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Degradation products of plastics

Polyethylene and styrene-containing thermoplastics — Analytical, occupational and toxicologic aspects

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Preface

Since 1977, problems associated with the possible health hazards of different degradation products of plastic materials have been discussed and studied in both Sweden and Finland. The Finnish factory inspectorate has demanded an examination of the effect of such degradation products, especially those arising from the handling of plastics materials in industry.

The need for investigations on the effects of the degradation products of plastics simultaneously arose in both countries. A literature review was carried out in the Department of Polymer Technology, the Royal Institute of Technology (KTH), in Stockholm to facilitate the evaluation of the degradation products that evolve during the processing of plastics. Laboratory investigations of the degradation products of polystyrene were carried out with the aid of gas chromatography at the Institute of Occupational Health in Helsinki. Toxicologic experiments were performed on exposed rats. The experience of the Institute of Occupational Health in this field was directly useful to industry in Sweden. Knowledge of polymer technology and the laboratory facilities at the Royal Institute of Technology were a primary condition for research on the relationship between temperature and the thermal degradation rates of various plastics materials during different processes.

However, both institutes lacked the equipment for gas chromatography-mass spectrometry. Such equipment and experience with it were available at the Department of Analytical Chemistry at the University of Stockholm, where methods for these analyses were developed in a project entitled "Chemical Analysis of Fire Gases."

Cooperation between the three institutes was established so that the products arising from the degradation of plastics at different temperatures and the health hazards involved could be studied. Collaboration between the three institutes made it possible to increase knowledge about the characteristics of plastics, the degradation products which arise, and the toxicologic effects of these degradation products.

Dr H Frostling acted both as the coordinator of the different subprojects and as the secretary of the task group. The Swedish labor market, the Swedish National Board of Occupational Safety and Health, the Swedish Confederation of Plastics, LM Ericsson, and the managers of the projects were all represented within the task group.

During the phase of the study concerned with the industrial hygiene measurements, L-M Westerberg, MSc, measured the radicals; S Vainiotalo, MSc, provided her skillful assistance with the analyses and the field measurements; Mr Y Peltonen and Ms T Hankimo provided technical assistance; and Ms T Salmi helped with the scanning electron micrographs. Mr E Meriluoto helped with the revision of the English text concerning this part of the study.

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Abbreviations

The following abbreviations are used throughout the text, tables and figures without explanation:

ABS	= poly(acrylonitrile-butadiene-styrene)
HDPE	= high-density polyethylene
IPS	= impact polystyrene
LDPE	= low-density polyethylene
MDPE	= medium-density polyethylene
NADPH	= reduced nicotinamide adenine dinucleotide phosphate
PE	= polyethylene
PP	= polypropylene
PS	= polystyrene
PVC	= polyvinyl chloride
SAN	= poly(acrylonitrile-styrene)
UDP	= uridine 5'-diphosphate

I. Background

by Harald Frostling

The name plastics is applied to compositions consisting of high molecular-weight compounds (polymers) containing additives. The latter are added to the polymer to impart certain useful qualities. The most widely used additives include antioxidants, stabilizers, pigments, and other components added in small amounts, about 2—3 % of the weight of the polymer (eg, PE, PP, and PS). Other additives, such as plasticizers and fillers, are sometimes added in considerably larger amounts, eg, soft PVC can contain as much as 70 % plasticizers. Plastics are widely used commercial materials that are consumed in large quantities (table 1).

The real increase in the annual consumption of plastics varied between 7—13 % in the 1970s, and the calculated increase for the 1980s is estimated to be the same. Plastics materials are being used more and more in building and construction work, in car production, and in the packing, color and electronic industries. The plastics processing industry thus contains a variety of different trades and different-sized companies. However, the industry producing polymers consists of a few large enterprises. There were, eg, around 20 production plants with a total of some 4,000 employees in Sweden in 1975 (47) and 7 Finnish production plants in 1977 with some 1,000 employees. All of the large commodity plastics, LDPE and HDPE vinyls, PP, PS, and polyurethane, are manufactured in Sweden and Finland. The production is dominated by PE and PVC plastics.

The plastics processing industry in Sweden consumed 437,000 t of commodity plastics in 1974 (47), and the Finnish consumption was around 453,000 t in 1978 (unpublished data of the Finnish Federation of the Plastics Industry). Thermoplastics dominate consumption. The number of plastics processing companies in Sweden was 730 with 27,000 employees in 1974, while, according to the Finnish Federation of the Plastics Industry (unpublished data), there were 165 plastics processing plants in Finland with 10,500 employees in 1978.

Processing techniques

The techniques used for processing thermoplastics depend to a large extent on the type of product required. Extrusion, injection molding, compression molding, and blow molding are widely used, though many other techniques are also employed. Processing temperatures vary with the type of thermoplastic, the type of application, and the flow index of the thermoplastic (table 2).

PE, PS, and related plastics are generally processed within the temperature range of 200—320°C. Somewhat higher temperatures can also be encountered. Table 3 shows some of the typical temperatures used during the injection molding of these substances (69).

Table 1. Consumption of common plastics in Western Europe in 1979 (29).

Material	Consumption (1,000 t)
HDPE	1,250
LDPE	3,430
PP	1,000
PS	1,600
ABS	270
Polyvinyls	3,430
Polyurethane	950

Chemical background

Polyethylene

More PE is produced than any other plastics in the world. Most processing methods for this substance are carried out at temperatures of 200—320°C, although temperatures as high as 370°C are occasionally used. The degradation that occurs during the processing of the plastics can be minimized but not eliminated. The amount and nature of the volatile organic products evolved during the processing are dependent on temperature and oxygen access to the heated plastics. The different methods of producing PE and the innumerable variations formed from the compounding of the polymer with various additives can influence the thermostability of the material considerably. Thus different amounts and types of organic volatiles can be expected to evolve during the processing of the various PE materials available on the market.

Table 2. Typical processing temperatures for PE and PS (91).

Processing method	Processing temperature (°C)	
	PE	PS
Extrusion (pipes)	140—170	—
Extrusion	—	150—280
Film and coatings	200—340	—
Injection molding	150—370	150—280
Compression molding	130—230	—
Blow molding	—	190—235

Investigations concerning volatiles formed during the thermal and thermooxidative degradiation of PE have mainly involved temperatures that do not correspond to those used in industrial processing (8, 9, 10, 66, 68, 81, 98) or those produced in the pyrolysis of the plastics (57, 60, 99, 100). Known toxic compounds formed during the thermooxidation of PE are oxygen-containing low-molecular-weight products such as aldehydes, ketones, and acids. According to the literature certain toxic compounds, eg, formaldehyde, formic acid, acrolein, and acrylic acid, are formed during the thermooxidation of PE (68, 72).

Styrene-containing thermoplastics

Styrene-containing thermoplastics are the third most produced type of plastics. In this group PS and IPS dominate, followed by ABS and SAN. PS is considered to be fairly thermostable at commercial molding and extrusion temperatures below 275°C. However, industrial grades of PS and IPS can contain varying amounts of occluded styrene monomer (up to 0.36 % of the weight) (94), which is released during processing. In addition the numerous commercial grades of PS, as well as the various grades of IPS, ABS and SAN, which differ in production method and additive content, could well have different thermostabilities during processing. It has been reported that the thermostability of PS and the other styrene-containing

Table 3. Parameters pertinent to the injection molding of some commodity plastics [modified from Milby (69)].

	Maximum thickness of part (cm)									
	ABS		SAN		PS & IPS		LDPE & MDPE		HDPE	
	< 0.32	> 0.63	< 0.32	> 0.63	< 0.32	> 0.63	< 0.32	> 0.63	< 0.32	> 0.63
Cylinder (°C)										
Zone 1	204—246	199—244	204—287	204—260	177—287	148—246	150—235	150—230	150—320	180—320
Zone 2	210—249	204—244	218—287	204—287	190—302	177—265	180—235	160—200	180—320	180—320
Zone 3	210—249	204—244	218—274	218—232	204—316	190—274	205—260	180—230	180—320	180—320
Nozzle temperature (°C)	210—249	204—244	204—277	190—246	190—302	177—260	205—260	160—230	210—290	210—260
Melt temperature (°C)	204—246	190—244	193—260	193—246	177—260	154—217	205—260	150—230	210—260	210—230
Mold temperature (°C)	50—100	50—100	50—82	50—82	32—65	32—65	up to 95	95	95	95
Injection time (s)	10—20	20—60	2—20	10—60	2—30	15—60	5—20	15—40	5—20	15—30
Total cycle time (s)	30—35	60—120	10—60	40—180	5—50	40—160	10—40	40—120	10—30	40—180

thermoplastics is dependent on molecular weight (17), the mode of polymerization (ionic or radical) (15, 17, 106), and composition (6, 33). Furthermore, the nature and amount of volatiles formed during the degradation of thermoplastics are dependent not only on the composition of the material, but also on the processing conditions (temperature, time, and access to oxygen).

