels in the polystyrene processing factories have been low when compared to the occupational exposure limits of individual components. For instance, Vainiotalo and Pfäffli (5) reported concentrations in the Finnish polystyrene processing industry (Table 1). Their results include processing of the homopolymer and copolymers of styrene. The authors state that there were no significant differences between the homopolymer and copolymers (ABS and SB).

3.5 Effects in animal and in vitro studies

Rats and mice were exposed to the fumes of oxidative thermal degradation (350°C) of polystyrene (9). Mice were exposed to four 35-min periods (10-min intervals between the doses) per day for 1, 2 and 4 days and also for 2 and 10 weeks (5 days per week). Rats received continuous 6-hour exposures (3 weeks, 5 d/week).

The mean styrene concentration in the exposures was about 640 mg/m³ (150 ppm). The level of reduced glutathione was lowered in the liver and lung in both species. The exposures also increased the cytochrome P-450 content in the mouse liver and the hepatic monooxygenase (ethoxy-coumarin O-deethylase) activity in both species. After a single exposure activity in mouse liver was doubled in 24 h. This enhancement gradually disappeared in the course of continued daily exposures. Ethoxy-coumarin O-deethylase activity and cytochrome P-450 contents were also increased in the rat liver and lung after the exposure. The degradation temperature in the study was much higher and the concentrations of degradation products approximate thousand-fold higher than in the processing industry. The results are not really relevant for exposure limit assessments.

Zitting et al. (8) exposed isolated rat hepatocytes to thermooxidative degradation products of polystyrene. The depletion of reduced glutathione was

induced in isolated rat hepatocytes exposed for 120 min. The depletion depended on the degradation temperature. Products from degradation at 200°C (concentration of styrene in exposure atmosphere 3 mg/m³ ≈ 0.7 ppm) had no detectable effect on glutathione levels in isolated hepatocytes. At higher degradation temperatures 250°C and 300°C, with styrene concentrations of 11 mg/m³ and 110 mg/m³ (2.5 and 25 ppm, respectively) a rapid depletion was detected. The cell viability (measured as the latency of lactate dehydrogenase) was not, however, affected. Copolymers of styrene (ABS, SB and poly(styrene–acrylonitrile) had similar effects (7).

3.6 Observations in man

McDonald et al. (3) analysed 193 current and previous pregnancies of Canadian women employed at the time of conception in the plastics industry. The ratio of observed to expected spontaneous abortions, corrected by logistic regression for seven nonoccupational confounding variables, was elevated (1.27; 90% confidence interval 0.91–1.72) in women engaged in the process work. The ratio was raised (1.58; 90% confidence interval 1.02–2.35) among women whose work included the processing of polystyrene (number of pregnancies 76). No excess was observed among women whose work did not include polystyrene. The hygienic measurement data was not available.

3.7 Conclusions for polystyrene

3.7.1 Critical exposing agents

Styrene seems to be the most significant degradation product. Other notable products are aerosols, carbonyl compounds, and formic and acetic acid. The spectrum of the impurities in the workroom air during the processing of styrene polymers is more complicated than could be expected from the laboratory experiments, e.g. low molecular weight carbonyl compound are quite abundant in the processing. The reason might be the decomposing additives in the materials and/or emissions external to the actual processing. The levels of the individual compounds in the processing industry have been very low compared to the occupational exposure limits in the Nordic countries. Aerosols are also formed in the processing of polystyrenes.

3.7.2 Critical effects

In the limited animal and *in vitro* studies, the exposure conditions have been much more severe than in the processing of styrene plastics. Thus extrapolations from the observed results in animals is questionable.

The only reported adverse effect in humans in Canadian polystyrene processing industry has been increased risk of abortions. In this case, no quantitative exposure assessment is available.

3.7.3 Approaches to workplace monitoring

Styrene is by far the most abundant and typical thermal degradation product of polystyrene and its styrene copolymers, and thus an obvious marker compound. Styrene is routinely quantified by gas chromatography.

3.7.4 Recommended basis for an occupational exposure limits

The dose–response data is insufficient and therefore a scientific basis for an occupational exposure limit to polystyrene fumes is not pertinent. The same applies to copolymers of styrene.

3.8 References

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4. Polyvinylchloride; PVC

4.1 Composition of PVC

Vinyl chloride is polymerised to PVC by free radical mechanisms in bulk, in suspension, and in emulsion. PVC is a rigid material with limited heat stability and usually it must be compounded with additives to be technically useful. The amount of the additives in the material often exceeds the amount of PVC resin.