As in the case of PE, investigations concerning volatile products formed during the thermal and thermooxidative degradation of PS and related thermoplastics have mainly employed temperatures that do not correspond to those used in industrial processing (18, 52, 55, 59, 70).

Toxicologic background

The widespread and increasing use of plastics warrants the evaluation of possible health hazards in their production and use. Toxicologic research on the different raw materials and additives used in plastics production has won increasing interest during recent years [see, eg, the report of the International Agency for Research an Cancer (43)]. Epidemiologic and toxicologic studies have revealed that many important plastics, which have been regarded as almost inert biologically, can have serious, long-term adverse effects. Well-known examples are vinyl chloride and the popular fire retardant tris(2,3-dibromopropyl)phosphate.

Research has also been focused on the hazards caused by different residues in consumer goods — Regulations on the approved maximum levels have been issued, and the use of some materials for food packaging has been banned.

The literature on the toxicologic aspects of chemicals used in the Swedish plastics industry was reviewed in order that the risks connected with plastics handling could be evaluated (95). It was found that in 1974 about 520 different products or substances were used in the plastics manufacturing and processing industry. Toxicologic estimations had been made for half of these substances.

Little research or interest has been paid to the possible health hazards of thermoplastics. They are generally regarded as biologically inert because they are not absorbed or metabolized by organisms (54). However, during their processing to end products, they are often subjected to relatively high temperatures, which may induce some breakdown of the polymer or additives and give rise to a complex mixture of products. And when these products are released to the atmosphere, they may cause a possible occupational risk to the workers processing them.

The main interest in the toxic effects of the degradation products of plastics has come so far from fire toxicologists. The basis for this research has been the fact that fatalities in fires have been caused, to a great extent, by toxic compounds from burning materials. It is, however, impossible to draw any conclusions with respect to occupational situations from the data obtained in fire research. In the fires the temperatures are essentially higher than in processing. The exposures are often massive, and the degradation products also differ. In the case of fire, the importance of some low-molecular products like carbon monoxide and hydrogen cyanide is great. These compounds are known, acute toxicants, and because of the nature of fire interest has primarily focused on acute effects (27).

The decomposition products of PVC can cause asthmalike symptoms, "meat wrappers' asthma," among workers wrapping meat in plastic film (97). Similar effects have been described in the literature for polyurethane (84) and PE (96). Low exposures to the degradation products of polytetrafluoroethylene (Teflon) cause so-called polymer fume fever (76). In all these cases the individual compounds causing the observed effects are unknown. Nevertheless, up to now, skin diseases have dominated the registered occupational diseases caused by plastics materials (47).

The only toxicologic studies which can be related to occupational situations are those in which the irritative effects of the degradation products on the respiratory tract of experimental animals have been evaluated (4). The temperatures have also been rather high in these studies, and direct extrapolation to processing exposures is impossible.

Main objectives of the project

The main objectives of the study were the following: (i) to compare the thermostability of different commercial grades of PE, PS, IPS, ABS, and SAN under conditions closely resembling those of industrial processing, (ii) to analyze the airborne products formed during the initial stage of the degradation of these plastics at low values of weight loss and develop methods for analyzing the compounds formed, (iii) to develop field sampling methods for hygienic measurements, (iv) to determine the correlation between the results of the laboratory experiments and the field measurements, and (v) to investigate the effects on biological material in studies of acute and subacute exposures.

II. Analysis of volatile products

by Ariel Hoff, Sven Jacobsson

MATERIALS

The different grades of LDPE, HDPE, PS, IPS, ABS, and SAN typically found in the Swedish plastics industry were chosen for the analysis of volatile products. They are listed in table 4.

METHODS

Thermogravimetric analysis

Thermogravimetric analysis was used to compare the thermostability of the thermoplastics in terms of weight loss at low values of weight loss (up to about 4 %). The experiments were carried out with a Cahn RG — HV thermobalance in nitrogen or in air at reduced pressure [400 torr (53.3 kPa)] to eliminate the noise due to aerodynamic effects.

Thermoplastic samples of 40—50 mg were used in pellet form. The temperature detector (thermocouple) was placed beneath a stirrup containing the sample at a distance of 3 mm. Normally the experiments were performed at a 4-mg recorder range.

The activation energies (E) for the samples at three temperatures of degradation were calculated by means of the following equation (89):

$$\log t_i/T^2 = -E/RT + \text{const},$$

where t_i is the time span of isothermal degradation, T the temperature of degradation in Kelvin degrees, and R the universal gas constant.

Gas chromatographic and gas chromatographic-mass spectrometric analysis

Procedure of degradation

The degradation experiments with PE and the styrene-containing thermoplastics PS, IPS, ABS and SAN reported in this paper were carried out on the thermal degradation unit depicted in fig 1. This apparatus consists basically of the following parts: a thermal degradation tube made of Pyrex glass, a movable thermostated furnace (0—600°C), and an enrichment section.

The thermoplastics sample was placed in the degradation tube, and helium or dry air was pumped through the tube and the enrichment section at a rate of 20—30 ml/min. To prevent the diffusion of laboratory air into the tube, an additional bypass flow of 20 ml/min was applied to the opening of the glass tube.

The degradation started when the furnace moved along the tube, and within 1—2 min the sample attained the same

temperature as the furnace. The evolved products were swept away and enriched in a glass trap cooled by liquid nitrogen. For the analysis with gas chromatography-mass spectrometry the glass trap was attached to a six-port valve (Carle 2821, Fullerton, CA, USA) (39). The desorption of the enriched compounds was carried out with heat in the case of analyses of compounds with a low boiling point and with solvent when degradation products with a higher boiling point were being analyzed.

Apparatus

An LKB 9000 gas chromatographic-mass spectrometric apparatus with a laboratory-made gas chromatograph and an Altema multiple ion detector (Altema AB, Solna, Sweden) was used in the analyses. The operating conditions were as follows: ionization energy 70 eV, ion source temperature 250°C, acceleration voltage 3,500 V, trap current 40 μA. The transfer line and the two-stage jet-separator were kept at 220°C.

In the selected ion monitoring, chromatograms were recorded on a three-channel, strip chart recorder (Linear 595, Linear Instruments Corp, Irvine, CA, USA) at an

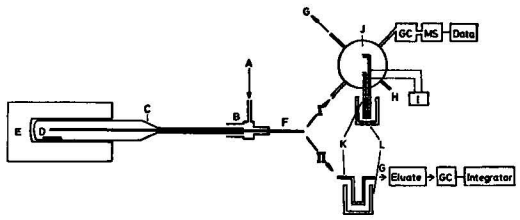


Fig 1. Thermal degradation system of the thermoplastics and the analytical pathways of the evolved products. I. Gas chromatographic-mass spectrometric analysis. II. Quantitative analysis of the degradation products from the styrene-containing thermoplastics. A = forced gas flow, 40—50 ml/min of degradation atmosphere; B = modified Swagelok reducing union 3.1 to 1.6 mm; C = degradation tube made of Pyrex glass; D = sample; E = furnace (0—600°C); F = glass capillary kept at 125 to 135°C; G = pumping (20—30 ml/min); H = helium fackflush; I = trap heater; J = six-port valve; K = glass trap (230 μl) filled with glass beads; L = Dewar flask. (GC = gas chromatograph, MS = mass spectrometer)

Table 4. Thermoplastics samples used.

Sample number	Thermo-plastics	Density (g/cm^3)	Additives	Melt index (g/10 min)	Trade name	Producer
1	LDPE	0.921	None	0.3	DFDS 6600	Unifos Kemi AB
2	LDPE	0.921	Release agent, antiblocking agent, antioxidant, titanium dioxide	0.3	DFDS 6607	Unifos Kemi AB
3	LDPE	0.921	Release agent, antioxidant, antiblocking agent	0.3	DFDS 6601	Unifos Kemi AB
4	LDPE	—	Release agent, antiblocking agent	—	NA 203-Z	USI Europe NV
5	HDPE	0.958	Antioxidant, carbon black	0.4	DGDS 2467	Unifos Kemi AB
6	HDPE	0.958	Unknown	8.0	Hostalen GC 7260	Hoechst
7	HDPE	0.958	Unknown	—	Dow 100 62	Dow Chemical
8	PS	—	Unknown	—	XP 5536	Dow Chemical
9	PS	1.04	Unknown	3.5	634	Dow Chemical
10	IPS	1.04	Unknown	3.5	461	Dow Chemical
11	IPS	1.05	Unknown	4	454 H	BASF
12	ABS	—	Unknown	—	Ugikral RA 10331	Ugine Kulman
13	ABS	1.04	Unknown	—	Cycolac AM 25139	Borg-Warner
14	SAN	1.08	Unknown	12	Luran 368 R 004	BASF

ionization energy of 70 eV, but for the determination of total ion current chromatograms an ionization energy of 20 eV was used.

Normalized mass spectra were received by an interfaced, laboratory-programmed M-8 Intertechnique computer (Intertechnique, 78-Plaisir, France) and displayed on a cathode ray tube.

The gas chromatograph was a Packard 427 (Packard-Becker Br, Delft, The Netherlands) equipped with capillary columns. It was connected to a LDC 308 integrator (Shannon, Ireland).

The columns used in this work are listed in table 5.

Analysis of the volatile organic products of polyethylene

The products that evolved from the PE samples were separated with columns 3—6 (table 5). PE samples, 2.8—4.0 mg, were heated for 3—12 min, dry air or helium being pumped through the tube at a rate of 20 ml/min. The samples were stamped out to have approximately the same size.

The volatile organic products were analyzed quantitatively with the use of external standards, calibration curves, and selected ion monitoring. The mean relative standard deviation in these experiments was 15 %.

Analysis of the volatile organic products of the styrene-containing thermoplastics

The identification and quantitative analysis of the products evolving from the styrene-containing thermoplastics was carried out with columns 1—3 and 7—8 (table 5). For the quantitative analyses capillary columns 7 and 8 and the internal standard technique were primarily used. Styrene-containing thermoplastics, in pellet form, were heated for 10 min. Ten to twenty milligrams of the sample was used for the analysis with gas chromatography-mass spectrometry. For quantitative analyses with the capillary gas chromatograph, 45—55 mg of the sample was used. During the heating dry air or nitrogen flowed through the tube at a rate of 25—30 ml/min.

Table 5. Chromatographic columns used for the analysis of the degradation products of PE and the styrene-containing thermoplastics.

Number	Type of column	Stationary phase/support	Temperature (°C)	Purpose
1	Packed, 2 m, 1.8-mm inner diameter, glass	SP 2100/Chromosorb W AW[a] 100/120 mesh	30—260	Qualitative analysis of degradation products of PE and the styrene-containing thermoplastics
2	Packed, 2 m, 1.8-mm inner diameter, glass	SP 1000/Chromosorb W, 100/120 mesh	50—225	Qualitative analysis of degradation products of the styrene-containing thermoplastics
3	Packed, 2 m, 1.8-mm inner diameter, glass	OS-138/Tenax GC, 60/80 mesh	30—220	Qualitative and quantitative analysis of low-molecular and oxygen-containing degradation products
4	Packed, 2 m, 1.8-mm inner diameter, glass	0.2 % SP 1000/Carbopack C, 100/120 mesh	30—210	Analysis of ketones and butyrolactone
5	Packed, 1 m, 1.8-mm inner diameter, glass	Porapak T, 60/80 mesh	130	Analysis of formaldehyde
6	Packed, 1 m, 1.8-mm inner diameter, Teflon	Fluorade FC-431[b] Tenax GC, 60/80 mesh	30—140	Analysis of C_1—C_4 acids, acetaldehyde
7	Wall-coated open tubular, 20 m, 0.2-mm inner diameter, glass	SP 2100[c]	30—210	Qualitative and quantitative analysis of non- and medium-polar degradation products of the styrene-containing thermoplastics
8	Wall-coated open tubular, 27 m, 0.24-mm inner diameter, glass	SE — 52[d]	25—250	Qualitative and quantitative analysis of non- and medium-polar degradation products of the styrene-containing thermoplastics

[a] Support Carbowax 20M deactivated according to Moseman (74).
[b] Fluorocarbon surfactant (11).
[c] Column deactivated according to Blomberg & Wännman (12).
[d] Column deactivated according to Grob et al (35).

The enriched compounds in the cooled trap were desorbed with solvent, 500 to 600 μl of either chloroform or toluene (analytical grade). One to two microliters of this eluate was then injected, in splitless mode, onto the capillary column.

The weight of each degradation product was calculated with the following equations:

$$c_i = (A_i c_{is} f_i)/A_{is}$$

and

$$f_i = (A_{is} m_i)/(A_i m_{is}),$$

where c_i = weight of product, c_{is} = weight of the internal standard, n-tridecane, in the eluate, A_i = area of product, A_{is} = area of internal standard, f_i = response factor, m_i = amount of sample compound, and m_{is} = amount of internal standard.

The quantitative results presented are the means of two thermal degradation/gas chromatographic runs, except for the thermooxidative degradation of SAN, for which five runs were made. In these experiments, the relative standard deviation varied between 5.4 and 9.9 % for the five most intense peaks. It was 6.3 % for styrene, 6.3 % for ethylbenzene, 5.4 % for isopropylbenzene, 9.9 % for benzaldehyde, and 6.6 % for n-propylbenzene.

For unresolved compounds or compounds for which this system was not suitable, ie, for compounds with too low a boiling point or too high a polarity, the thermal degradation/gas chromatographic-mass spectrometric system and packed columns were used. The compounds were quantified from the areas seen in the total-ion-current chromatogram and from the appropriate response factors that were normalized to the response factor of ethylbenzene.

THERMAL DEGRADATION OF POLYETHYLENE

Results

The thermogravimetric curves for seven different PE samples at 368°C are shown in fig 2. The reproducibility of the experimental points on the curves was about 0.02 % for three experiments with the same sample. Small differences in weight loss among the LDPE samples were observed. In the initial stage of weight loss, the LDPE samples were more stable than the HDPE samples. The differences in weight loss among the three HDPE samples studied were much more pronounced. One of these samples (number 7) was more stable in terms of weight loss than the two other samples (numbers 5 & 6). The weight loss of one of the "unstable" HDPE samples (number 5) commenced below 200°C. After the initial weight loss of the HDPE samples (0.4—0.9 %) the rate of loss decreased markedly.

Two samples were studied by gas chromatography-mass spectrometry. One of the samples was an LDPE (sample 1); it contained no additives and was the most stable according to thermogravimetric experiments. The other (sample 5) was an HDPE; it was one of the least "thermostable" among the samples studied. The results of gas chromatography of the thermodegradation products of these samples are shown in fig 3. The products identified by mass spectrometry after separation by gas chromatography are shown in table 6.

Altogether 27 products were identified. In the HDPE gas chromatogram small peaks of short chain hydrocarbons were seen. On the other hand, the LDPE chromatogram revealed an abundance of short

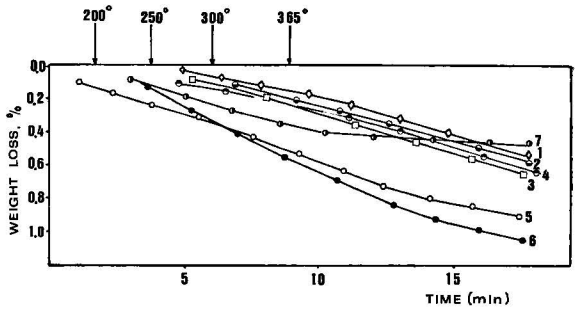


Fig 2. Thermal gravimetric curves of PE in helium at 368°C. Sample numbers as in table 4. The arrows indicate the time when a certain temperature was reached.

chain hydrocarbons. Linear, as well as branched, hydrocarbons were identified in the case of LDPE, whereas almost exclusively linear hydrocarbons were found in the analysis of HDPE.

The results of quantitative gas chromatography-mass spectrometry of the C_2—C_7 linear hydrocarbons are given in table 7. These results indicate that the amounts of C_2—C_7 linear hydrocarbons formed during the initial stage of the thermal degradation of LDPE and HDPE are roughly the same. The major products among the components quantified are C_4 hydrocarbons.

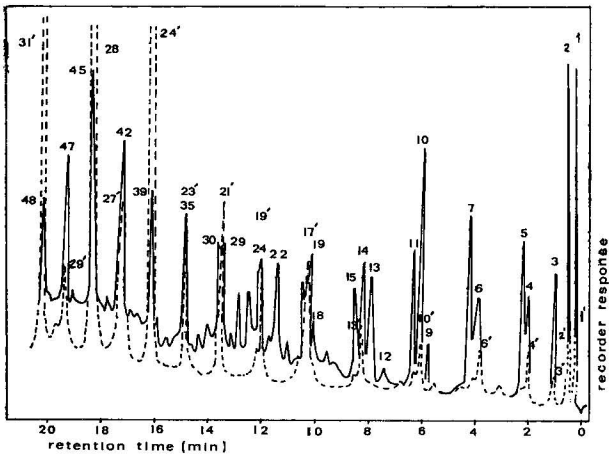


Fig 3. Gas chromatographic analysis of the products of thermal degradation of PE at 360°C on column 1 (see table 5). Peak numbers refer to the numbers in table 6. (——— LDPE sample 1, ---- HDPE sample 5)

Table 6. Thermal degradation of PE at 360°C in helium.