Polyvinylchloride based material may have the following ingredients (the number of different additives is great and the list gives only some examples):

Stabilisers

- lead compounds (e.g. carbonate, sulphate, phthalate)
- Cd, Ba, Ca, and Zn salts and soaps
- organotin compounds

Plasticisers

- phthalates, adipates
- polymeric plasticisers (e.g. polypropylene adipate)

Extenders (replacing partly more expensive plasticisers)

- chlorinated paraffins (waxes and liquids)
- oil extracts

Lubricants (preventing sticking to processing equipment)

- Al , Mg, Ca and Pb stearates

Fillers

- china clay, Ca carbonates

Pigments

Polymeric processing aids and impact modifiers

- Butadiene based rubbers, ABS materials

4.2 Processing of PVC

PVC is processed by various techniques like extrusion, injection, and blow moulding. The processing conditions vary much depending on product, the formulation of the material and the equipment. Typical processing temperatures are 140 – 250°C.

PVC films are used for wrapping material and subjected to elevated temperatures when thermally cut and shrunk.

Welding of PVC parts is also a common procedure where human exposures to the degradation products are possible.

4.3 Products of thermooxidation

In addition to the degradation temperature and the type of processing, the various additives in the PVC material greatly affect the composition of degradation products. The initial decomposition reaction of the polymer chain itself is the elimination of hydrogen chloride, with a subsequent fragmentation of the remaining polyene chain and the combination of some fragments to aromatic hydrocarbons (benzene usually the most abundant at high temperatures exceeding 500°C).

The additives, like plasticisers, e.g. phthalates (2, 22) and blowing agents, e.g. azodicarbonamide (25), are also emitted. They may react further, e.g. di-2-ethylhexylphthalate decomposes to some extent to phthalic anhydride (24).

There are many studies concerning degradation products of PVC. The study of Andersson (2) exemplifies the results (Table 1). She carried out the degradation at 170°C. McNeill et al. (14) for example have obtained similar results.

Table 1. Degradation products from PVC samples at 170°C. Modified from Andersson (2)

Group	Compound
Aliphatic hydrocarbon	C ₄ -, C ₈ -, C ₁₁ -, C ₁₂ -, C ₁₃ -hydrocarbons
Halogenated hydrocarbon	1,1-Dichloroethylene
Aromatic hydrocarbon	Trimethylbenzene
Alcohol	1-Nonanol 1-Decanol
Alkoxyalcohol	2-(2-Butoxyethoxy)ethanol
Aldehyde	Formaldehyde Acetaldehyde Hexanal Nonanal
Ketone	Cyclohexanone
Acid	2-Ethylhexanoic acid
Ester	Diethyl phthalate Di-n-butyl phthalate Di-2-ethylhexyl phthalate
Hydrogen chloride	

4.4 Occupational exposure data

Because hydrogen chloride is always present in the decomposition products of PVC polymer and is the major product at processing temperatures – it has been used as a marker substance in industrial hygienic measurements. The exposure levels vary widely depending on the process and material type. Two examples are given on industrial hygienic measurements.

Table 2. Concentrations of PVC degradation products in processing at 165–200 °C. Modified from Madsen et al. (12)

	Average ± SEM (mg/m ³)	Number of samples
Hydrogen chloride	0.07 ± 0.03	4
Phthalic anhydride	0.001 ± 0.001	4
Vinyl chloride	< 0.003	4
Benzene	< 0.03	4
Carbon monoxide	< 1	4
Aerosols*	0.5 ± 0.1	8
Di-(ethylhexyl)phthalate	0.3 ± 0.1	4

* Includes phthalate

Table 3. Concentrations of PVC degradation products in processing. Modified from Vainiotalo and Pfäffli (24)

Processing method	Hydrogen chloride (mg/m ³)	Di-(ethyl-hexyl)phthalate (mg/m ³)	Phthalic anhydride (µg/ m ³)	Processing temperature (°C)	Amount of plasticiser (%)
Extrusion	0.15±0.06 (6)	0.05±0.03 (4)	– ^a	150–200	2.4
Extrusion	0.09±0.10 (3)	0.30±0.2 (5)	0.3±0.5 (16)	150–195	Nk
Calendering	0.15±0.03 (6)	0.50±0.5 (7)	0.2±0.1 (8)	130–200	6.5–15
Hot embossing	0.03±0.02 (2)	0.05±0.02 (5)	– ^a	~ 180	Nk
Welding	0.30±0.02 (3)	0.3±0.05 (4)	5.0±2.0 (4)	400 (at lamp)	Nk
Injection moulding	0.05±0.00 (2)	0.02±0.01 (2)	< 0.02 (2)	180–190	Nk
Compounding	– ^a	0.02±0.01 (5)	– ^a	120	20
Thermoforming	– ^a	0.02±0.02 (2)	0.1±0.05 (2)	120–130	Nk
High-frequency welding	< 0.03 (2)	< 0.02	– ^a	Nk	Nk
Spread coating	– ^a	– ^b	1.2±0.2 (4)	160–205	35
Blow moulding	0.05±0.02 (2)	– ^c	– ^c	150–190	–
Compression moulding	0.04±0.01 (2)	– ^c	– ^c	150	–