Number	Peak number [a]	Product	LDPE [b]	HDPE [b]	Identification [c]	
					Gas chromatography	Mass spectrometry
1	1,1'	Ethene, ethane	+	+	A	B
2	2,2'	1-Butene, butane	+	+	A	B
3	3,3'	1-Pentene, pentane	+	+	A	B
4	4,4'	1-Hexene	+	+	A	B
5	5,5'	Hexane	+	+	A	B
6	6,6'	1-Heptene	+	+	A	B
7	7,7'	Heptane	+	+	A	B
8	9	3-Methyl-1-heptene	+	—	Not used	C
9	8'	Methylcyclohexene	—	+	Not used	C
10	10	2-Ethyl-1-hexene	+	—	Not used	C
11	10'	Octane	—	+	A	B
12	11	2,4-Dimethylhexane	+	—	Not used	C
13	13'	1-Nonene	—	+	A	B
14	14	Trimethylcyclopentane	+	—	Not used	C
15	15	Nonane	+	—	A	B
16	19,17'	1-Decene	+	+	A	B
17	19'	1-Undecene	—	+	A	Not used
18	29,21'	1-Dodecene	—	+	A	Not used
19	22	2-Methyl-4-ethylhexane	+	—	Not used	C
20	35,23'	C_{13}	+	+	A	Not used
21	24	3,3-Dimethylheptane	+	—	Not used	C
22	39,25'	C_{14}	+	+	A	Not used
23	42,27'	C_{15}	+	+	A	Not used
24	45,28'	C_{16}	+	+	A	Not used

[a] Peak numbers according to fig 3.
[b] + = detected, — = not detected.
[c] A: according to retention time, B: according to mass spectra of individual compounds, C: according to mass spectra compared with those of Cornu & Massot (22).

Discussion

When the thermal stability of different PE samples is compared in terms of their initial weight loss, the following factors should be considered: (i) the nature and the amounts of stabilizers in PE, (ii) the chemical structure of the sample, and (iii) the molecular weight distribution of the sample or, more precisely, the presence of extractable oligomers with low molecular weights.

The information about the stabilizers in the samples studied was rather scanty. The most thermostable sample in terms of initial weight loss was LDPE (sample 1), which contained no additives at all. The stabilizers in the other samples were perhaps exhausted before the isothermal conditions were reached.

The essential difference in structure between HDPE and LDPE is that LDPE molecules may have 8—40 (usually 20—30) branches, some exceeding 10 carbon atoms in length, while HDPE molecules may have less than five short branches and are therefore nearly linear in structure. Thus LDPE contains a considerably higher number of tertiary carbon-hydrogen bonds than HDPE. The tertiary carbon-hydrogen bonds have a lower bond dissociation energy than secondary carbon-hydrogen bonds. Consequently, HDPE may be expected to be more thermostable than LDPE. Actually, after the initial weight loss (0.4—0.9 %), the rate for the HDPE samples diminished below that for the LDPE samples. Thus, after a weight loss of 0.4—0.9 %, the HDPE samples were more thermostable than the LDPE ones.

The difference in the initial weight loss of the LDPE and HDPE samples can also depend on the third factor mentioned, ie, a difference in the molecular weight distribution of the samples studied. This distribution was unknown for most of the samples, the exception being LDPE sample 1. The LDPE with the known molecular weight distribution (41) contained a small portion of oligomers with molecular weights as low as 500. The activation energy of the thermal degradation of LDPE sample 1 measured at 334, 355, and 368°C at the same value of weight loss (0.2 %) was found to be about 20 kcal/mol (84 kJ/mol). This value is much lower than the energy expended in the thermal degradation of HDPE [about 70 kcal/mol (293 kJ/mol)] (104).

The two HDPE samples (numbers 5 & 6) which had the largest initial weight loss presumably contain a greater portion of oligomers with low molecular weights than the other samples. Thus it seems plausible that the difference in the initial weight loss among the samples studied was caused by the difference in the content of low molecular oligomers. This conclusion is supported by the results of the gas chromatographic-mass spectrometric analyses.

Actually, a comparison of the chromatograms of the most (LDPE, sample 1) and least (HDPE, sample 5) "thermostable" samples shows a considerably larger amount of hydrocarbons with a high boiling point from HDPE than from LDPE (fig 3). On the other hand, the hydrocarbons C_2—C_7, which are formed in the course of thermal degradation, are found in approximately the same amounts for both HDPE and LDPE (samples 1 & 5, table 7).

THERMOOXIDATIVE DEGRADATION OF POLYETHYLENE

Results

The thermogravimetric curves for the thermooxidation of the different PE samples at 296°C are shown in fig 4. The substances used for these experiments were in pellet form. Only pellets with approximately the same size and form were used so that nearly the same surface-volume relation would exist for the melted samples. The weight loss seen in fig 4 was probably the net weight loss after the

Table 7. Some products (μg/kg) of thermal degradation of LDPE and HDPE at 360°C in helium.[a]

Compound	LDPE (sample 1)	HDPE (sample 5)
Ethene, ethane	80	54
Propene, propane	79	54
1-Butene, butane	150	114
1-Pentene, pentane	83	57
1-Hexene, hexane	71	52
1-Heptene, heptane	75	50

[a] Reaction time 4 min.

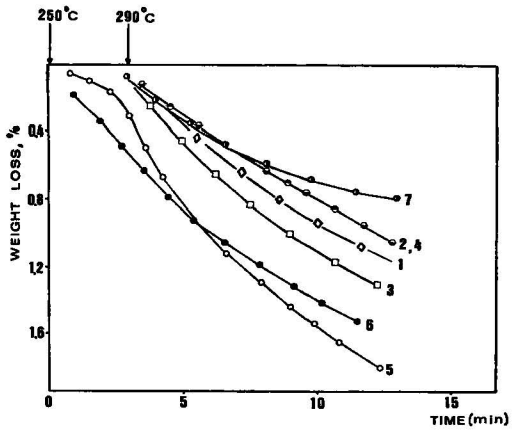


Fig 4. Thermogravimetric curves of PE in air at 296°C. Sample numbers as in table 4. The arrows indicate the time when a certain temperature was reached.

Table 8. Products of PE thermooxidation.

Number	Compound	Identification[a]	
		Gas chromatography	Mass spectrometry
1	Carbon dioxide	A	B
2	Water	A	B
3	Ethene	A	B
4	Propene	A	Not used
5	Propane	A	Not used
6	Cyclopropane	Not used	C
7	Butene[b]	A	Not used
8	Butane[c]	A	Not used
9	Pentene	A	Not used
10	Pentane	A	Not used
11	Hexene	A	Not used
12	Hexane	A	Not used
13	Heptene	A	Not used
14	Heptane	A	Not used
15	Octene	A	Not used
16	Octane	A	Not used
17	Methanol	A	B
18	Ethanol	A	B
19	Furan	Not used	C
20	Tetrohydrofuran	Not used	C
21	Formaldehyde	A	B
22	Acetaldehyde	A	B
23	Propanol	A	B
24	Acrolein	A	B
25	Butanal	A	B
26	Isobutanal	Not used	C
27	Pentanal	A	B
28	Acetone	A	B
29	Methyl vinyl ketone	A	B
30	Methyl ethyl ketone	A	B
31	2-Pentanone	Not used	C
32	2-Hexanone	Not used	C
33	2-Heptanone	Not used	C
34	Formic acid	A	B
35	Acetic acid	A	B
36	Propionic acid	A	B
37	Acrylic acid	A	B
38	Butyric acid	A	B
39	Isovaleric acid	Not used	C
40	Hydroxyvaleric acid	Not used	C
41	Crotonic acid	A	B
42	Caproic acid	Not used	C
43	Butyrolactone	A	B
44	Valerolactone	Not used	C

[a] A: according to retention time, B: according to mass spectra of individual compounds, C: according to mass spectra compared with those of Cornu & Massot (22).
[b] 1-Oletins.
[c] N-alkanes.

thermoplastics had taken up an unknown amount of oxygen and lost an unknown amount of carbon and oxygen. However, these curves serve only for comparative purposes. The relative thermostability of the samples, judged in terms of weight loss, resemble the results found for thermal degradation experiments with the same samples. Most of the LDPE samples and one HDPE sample (number 7) showed relatively small differences in isothermal weight loss, at least up to 0.4—0.5 % of weight loss. The weight loss of these samples was observed in the vicinity of 290°C. For two other HDPE samples (number 5 & 6), the weight loss commenced at a temperature below 250°C. These two samples (numbers 5 & 6), which were the least stable during the thermal degradation experiments, revealed a greater thermolability, at least at weight losses of up to 1.0—1.5 %. The results of the identification of the volatile products detected by gas chromatography-mass spectrometry are summarized in table 8.

Altogether, 44 products representing hydrocarbons, alcohols, aldehydes, ketones, acids, lactones, cyclic ethers, and cyclic esters were found. The oxygen-containing compounds constituted the majority and the hydrocarbons a minority of the products detected after the thermooxidation of LDPE. The gas chromatographic chromatograms for LDPE and HDPE were essentially the same. The results of the quantitative measurements of some volatile, oxygen-containing products formed during the oxidation of LDPE and two HDPE samples are given in table 9.

Table 9 shows that, among the oxygen-containing products, fatty acids were the most abundant, followed by aldehydes. Formic acid was the main component detected. It was followed in abundance by formaldehyde and acetaldehyde. With respect to the formation of volatile, oxygen-containing products during the thermal oxidation of one LDPE sample (number 1) and two HDPE samples (numbers 5 & 7), the following observations can be made: (i) the oxidation of the LDPE sample and the most "thermostable" HDPE sample (number 7), in terms of weight loss, resulted in the formation of approximately the same amounts of oxygen-containing volatile products, and (ii)

the oxidation of one of the least "thermostable" HDPE samples (number 5), in terms of weight loss, resulted in the formation of somewhat higher amounts of oxygen-containing volatiles, especially evident for formic acid and formaldehyde.

The effect of temperature (264—289°C) on the yield and rate of formation of volatile acids and aldehydes during LDPE oxidation is shown in fig 5 and 6.

Discussion

The difference between the amounts of acids formed during the thermooxidation of HDPE and LDPE is considered in the literature to be the result of differences in the crystallinity of these thermoplastics (10, 66, 72). However, this explanation seems inadequate for the experimental results found in our study.

The difference in the volatilization of the samples, as evidenced by the thermogravimetric curves (fig 4), and the difference in the yields of the fatty acids, as evidenced by the gas chromatographic-mass spectrometric analysis (table 9), during thermooxidation can be explained as follows. The least "thermostable" HDPE sample (number 5) presumably contained a larger portion of oligomers with low molecular weights than the two other samples, LDPE sample 1 and HDPE sample 7. The oligomers of PE that are volatile under experimental conditions (eg, 280°C) are oxidized in the gas phase. This gas phase oxidation could be expected to proceed at a considerably higher rate than the oxidation on the thermoplastics surface. Thus more complete oxidation (acids instead of aldehydes) could be achieved.

The thermooxidation of PE in the temperature range of 264—289°C results in the formation of a very complex mixture of oxidation products. As has already been shown, 44 compounds representing 10 classes of organic products were identified. The most abundant products formed were fatty acids, followed in abundance by formaldehyde and acetaldehyde. These results generally coincide with those obtained by Matveeva and coworkers (66), who studied the oxidation of PE in oxygen at 150 and 170°C. They found that fatty acids are the predominant products, followed by formaldehyde and acetaldehyde. The aldehydes consti-

Table 9. Thermooxidative degradation of LDPE and HDPE at 280°C (4 min) — Concentration of some of the volatile products (μmol/g of LDPE or HDPE).[a]

Compound	Molecular weight	LDPE (sample 1)	HDPE (sample 5)	HDPE (sample 7)
Aldehydes				
Formaldehyde	30	59.3	88.3	59.3
Acetaldehyde	44	44.3	30.7	23.6
Propanal	58	6.4	5.3	3.4
Acrolein	56	5.0	6.4	4.1
Butanal	72	9.7	7.5	5.4
Pentanal	86	6.3	6.5	4.7
Ketones				
Acetone	58	4.3	4.6	2.1
Methylethylketone	72	4.4	8.9	—
Methylvinylketone	70	0.43	1.7	—
2-Pentanone	86	3.4	7.2	—
Acids				
Formic	46	75.0	106.5	84.8
Acetic	60	23.3	30.0	23.0
Propionic	74	9.4	9.7	9.2
Acrylic	72	2.5	4.6	3.2
Butyric	88	2.6	3.9	2.7
Lactones				
Butyrolactone	86	3.4	5.3	—

[a] Mean values for at least three experiments, the relative standard deviation being about ± 15 %.

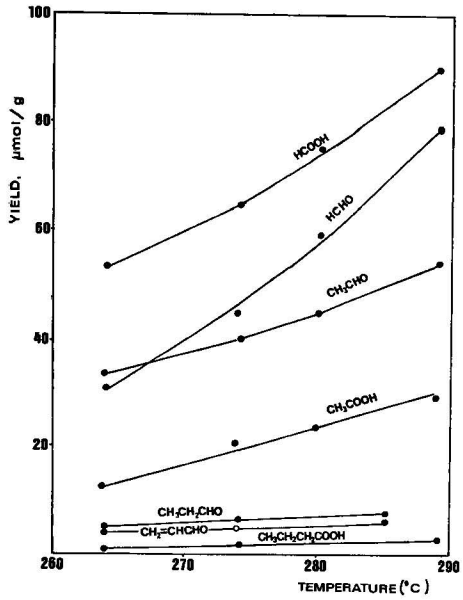


Fig 5. Effect of temperature on the yields of some aldehydes and acids during the thermal oxidation of LDPE sample 1. (HCOOH = formic acid, HCHO = formaldehyde, CH_3CHO = acetaldehyde, CH_3COOH = acetic acid, CH_3CH_2CHO = propionaldehyde, $CH_2{=}CHCHO$ = acrolein, $CH_3CH_2CH_2COOH$ = butyric acid)

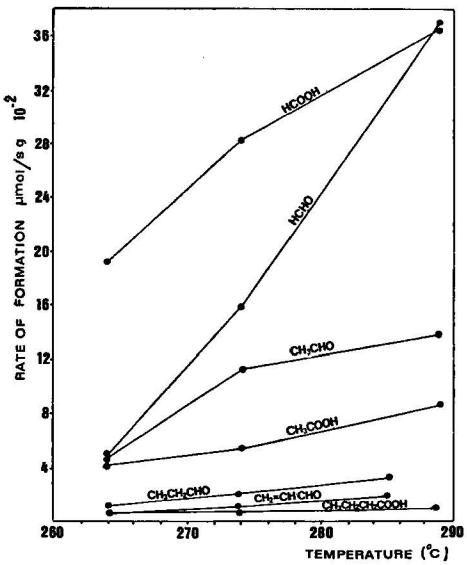


Fig 6. Effect of temperature on the rates of formation of some aldehydes and acids during the thermooxidation of LDPE sample 1. (HCOOH = formic acid, HCHO = formaldehyde, CH_3CHO = acetaldehyde, CH_3COOH = acetic acid, CH_3CH_2CHO = propionaldehyde, $CH_2{=}CHCHO$ = acrolein, $CH_3CH_2CH_2COOH$ = butyric acid)

tute about 30 % of the total amount of the acids produced.

However, other results have been published. The oxidation of PE in oxygen at 150 and 160°C (9) and in oxygen concentration levels of 0—100 volume % at 75—200°C (98) result in the formation of different volatile products. Acetaldehyde was found to be the main product (9), or among the main products (98).

The evolution of fatty acids, acrolein, and formaldehyde during smoldering combustion of PE was studied by Morikawa (72). He found that the maximum yield of these volatiles was obtained at 300—400°C. At 350°C during 30 min of heating, the yield was about 78,000 μg/g for formaldehyde, 16,500 μg/g for acrolein, 9,500 μg/g for acetic acid, 8,700 μg/g for formic acid, and 2,300 μg/g for propionic acid.

The discrepancies in the results obtained by different authors might arise from different experimental conditions (temperature and atmosphere) and from different analytical conditions, eg, the use of gas chromatographic columns that are not proper for the separation of acids.

The formation of oxidized volatiles in the thermal degradation sampling system probably proceeds in the two possible phases: partially on and under the surface of the melted thermoplastics, with restricted access to oxygen, and partially in the gas phase, rich with oxygen. In the latter case, the volatiles are formed by the oxidation of the decomposed thermoplastics, a situation which compares to industrial conditions.

The mechanism for the formation of some products of the thermooxidation of LDPE has been discussed in a paper published elsewhere (39). The volatile short-chain acids and aldehydes formed at the surface of the melted thermoplastics would probably be decarboxylate and decarbonylate at the experimental temperatures used (264—289°C). Therefore it seems plausible that the short-chain aldehydes and acids are formed predominantly by gas-phase oxidation of the oxidized fragments and the escaped hydrocarbons. In this connection it is pertinent to mention that the gas-phase oxidation of n-hexane in air at 300—400°C results in a high yield of fatty acids and formaldehyde (72).

The study of the temperature effect on

the oxidation of LDPE (fig 5 & 6) shows that the increase of the temperature of oxidation favors the formation of formaldehyde.

THERMAL AND THERMOOXIDATIVE DEGRADATION OF THE STYRENE-CONTAINING THERMOPLASTICS

Results and discussion

For the study of the composition of the volatile organics formed during the degradation of the styrene-containing thermoplastics, a range of 0.2—1.2 % was chosen for loss in weight. The temperatures used in these experiments were within the range used in the industrial processing of these thermoplastics. In fig 7 and 8 the isothermal thermogravimetric curves of all the samples run in nitrogen and air are shown. Because the thermogravimetric experiments were conducted at a somewhat reduced pressure, while the thermal degradation/gas chromatographic experiments were run at atmospheric pressure with a forced gas flow (nitrogen or air), the actual loss in weight in air differed in these experiments. For the calculation of the actual yield of the volatiles formed, special experiments were conducted in which the thermoplastics samples were weighed before and after the thermal degradation runs.

Thermal degradation

Table 10 presents the volatile products formed during 10 min of thermal degradation. The yield of the volatiles, judged on the basis of the yield of styrene, comprises only a part (sometimes a minor part) of the products evolved during the heating of the samples. This conclusion is drawn on the basis of the weight loss experiments. Thus a considerable part of the volatiles are products with a high boiling point that are retained in the glass capillary connecting the degradation tube with the trap for gaseous components. This finding was proved in separate experiments in which the products condensed in the capillary were analyzed. As an example thermal degradation of IPS (sample 11) has been chosen.