The results are given as the mean ± SD (number of samples)

Nk = not known

^aNot measured

^bDiisononylphthalate plasticiser

^cUnplasticised PVC

Madsen et al. (12) measured degradation products of PVC processing at 165 – 200°C. The plastics contained 40–59% di-(ethylhexyl)phthalate as a plasticiser. The results are given in Table 2.

Vainiotalo and Pfäffli (24) studied several types of PVC processing facilities. The results are given in Table 3.

4.5 Effects in animal and in vitro studies

The toxicity of thermal decomposition products of PVC plastics has been widely studied in the area of combustion toxicology where the attention has been targeted on the acute toxicity like lethality, pulmonary damage and irritation. Due to the high temperatures and very high concentrations used in the experiments the results cannot be extrapolated to processing conditions.

Schaper et al. (20) studied in mice the irritating effects of a plasticised PVC (containing 40 – 60% PVC resin; no other data given) which was degraded at 150 and 230°C. At the lower temperature, it was not possible to elicit a 50% decrease response in the respiratory rate. The observed RD₅₀ value at the higher temperature was 11.51 (95% confidence interval 4.66 – 23.07) mg/m³. The concentration applies to particulates drawn onto polytetrafluoroethylene filters (the pore size was not indicated). Alarie (1) has proposed that to prevent sensory irritation in humans, the RD₅₀ should be multiplied by 0.03. Schaper et al. (20) suggest that the exposure limit of 0.35 mg/m³ would be set for degradation products of PVC.

Detwiler–Okabayashi and Schaper (6) performed a similar study using guinea pigs. The results have been referred before in the polypropylene chapter of this document.

4.6 Observations in man

The first cases of “meat wrapper’s asthma” were reported 1973 (23). Hot–wire cutting of PVC film was one of the processes used in each of the three cases. It was not determined whether the effect was an allergic or irritant response. Numerous case reports on PVC fume induced asthma have been published after this finding.

A limited epidemiological study (without quantitative exposure data) (18) indicated that many meat wrappers had the respiratory impairment (decreases in forced expiratory volume (FEV₁) and forced expiratory flow 50% (FEF₅₀)). The cause was thought to be the thermal degradation products of the PVC film.

Falk and Portnoy (7) concluded in an epidemiological report (without quantitative exposure data) that several meat wrappers had “meat wrapper’s asthma” and that in some cases it progressed to clinical asthma.

Bronchial provocation studies (3, 4) showed that fumes from price label adhesive decreased the FEV₁ much more effectively than PVC fumes. Further in-

vestigations (16) after three new cases of “meat wrapper’s asthma” indicated that the primary agent was phthalic anhydride and the secondary one was epoxidised soybean oil. The adhesive was a reaction product of phthalic anhydride and epoxidised oil. The heat produced these constituents.

Rasmussen et al. (19) described that workers who were thermocutting plastic films complained of irritative symptoms in the eyes and upper respiratory tract, neurological symptoms and an itching skin eruptions on their hands, arms, neck and face. The clinical skin allergy tests were negative. The workers were using intermittently polyethylene and polyvinyl chloride. No industrial hygiene measurements were conducted.

Froneberg et al. (8) described an incidence with general and respiratory symptoms in a PVC fabrication plant. An extruder overheated from 148°C to 338°C and released heavy irritant fumes into the workroom. Workers started to complain of burning eyes, sore throat, and breathing difficulties. Workers, however, had to continue the production, although the plant ventilation was unsatisfactory. Some of the workers collapsed and were hospitalised. Altogether 62 of 201 workers and one of the management personnel developed acute upper and lower respiratory irritation, headache, nausea and fainting. Two and 14 weeks later, pulmonary function testing (Vitalograph®) of workers with persistent symptoms showed abnormalities among 13 of 16 examined persons and in 9 of 11, respectively; the group with persistent symptoms contained an excess of non-smokers and persons with previous respiratory illnesses. The report is not useful in the evaluation of exposure limits, because no quantitative exposure data were available, and was not estimated because the amount of degraded PVC could not be ascertained.