Fig 9 presents two chromatograms, one of the volatile fraction and one of the products with a high boiling point that were retained in the capillary. It can be seen that the products with a high boiling point dominated over styrene, which was the main compound quantified (table 10). The proportion of products with a high boiling point was much larger for the PS and IPS samples than for the ABS and SAN samples.

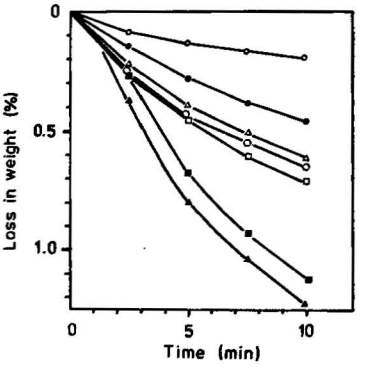


Fig 7. Thermogravimetric curves of some styrene-containing thermoplastics in nitrogen at 400 torr (53,320 Pa) under isothermal conditions. (O = PS sample 8, 260°C; ● = PS sample 9, 252°C; □ = IPS sample 10, 252°C; ■ = IPS sample 11, 240°C; △ = ABS sample 12, 209°C; ▲ = ABS sample 13, 210°C; ○ = SAN sample 14, 208°C)

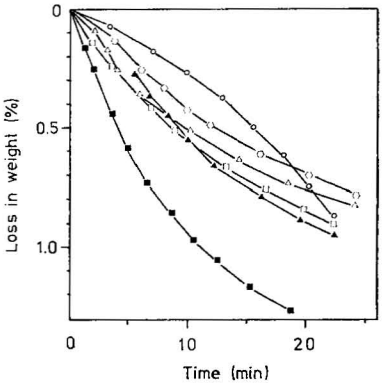


Fig 8. Thermogravimetric curves of some styrene-containing thermoplastics in air at 400 torr (53,320 Pa) under isothermal conditions. (O = PS sample 8, 250°C; □ = IPS sample 10, 250°C; ■ = IPS sample 11, 224°C; △ = ABS sample 12, 208°C; ▲ = ABS sample 13, 197°C; ○ = SAN sample 14, 218°C)

Polystyrene and impact polystyrene. PS is the most thermostable of the styrene-containing thermoplastics studied (fig 7 & 10). The activation energies found for the isothermal degradation of the PS samples at a low degree of loss in weight (0.3 %) were 23 kcal/mol (96 kJ/mol) (sample 8) and 11 kcal/mol (46 kJ/mol) (sample 9), the corresponding values for IPS polymers under the same conditions were 11 kcal/mol (46 kJ/mol) (sample 10) and 7.6 kcal/mol (32 kJ/mol) (sample 11).

The activation energy for the thermal degradation of PS is dependent on the

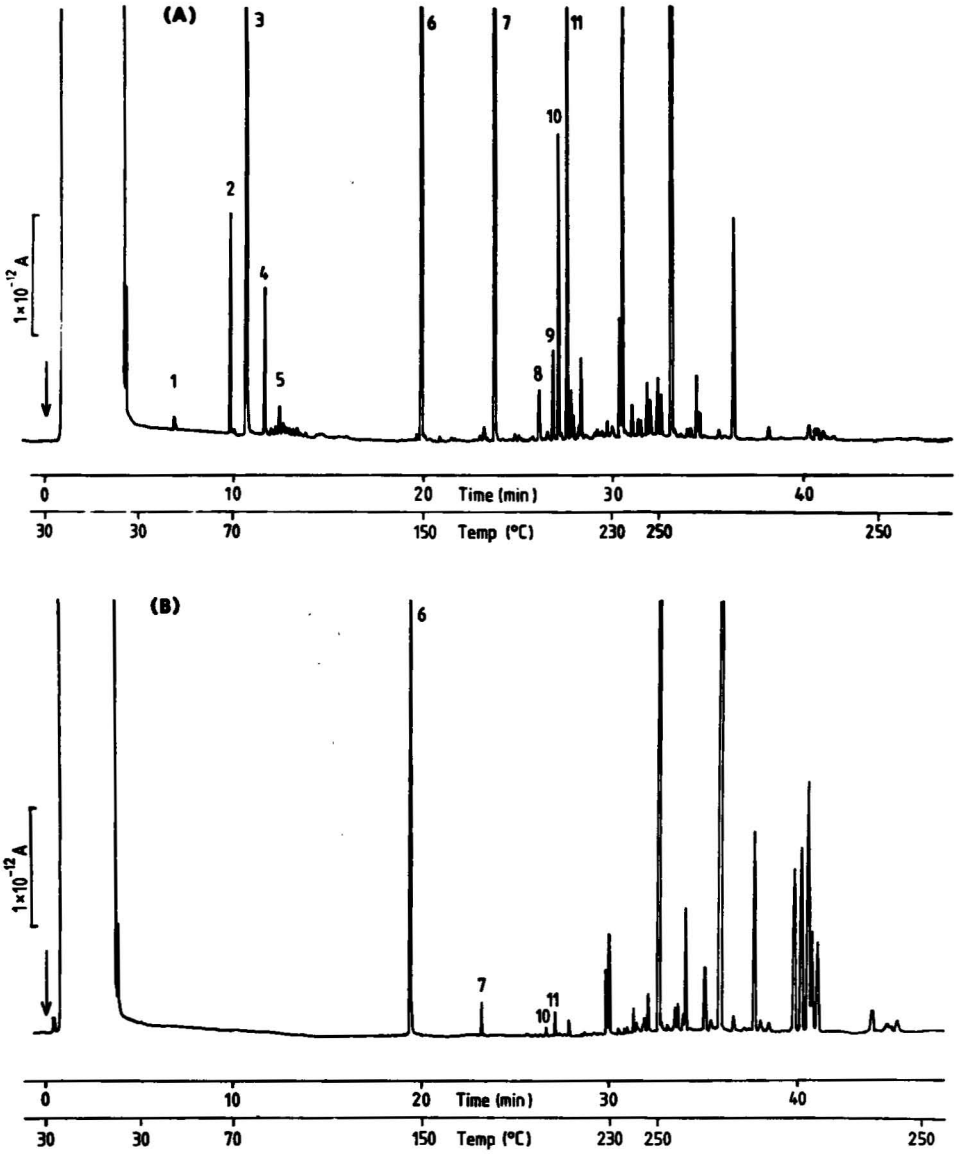


Fig 9. Gas chromatograms of the degradation products obtained by heating sample 11 at a final temperature of 240°C in an atmosphere of nitrogen for 10 min. Gas chromatogram A shows degradation products enriched in the glass trap cooled by liquid nitrogen. Gas chromatogram B presents degradation products retained in the capillary, kept at 135°C. The capillary connects the degradation tube with the trap (see fig 1). [Peak identification: 1 = toluene, 2 = ethylbenzene, 3 = styrene, 4 = iso-propylbenzene, 5 = n-propylbenzene, 6 = n-tridecane, 7 = 2,6-di-t-butyl-4-methylphenol, 8 = 1,3-diphenylpropane, 9 = styrene dimer a (see fig 11), 10 = styrene dimer b, 11 = styrene dimer c]

Table 10. Thermal degradation products (μg/g of thermoplastic) of the styrene-containing thermoplastics.[a]

Product	PS (sample 8, 255°C)	PS (sample 9, 260°C)	IPS (sample 10, 260°C)	IPS (sample 11, 240°C)	ABS (sample 12, 210°C)	ABS (sample 13, 210°C)	SAN (sample 14, 210°C)
Hydrocarbons							
4-Vinyl-1-cyclohexene	—	—	—	—	13	88	—
Aromatic hydrocarbons							
Toluene	< 10	< 10	< 10	< 10	—	—	< 10
Styrene[b]	330 (9.1)	520 (13)	290 (3.1)	390 (3.3)	2400 (30)	7400 (55)	2400 (34)
Ethylbenzene	24	38	24	39	23	54	670
Di-methylbenzene	—	—	—	—	14	—	—
α-Methylstyrene	< 10	< 10	< 10	< 10	12	230	—
β-Methylstyrene	< 10	< 10	< 10	< 10	< 10	18	11
3-Phenyl-1-propene	—	—	—	—	< 10	—	—
n-Propylbenzene	< 10	19	23	< 10	18	32	69
Iso-propylbenzene	11	25	18	25	42	190	130
Ethyl-methylbenzene	< 10	15	20	< 10	11	39	49
Phenylcyclohexene	—	—	—	—	18	—	—
1,3-Di-phenylpropene	< 10	< 10	< 10	—	—	—	< 10
1,3-Di-phenylpropane	< 10	< 10	< 10	11	—	—	< 10
Styrene dimer							
A[c,d]	29	43	< 10	50	—	—	15
B[c,d]	14	26	24	15	—	—	—
C[c,d]	120	250	180	100	—	—	19
Alcohols							
Phenol	—	—	—	—	33	—	—
Cresol	—	—	—	—	48	—	—
2-Phenyl-2-propanol	—	—	—	—	20	580	—
2,6-Di-t-butyl-4-methylphenol	—	—	88	440	—	—	—
Aldehydes							
Benzaldehyde	—	—	—	—	33	75	24
Ketones							
Acetophenone	—	—	—	—	23	420	—
Miscellaneous							
Acrylonitrile[e]	—	—	—	—	15	< 10	11
Styrene-acrylonitrile							
A[d,f]	—	—	—	—	—	—	< 10
B[d,f]	—	—	—	—	—	—	14
C[d,f]	—	—	—	—	—	—	35
D[d,f]	—	—	—	—	—	—	21