Baser et al. (5) performed spirometry among 174 males in a plant producing PVC sheeting and wall covering. There were no significant differences between the in-plant comparison group (from departments where no exposures to vinyl chloride monomer, PVC dust, or PVC thermal degradation products were possible) and any department with potential exposures. However, when the comparison group and the exposed group were combined, the duration of employment (two groups: <0.5 year and ≥0.5 year) was significantly associated with decrements in FEV₁/FVC, preshift FEV₁/FVC, and prevalence (from a questionnaire) of chronic cough and chronic phlegm. The prevalences of chronic wheeze (36%) and chest tightness (50.5%) were high in non-smokers. The authors note that the agents causing pulmonary effects could not be identified, but the industrial hygiene measurements rule out vinyl chloride monomer, PVC dust, or thermal degradation products. Additives which are volatile at 200°C, and/or chemicals used in noncalendering areas of the plant might have contributed to the development of the symptoms. No other results from the industrial hygiene measurements were given other than the comment that the concentrations of hydrochloric acid were below detection limits. The authors state that they cannot differentiate between cohort effects, in which time-dependent effects would be due to high past exposure levels, and effects caused by longer exposure to a similar dose level. They also note about a possible cohort effect due to earlier

high accidental exposures, because of the anecdotal reports of PVC overheating in the plant.

Rasmussen et al. (19) reported on nine women, employed in a plant producing polyethylene and PVC goods, who complained of irritative symptoms in the eyes and upper respiratory tract, neurological symptoms (headache, tiredness, impairment of memory and poor concentration). No clinical signs were observed. No quantitative exposure data were given.

Nielsen et al. (15) studied a group of 20 PVC processing workers and used 19 unexposed workers as a control group. The exposures to the thermal degradation products were not measured, but the levels of phthalates were up to 2 mg/m^3 . Two (10%) exposed workers had a mild work related asthma vs none in controls; five (25%) vs one (5%) exhibited symptoms of unspecific bronchial hyperreactivity. The exposed workers had significantly more subjective symptoms from eyes (conjunctivitis) and upper airways (dry cough) than the unexposed workers. No significant differences between the groups were found in lung function tests.

Petersen and Sabroe (17) undertook a cross-sectional questionnaire investigation on the frequency of occupational symptoms among 34 linoleum-layers who were exposed to the degradation products when welding vinyl floorings and also to organic solvents from adhesives. The control group consisted of 108 linoleum-layers and upholsterers who did not weld vinyl. Significant excess frequency of symptoms was found, including impairment of memory, poor concentration, visual disturbances and disturbances in the senses of taste and smell and symptoms of mucous membrane irritation. A non-significant increased frequency of symptoms of chronic bronchitis was also found. The authors pointed out that vinyl-welders are exposed to solvents to a much greater extent than the non-vinyl-welders.

The interest of the epidemiologists on PVC processing awoke after vinyl chloride monomer had been shown to be carcinogenic. PVC contained earlier significant amounts of vinyl chloride monomer residues, but the modern manufacturing technologies eliminate its presence now almost totally. The concentrations of vinyl chloride in the processing facilities are below the detection limit nowadays.

Maltoni et al. (13) reported two cases of liver angiosarcoma among PVC extruders in a small factory producing PVC bags and other containers. No data on the exposures were given. No other reports of angiosarcoma among PVC processing workers have been found.

A Swedish cohort study (9) was performed among 2031 male workers at a PVC processing plant. They had been employed for at least 3 months during 1945 – 1980. A significant increase in total cancer morbidity was observed (SMR = 128, 95% confidence interval 101 – 161) as well as an increase of respiratory cancers (SMR = 213, 95% confidence interval 127 – 346). No significant exposure-response associations between exposure estimates for vinyl chloride monomer, asbestos (which was used until 1977), or plasticisers and cancer morbidity were found. The exposures to the thermal degradation products of PVC were not estimated.

Another Swedish study (11) examined the mortality pattern and cancer incidence among 717 men who had been employed for at least 3 months during 1964 – 74 in three PVC-processing plants. The mortality was followed-up from 1964 through 1986 and the cancer incidence from 1964 through 1984. Among the native Swedes, the observed mortality and cancer incidences were close to those expected for most diagnoses, but among immigrants, mostly from Finland, there was a marked excess of circulatory deaths. This finding was probably due to the higher incidence of coronary mortality in Finland compared to Sweden. All the expected figures in the study were calculated from Swedish national rates. In the cohort, five cases of malignant melanoma were found as compared to 1.5 expected (SMR = 3.4, 95% confidence interval 1.1. – 7.9). Exposure estimations were done only for vinyl chloride monomer, not for plasticisers or thermal degradation products. Vinyl chloride concentrations (8 h TWA) never exceeded 15 mg/m³ (10 ppm) before 1975 and were much lower after that. In the other departments, they were below 7.5 mg/m³ before 1975 and below 1.5 mg/m³ (1 ppm) after that.

A nested case-control study (21) was conducted to investigate whether an excess of pancreatic cancer was associated with workplace exposures at a plastic manufacturing and research and development facility. The study population included 28 male pancreatic cancer cases and 140 randomly selected controls, matched for year of birth and vital status at the time of death. Workers assigned to a work area that processed vinyl resins and polyethylene were shown to be at increased risk. Men assigned more than 16 years to this department had a significantly increased risk ratio of 7.15 (95% confidence intervals 1.28 – 40.1). No excess was seen with shorter duration assignments. Over the study period, significant process changes had occurred. In addition, numerous chemical additives were used. The authors state that the identification of the causative agent or combination of agents would require investigations with more detailed exposure information. There is, however, a possibility that the workers have been exposed also to the thermal degradation products of plastics.

A small Swedish case-control study (10) on testicular cancer using self-administered questionnaires linked the incidence of testicular cancer and work with PVC. Answers were obtained for 148 cases and 315 controls. Of the cases, 7 were exposed to PVC and 2 of the controls. Odds ratio (OR) was 6.6 with a 95% confidence interval of 1.4–32. The quality of exposure was not reported clearly. Because of the shortcomings in the exposure assessment and few cases, the authors state that the results must be regarded only as hypothesis generating.

There are several other epidemiological studies on PVC workers. Any possibilities of exposure to thermal degradation products were not, however, considered.

4.7 Conclusions for polyvinylchloride

4.7.1 Critical exposing agents

Hydrogen chloride is the main degradation product of PVC in the processing temperatures. Its monitored concentrations in the processing industry under normal working conditions have been significantly lower than the occupational exposure limits in the Nordic countries. It is an irritant. Other degradation products tend to be emitted from the actual polymer at much higher temperatures than those in processing. Usually the most abundant airborne compounds from PVC plastics in these conditions originate from additives. The most abundant among these are plasticisers like phthalates. Their degradation products, e.g. phthalic anhydride, have also been monitored. Aerosols are also emitted to the workroom air – they contain low boiling additives and probably their reaction products as well as absorbed hydrogen chloride. The broad spectrum of PVC compositions makes it difficult to assess the exposures, e.g. the amount of PVC polymer may vary from almost 20–100%.

4.7.2 Critical effects

The animal experiments with PVC in fire toxicology are common and the measured endpoints have been death, incapacitation, and irritation. The degradation temperatures in these are not occupationally relevant. Only a few studies on the irritative effects have been performed with degradation temperatures which are close to those in the industry. The PVC processing workers have complained of irritation in eyes and respiratory tract. In these cases the degradation temperatures have been unusually high.

The most well known adverse effect of the degradation products of PVC plastics is the meat wrapper's asthma. It is not known, which is the causative agent. It has been proposed that some additives and their reaction products (e.g. azodicarbonamide, phthalic anhydride) might be the cause. Dose (for any marker substance) –response relations are not well known.

There are a few reports that the fumes also adversely affect the lung functions of workers.

Melanoma risk has been connected in one epidemiological study to PVC work. One report on angiosarcoma in PVC processing cannot be properly connected to the decomposition product exposure.

4.7.3 Approaches to workplace monitoring

The most common marker for PVC polymer degradation is hydrogen chloride, which is analysed by ion-selective electrode or ion chromatograph. The additives have been measured by chromatography.

4.7.4 Recommended basis for an occupational exposure limits

There exist no relevant dose–response relations and therefore a scientific basis for an occupational exposure limit is not pertinent. The animal studies on the irritative effects on the respiratory tract are still very limited.

4.8 References

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5. Polytetrafluoroethylene; PTFE

5.1 Composition of PTFE

PTFE is a linear polymer, which is made from tetrafluoroethylene. The chemical bond strengths in the polymer are high making it thermally and chemically very stable. It is an excellent electrical insulator. The material is non-adhesive and has a very low coefficient of friction. The melting point is 327°C. There are no solvents for PTFE at room temperature. The applications of PTFE are ascribed to these properties. Some examples of the use of PTFE are:

- Seals, gaskets, packings, valve parts, pumps, laboratory equipment
- Seals for condensers, wire insulators, and many other electrical applications
- Coating for chemically resistant vessels
- Aircrafts and missiles
- Textiles (for example Gore-Tex®)
- Lubricating sprays
- Adhesives

5.2 Processing of PTFE

Very high melt viscosity of PTFE prevents the use of usual processing techniques for thermoplastics. Like in powder metallurgy, PTFE material is first preformed usually at room temperature, then sintered above the melting point (typically 370°C), and then cooled. The thermal degradation is negligible in the processing. Additives are seldom used with PTFE.