[a] Activation energy (kcal/mol), measured in the temperature range of ± 15°C from the temperature indicated with the name of the thermoplastic in the heading and referring to the loss in weight given in parentheses: PS sample 8: 23 (0.3); PS sample 9: 11 (0.3); IPS sample 10: 11 (0.3); IPS sample 11: 7.6 (0.3); ABS sample 12: 16 (0.8); ABS sample 13: 17 (0.8); SAN sample 14: 18 (0.9).
[b] The styrene yield is given in parentheses as the percentage of total loss in weight.
[c] See fig 11.
[d] Compounds assumed to have the same response factor as n-tridecane.
[e] Compounds quantified from the gas chromatographic-mass spectrometric chromatogram.
[f] See fig 12.

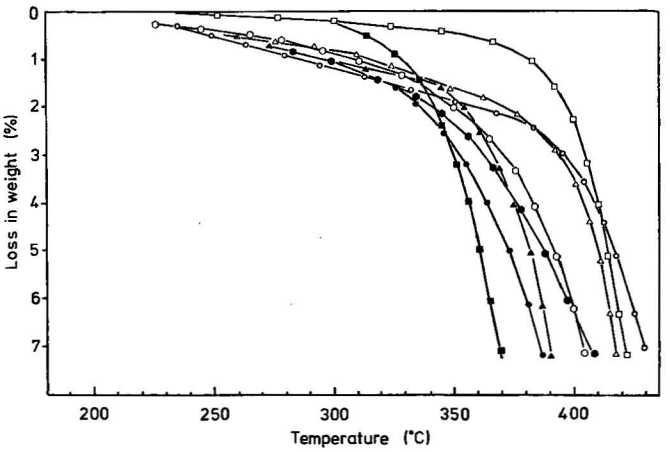


Fig 10. Thermogravimetric curves of styrene-containing thermoplastics in air and nitrogen at 400 torr (53,320 Pa), heating rate 16°C/min. (Air atmosphere: ■ = PS sample 8, ● = IPS sample 9, ⬢ = ABS sample 12, ▲ = SAN sample 14; nitrogen atmosphere: □ = PS sample 8, O = IPS sample 11, ⬡ = ABS sample 12, △ = SAN sample 14)

molecular weight and the mode of polymerization; it is in the range of 41—51 kcal/mol (172—214 kJ/mol) (17). The corresponding value for decompositions of the "weak bonds" in PS is 23 kcal/mol (96 kJ/mol) (6). Commercial samples of PS and IPS sometimes contain small amounts of styrene (up to 0.36 %) and other compounds (toluene, ethylbenzene, propylbenzene) in minor amounts (94). These compounds are occluded by the polymer during polymerization.

Among the volatiles identified and quantified, styrene was the main product, followed by styrene dimer. This conclusion coincides with the observations based on the results of chromatographic separation made elsewhere (70). In one case, for IPS (sample 11), a rather large amount of 2,6-di-t-butyl-4-methylphenol (an antioxidant) was detected. This sample showed the lowest value of activation energy. Thus, for a low degree of volatilization, there are two factors which can influence the initial weight loss of PS and IPS, ie, evaporation of the occluded monomer and/or additives (characterized by very low activation energy) and thermal degradation of the polymer.

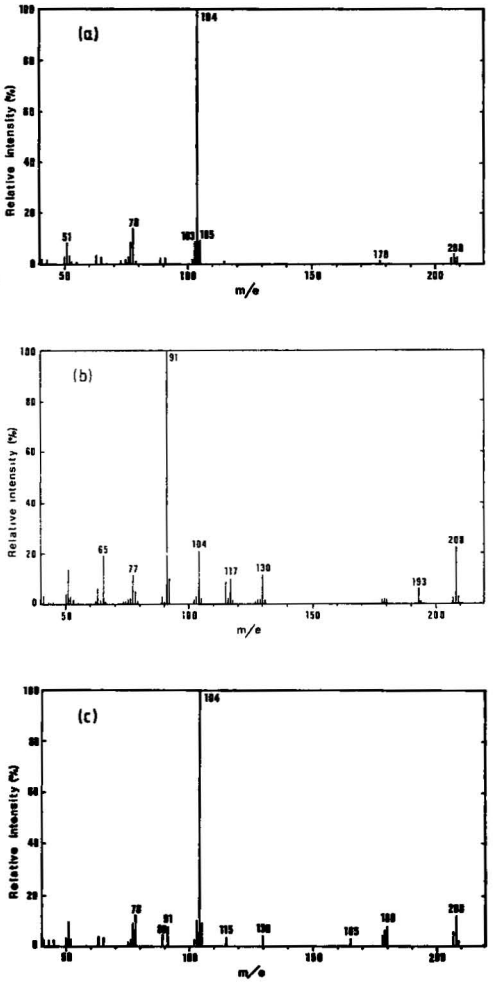


Fig 11. Mass spectra of the styrene dimers appearing as peaks 9 (= a), 10 (= b), 11 (= c) in fig 9.

The presence of styrene dimers in the case of PS, as well as the formation of compounds with high boiling points, indicates that some degradation of the original samples took place. The low values of activation energy indicate a considerable impact of evaporation on the weight loss of the samples. As was pointed out earlier, styrene was the main volatile product found during the thermal degradation of PS. However, the yields of styrene (3.1—13 %) were much lower than the value of 40 % found for PS by Madorsky & Straus (59) at 300—400°C. The low yield of styrene could be explained by the fact that the activation energies for the formation of dimer, trimer, and other fragments with high boiling points were considerably lower than for styrene (93). Thus at low degradation temperatures the formation of these products is favored over that of styrene.

The formation of styrene dimers has been discussed in several papers. Noffz et al (80) found 1-benzyl-2-methyl-3,4-benzocyclobutene to be the predominant dimer product during the pyrolysis of PS at 768°C. Cascaval et al (18) stated that 1,3-diphenyl-1-butene would be the major dimer product during thermal degradation at 600°C. Tsuge et al (101) studied the thermal degradation of PS at 580°C and found 1,3-diphenylbutene to be the major dimer product.

In our work we found three peaks with different retention times and a molecular weight of 208 (fig 9 & 11). Noffz et al (80) considered 1,3-diphenyl-1-butene and 2,4-diphenyl-1-butene to be the precursors of the predominant dimer 1-benzyl-2-methyl-3,4-benzocyclobutene. The dimer 2,4-diphenyl-1-butene would probably give rise to a large m/e 91 due to the double-allylic position in that compound. The

loss of a methyl group could be explained by a double bond migration to the conjugated position followed by allylic cleavage. To assign the right structure to the dimer products of styrene-containing thermoplastics, a definitive study of these compounds would be necessary, and such a study was outside the scope of the present work.

Poly(acrylonitrile-butadiene-styrene) and poly(acrylonitrile-styrene). One of the ABS samples (number 12) and the SAN sample showed a similar pattern of loss in weight (fig 10), and the composition and amount of the degradation products corresponded also to some degree, especially for styrene. On the other hand the two ABS samples differed. Sample 13 decomposed considerably faster and formed about three times more styrene than sample 12. The activation energies for degradation were roughly the same for all three samples. In addition the degradation pattern of the least thermostable ABS (sample 13) revealed higher amounts of some volatiles, namely, α-methylstyrene, 2-phenyl-2-propanol and acetophenone, than the other ABS sample (number 12) and the SAN sample. Grassie & Bain (33) showed that the rate of volatilization of SAN is directly proportional to the acrylonitrile content in the thermoplastic. The increase of acrylonitrile content in SAN favors the higher styrene yield during degradation. Thus the difference in the rates of degradation and the amounts of styrene evolved by these ABS grades can be assumed to be related to a difference in acrylonitrile content. The styrene yield of the total loss in weight was considerably higher for the ABS and SAN samples than for the PS and IPS samples (table 10).

According to Grassie & Bain (34) styrene and acrylonitrile are the main volatile products formed during the thermal degradation of SAN at 330°C, styrene being dominant. In our study, at 210°C, acrylonitrile was a minor component found in a very low amount (0.1—1.2 mole % of styrene content).