Table 1. Thermal decomposition products of PTFE

Identified compound	Decomposition in air	Decomposition in inert atmosphere
Hydrogen fluoride	+	+
Tetrafluoromethane ; CF_4	+	
Carbonyl fluoride; $\text{CF}_2=\text{O}$	*	
Hexafluoroethane; CF_3-CF_3	+	
Tetrafluoroethylene; $\text{CF}_2=\text{CF}_2$	+	+
Hexafluoropropene; $\text{CF}_3-\text{CF}=\text{CF}_2$	+	+
Octafluoropropene; $\text{CF}_3-\text{CF}_2-\text{CF}_3$	+	
Octafluoroisobutene; $(\text{CF}_3)_2=\text{CF}_2$		*
Trifluoroacetyl fluoride; CF_3COF	+	

+ = compound identified; * = major reaction products

5.3 Products of thermal decomposition

Decomposition products of PTFE have been studied under various temperatures and oxygen availability. Hydrogen fluoride was first detected by Adams (1). The data in Table 1 have been collected from references (1, 2, 7, 11, 29).

5.4 Occupational exposure data

Atmospheric concentrations of fluorocarbon polymer dust and decomposition products have been measured in several industrial situations, but no correlations have been found between the measurements and adverse effects in workers. The majority of reports on polymer fume fever are linked to the smoking of contaminated cigarettes, and in these cases the contamination most probably occurs via unwashed hands. The documented outbreaks of the polymer fume fever involving exposure mechanisms other than contaminated tobacco products are almost always connected to accidental situations like welding near a PTFE block. No exposure data in these cases are available.

5.5 Effects in animal and in vitro studies

The toxicity of PTFE decomposition products has been studied in rats, rabbits, guinea pigs and mice. Very high degradation temperatures (typically 500 – 800°C) differ significantly from processing temperatures and the resulting high exposure concentrations make their use not relevant in the evaluation of exposure limits. The pathological changes have been pulmonary haemorrhage and oedema. The survived animals have showed focal emphysema and interstitial fibrosis (15, 29-31).

It seems that ultrafine particles with a median diameter of ~ 26 nm cause the high pulmonary toxicity and mortality, e.g. (17, 21, 26). The effects are eliminated if the particles are filtered away from the exposure atmosphere. It has been suggested that particles contain very reactive compounds, e.g. free radicals. If an additional vessel is placed into the degradation product stream between the degradation system and the animals, thus ageing of the particles, the toxicity decreases. In the study of Johnston et al. (15), the degradation temperatures of PTFE were 450 – 460°C, the exposure concentration was $5 \cdot 10^5$ particles/cm³ (≈ 50 mg/m³) and the exposure time 15 min. Many parameters of inflammation increased in the lungs of exposed rats. According to the authors, the responses suggested an oxidative injury. Lee and Seidel (17) used in their study tetrafluoroethylene–hexafluoropropylene copolymer, a close relative of PTFE. The lowest degradation temperature was 370°C, which is a common sintering temperature of PTFE. The exposure time was 30 min. The mortality (4-hour follow-up) of rats was 8/8 while they were exposed to the fresh fume (particle concentration 0.2

mg/m³), 4/24 when exposed to the aged fume (particle concentration 0.4 mg/m³), and 0/18 when exposed to the filtered fume.

Cavagna et al. (5) reported an experimental model of polymer fume fever in the rabbit, but the results could not be reproduced (6).

5.6 Observations in man

PTFE fumes have caused pulmonary oedema when acetylene torch has been used for metal cutting, and PTFE has been accidentally exposed to very high temperatures (10). The oedema has also been described after inhaling fumes produced in welding (16, 22) and after grinding PTFE coated metal (14). In the latter case, pericarditis was also diagnosed.

Polymer fume fever is a flu-like self-limiting symptom complex, which is induced after inhalation of thermal degradation products of PTFE.

Harris (13) reported the first polymer fume fever cases in 1951 – the smoking habits of these workers were not noted. The decomposition temperatures were 350–500°C. Four workers reported chills, fever, and myalgias with onset by at least 3 hours after the initial exposure. A case series consisting of seven cases was reported in 1955 (23). The measured concentration of the airborne fluoride (both in gaseous and particulate phase) was equivalent to 3.5 mg PTFE/m³. All the affected workers were smokers. The link of symptoms to smoking was strengthened later (1).

Polymer fume fever cases were later reported at work with/within:

- PTFE mould-release compounds (18)
- Print shop (3)
- Aircraft repair (4)
- Aerosol product in printing (3)
- Lubricating spray (4)
- Textile manufacturing (27)
- Textile coating (27)
- Rubber stamp shop (19)
- Electronic instrument testing (12)
- Ski wax (8, 25)

The affected persons that were reported in each case had been smoking cigarettes without prior hand washing.

Human volunteer studies showed that the lowest amount of PTFE in a burning cigarette necessary to produce polymer fume fever was 0.4 mg. The effect was the same irrespective of whether the dose was given in a single cigarette or fractionated among several cigarettes (6).

Cases of polymer fume fever with exposure mechanisms other than contaminated tobacco has also been documented in welders (9, 22), when grinding PTFE coating, and in context of pyrolysis of PTFE (20, 24).

Higher rate of the polymer fume fever among the smokers than non-smokers has been reported after the exposure to fumes from a charred electrical cable in a laboratory (28).

The polymer fume fever causing agents in the PTFE degradation products have remained unidentified. The effect has not been shown to occur in animal experiments.

5.7 Conclusions for polytetrafluoroethylene

5.7.1 Critical exposing agents

The major gaseous degradation products of PTFE are hydrogen fluoride, carbonyl fluoride, and various fluorinated hydrocarbons. The health effects of the gaseous fraction at the concentrations, which occur in the PTFE processing industry, are not clearly known.

The ultrafine particles, which are produced in the degradation, have turned out to be the cause of the toxic pulmonary and lethal effects in the experimental animals. These particles probably carry to the lungs small molecular products (e.g. hydrogen fluoride, carbonyl fluoride) and very reactive compounds like free radicals, because their effectiveness strongly depends on the age of the particle.

The agents in the degradation products, which cause polymer fume fever, are not known.

5.7.2 Critical effects

Large doses of PTFE fumes cause pulmonary inflammation, haemorrhage, oedema and even death in experimental animals. Similar effects have occurred in humans who have accidentally inhaled fumes from the degradation processes at exceptionally high temperatures.

In humans, the well-known health effect of PTFE degradation products is the polymer fume fever with flu-like symptoms. The smoking of even slightly PTFE contaminated tobacco products is the cause in the great majority of reported cases.

5.7.3 Approaches to workplace monitoring

Hydrolysable fluoride (hydrogen fluoride, inorganic fluoride, carbonyl fluoride and other organic forms of fluoride, which are hydrolysed in alkaline solution) has been used as a marker of the decomposition products of fluorocarbon polymers. The quantification uses fluoride-ion-selective electrode or ion chromatography. Fluorinated hydrocarbons can be monitored by gas chromatography.

5.7.4 Recommended basis for an occupational exposure limits

There exists no relevant scientific basis for occupational exposure limits for the thermal degradation products of PTFE.

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Summary

Zitting A. 124. Thermal Degradation Products of Polyethylene, Polypropylene, Polystyrene, Polyvinylchloride and Polytetrafluoroethylene in the Processing of Plastics. The Nordic Expert Group for Criteria Documentation of Health Risks from Chemicals. *Arbete och Hälsa*, 1998;12:1-40

Plastics are subjected to elevated temperatures in the processing. This gives rise to complex mixtures of substances. The quality and quantity of these depends, e.g. on the type of the polymer, additives, and the degradation temperature. This criteria document covers the occupational health effects caused by the thermal degradation products from five plastics at processing temperatures. The industrial hygienic measurements have shown that the concentrations of individual compounds in normal processing are much lower than their Nordic occupational exposure limit values. The dose-response data is insufficient and so there are no scientific foundations for occupational exposure limits.

Polyethylene and polypropylene. The major degradation products under relevant conditions are formaldehyde, formic acid, acetaldehyde, and acetic acid and other aldehydes and acids. Aerosols are formed in significant amounts. Alkoxy radicals have also been detected. Respiratory irritation found in animal studies suggest that this might be used as a critical effect. Observed effects in man are mainly case reports of bronchoconstriction.

Polystyrene. Styrene is the most significant degradation product. Other notable products are aerosols, carbonyl compounds and formic and acetic acid. The only reported adverse effect in humans in the processing industry has been increased risk of abortions but no quantitative exposure assessment is available.

Polyvinylchloride. Hydrogen chloride is the main product from polyvinylchloride. Other products are emitted at much higher temperatures than in processing. The most abundant emissions usually originate from additives (like phthalates). Aerosols are also emitted. Workers have complained of irritation in eyes and respiratory tract. In these cases the degradation temperatures have been, however, unusually high. The best-known adverse effect is the meat wrapper's asthma but the causative agent is not known. The fumes can also affect adversely lung functions.

Polytetrafluoroethylene. The major gaseous products are hydrogen fluoride, carbonyl fluoride and fluorinated hydrocarbons. Ultrafine particles have been the cause of toxic pulmonary and lethal effects in experimental animals. Large doses of fumes cause pulmonary inflammation, haemorrhage, oedema and even death in experimental animals. Similar effects have occurred in humans who have accidentally inhaled fumes from degradation at exceptionally high temperatures. The best-known adverse effect is polymer fume fever with flu-like symptoms. Smoking of contaminated tobacco products has been the cause in the majority of cases.

Keywords: Human toxicity, occupational exposure, occupational exposure limits, plastics, processing, review, risk evaluation, thermal degradation.

Summary in Swedish

Zitting A. 124. Thermal Degradation Products of Polyethylene, Polypropylene, Polystyrene, Polyvinylchloride and Polytetrafluoroethylene in the Processing of Plastics. The Nordic Expert Group for Criteria Documentation of Health Risks from Chemicals. *Arbete och Hälsa*, 1998;12:1-40.

Plaster utsätts för upphettning vid bearbetning. Detta ger upphov till en komplex blandning av nedbrytningsprodukter. Hur mycket och vilka nedbrytningsprodukter som bildas beror på vilken plast som bearbetas, vilka tillsatser som används och vid vilken temperatur de bearbetas. Detta kriteriedokument omfattar de yrkesrelaterade hälsoeffekter som orsakas av de termiska nedbrytningsprodukter som bildas vid uppvärmning, till bearbetningstemperatur, av fem olika plaster. Yrkeshygieniska mätningar har visat att koncentrationen av de bildade nedbrytningsprodukterna är mycket lägre än de i Norden gällande hygieniska gränsvärdena för de individuella ämnena. Dos-respons data är för ofullständiga för att något vetenskapligt underlag som grund till ett hygieniskt gränsvärde skall kunna göras.

Polyetylen och polypropylen. De huvudsakliga nedbrytningsprodukterna som bildas under relevanta förhållanden är formaldehyd, myrsyra, acetaldehyd och ättiksyra samt andra aldehyder och syror. Aerosoler bildas i betydande mängd. Alkoxyradikaler har också påvisats. Baserat på djurstudier kan irritation av luftvägarna eventuellt anses utgöra den kritiska effekten. Observerade effekter på människa inskränker sig till fallrapporter av bronkokonstriktion.

Polystyren. Den huvudsakliga nedbrytningsprodukten är styren. Andra noterbara produkter är aerosoler, formaldehyd och ättiksyra och andra karbonylföreningar. Den enda skadliga effekt som rapporterats hos människa inom processindustrin är en ökad risk för abort. Inga kvantitativa exponeringsdata finns dock tillgängliga.

Polyvinylklorid. Den huvudsakliga termiska nedbrytningsprodukten från polyvinylklorid vid bearbetning är väteklorid medan andra produkter bildas vid betydligt högre temperaturer. Andra kvantitativt viktiga ämnen härstammar från tillsatser, t ex ftalater. Aerosoler bildas också. Arbetare har klagat över irritation i ögon och luftvägar men vid dessa tillfällen har processtemperaturen varit onormalt hög. Den bäst beskrivna skadliga effekten är köttpackarastma, men vad som orsakar denna är okänt. Ångorna kan också negativt påverka lungfunktionsvärden.

Polytetrafluoroetylen. De huvudsakliga flyktiga nedbrytningsprodukterna är vätefluorid, karbonylfluorid och fluorerade kolväten. De mycket små partiklar som bildas vid upphettning har i djurförsök orsakat lungtoxicitet och dödlighet. Stora doser ånga orsakar lunginflammation, blödningar, ödem och död hos försöksdjur. Liknande symptom har observerats hos människa som på grund av olyckshändelse inandats ångor efter mycket höga degradationstemperaturer. Den mest välkända skadliga effekten hos människa är polymerröksfeber "teflonfrossa" med influensaliknande symptom. Rökning av kontaminerade tobaksprodukter har varit den vanligaste orsaken.

Nyckelord: Bearbetning, humantoxicitet, hygieniskt gränsvärde, plaster, riskvärdering, termisk nedbrytning, yrkeshygienisk exponering, översikt.

Databases Used

Medline

Toxline

The search-words used were "thermal degradation", "polyethylene", "polypropylene", "polystyrene", "PVC", "PTFE", "polyvinyl chloride", "polytetrafluoroethylene", and "pyrolysis".

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