From the thermal and thermooxidative degradation studies of the SAN sample,

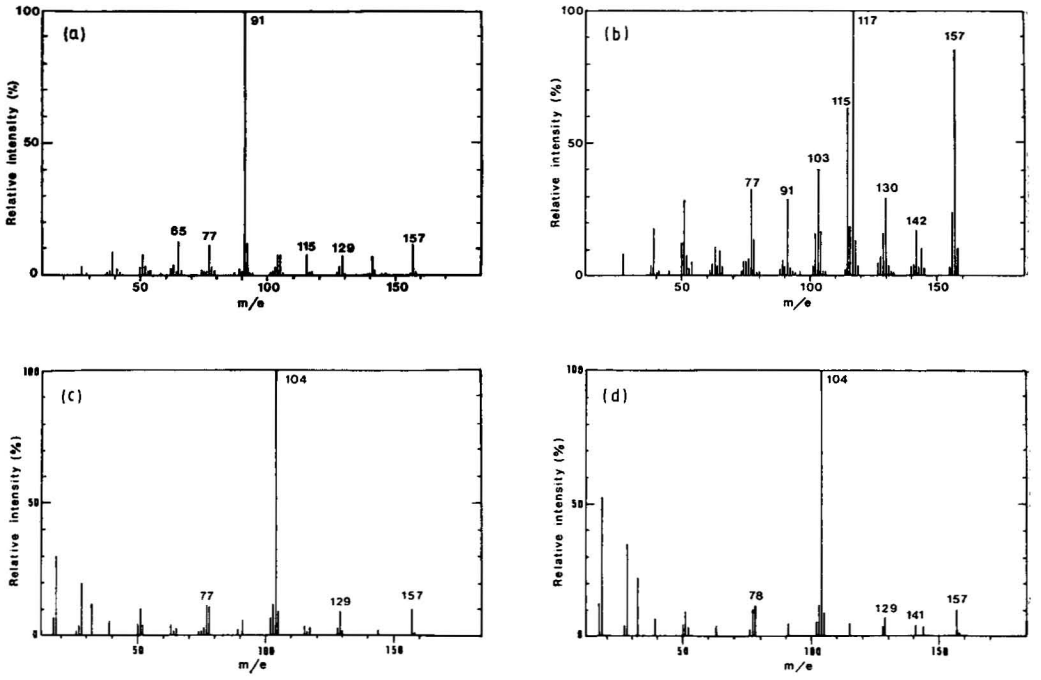


Fig 12. Mass spectra of styrene-acrylonitrile dimers found during the thermal and thermooxidative degradation of SAN. Mass spectra a and b correspond with those reported by Grassie & Bain (35).

four different styrene-acrylonitrile dimers with the molecular weight of 157 were found in very small amounts. Two of these correspond to the two reported by Grassie & Bain (34). Mass spectra of these compounds are given in fig 12.

Thermooxidative degradation

In fig 10 the thermogravimetric curves for the thermal and thermooxidative degradation of PS, IPS, ABS, and SAN are shown. It can be seen that, in terms of loss in weight, PS was the most sensitive and ABS the least sensitive to the influence of air during thermal stress. IPS and SAN show an intermediate behavior. In the initial stage of weight loss the isothermal thermogravimetric curves (fig 8) for all the samples in air were similar to those obtained in nitrogen. The only exception was PS. The thermogravimetric curve for PS was typical for autoxidation reactions. Table 11 gives the amounts of volatiles formed during 10-min thermooxidative degradation of the samples in dry air (flow conditions 25—30 ml/min).

Table 11. Thermooxidative degradation products (μg/g of thermoplastic) of the styrene-containing thermoplastics.

Product	PS (sample 8, 250°C)	PS (sample 9, 240°C)	IPS (sample 10, 250°C)	IPS (sample 11, 224°)	ABS (sample 12, 208°C)	ABS (sample 13, 197°C)	SAN (sample 14, 218°C)
Hydrocarbons							
4-Vinyl-1-cyclohexene	—	—	—	—	10	82	—
Aromatic hydrocarbons							
Benzene[a]	14	< 10	< 10	< 10	—	—	—
Toluene	< 10	< 10	< 10	< 10	—	—	< 10
Styrene[b]	740 (7.0)	520 (8.0)	280 (3.8)	310 (3.4)	2300 (32)	7800 (68)	2700 (32)
Ethylbenzene	24	37	26	32	20	56	760
Di-methylbenzene	—	—	—	—	12	—	—
α-Methylstyrene	29	13	< 10	< 10	< 10	120	—
β-Methylstyrene	13	< 10	< 10	< 10	< 10	17	12
3-Phenyl-1-propene	—	—	—	—	< 10	—	—
n-Propylbenzene	< 10	16	14	< 10	18	35	80
Iso-propylbenzene	< 10	23	14	19	35	190	140
Ethyl-methylbenzene	< 10	17	17	< 10	14	38	52
Phenylcyclohexene	—	—	—	—	16	—	—
1,3-Di-phenylpropene	11	< 10	< 10	< 10	—	—	—
1,3-Di-phenylpropane	12	< 10	< 10	< 10	—	—	< 10
Styrene dimer							
A[c, d]	74	51	17	48	—	—	13
B[c, d]	40	50	27	14	—	—	—
C[c, d]	110	260	200	100	—	—	17
Alcohols							
Phenol	120	50	27	17	25	—	—
Cresol	—	—	—	—	37	—	—
Benzyl alcohol	34	18	—	—	—	—	—
2-Phenyl-2-propanol	—	—	—	—	< 10	700	—
2,6-Di-t-butyl-4-methylphenol	—	—	69	290	—	—	—
Aldehydes							
Ethanal[a]	—	—	32	20	11	38	—
Acrolein[a]	—	—	80	22	15	50	—
Benzaldehyde	2300	810	300	130	43	130	60
Cinnamaldehyde	55	16	—	—	—	—	—
Ketones							
Acetophenone	380	180	58	44	35	450	—
Acids							
Benzoic acid[a]	570	300	160	80	—	—	—
Miscellaneous							
Acrylonitrile	—	—	—	—	19	< 10	25
Styrene-acrylonitrile							
A[d, e]	—	—	—	—	—	—	< 10
B[d, e]	—	—	—	—	—	—	14
C[d, e]	—	—	—	—	—	—	35
D[d, e]	—	—	—	—	—	—	18
M-132[d, f]	320	130	31	21	—	—	—

[a] Compounds quantified from the gas chromatographic-mass spectrometric chromatogram.
[b] The styrene yield is given in parentheses as the percentage of total loss in weight.
[c] See fig 11.
[d] Compounds assumed to have the same response factor as n-tridecane.
[e] See fig 12.
[f] Unidentified compound M-132. The eight most intense ions (m/e) with relative intensity (in parentheses) in the mass spectrum of this compound are 103 (100), 77 (61), 132 (49), 104 (47), 51 (37), 79 (23), 107 (21), and 55 (19).

Polystyrene and impact polystyrene. Of the thermoplastics studied, PS was the most susceptible to thermooxidation (fig 10). The main products, formed during the initial stage of the thermooxidative degradation of PS and IPS, were benzaldehyde, styrene, benzoic acid, and acetophenone.

The amounts of volatiles detected for IPS were considerably lower than those for PS. The styrene yield, as percentage of the total loss in weight, for both PS and IPS was similar to that found during thermal degradation. Among the products identified during the thermooxidative degradation of PS, a compound with a molecular ion of 132 was found. Mitera et al (70) suggested that vinylbenzaldehyde should be a major thermooxidative degradation product of PS at 280°C. However, the mass spectrum of the compound with a molecular weight of 132 did not correspond to the reference spectrum of vinylbenzaldehyde. The resemblance with the fragmentation pattern of 2-phenylpropanal (22) indicates that the unknown compound is more likely to be 2-phenylpropenal. This probability could however not be verified since no reference spectrum or reference compound was available. The amount of the unknown compound and the mass spectrum of the eight most intense ions of this compound can be found in table 11.

Poly(acrylonitrile-butadiene-styrene) and poly(acrylonitrile-styrene). The losses in weight of both ABS grades and SAN at low degrees of volatilization were dependent to some extent on access to oxygen during degradation (fig 10). The composition of the products formed during thermal and thermooxidative degradation was similar. The major compound formed in the course of thermooxidative degradation was styrene.

III. Industrial hygiene measurements

by Pirkko Pfäffli

Materials

The same types of plastics that were used for the laboratory experiments (table 5) were chosen to test both the field sampling methods and the methods of analysis. They were typical grades used in actual industrial processes. Some plastics obtained from Finnish manufacturers were also tested; they were Peten 3022 and Peten 5022 (Pekema Ltd) and Polystyrene BN (Stymer Ltd).

Methods

Experimental degradation of plastics

In the qualitative and semiquantitative laboratory experiments, the plastics material (100 mg) underwent degradation in a J-shaped glass tube (diameter 4 mm, wall thickness 1 mm, total length 30 cm) inserted into a laboratory oven through a hole (fig 13) (85). In order for the temperature within the tube to equal the temperature within the oven, the short arm of the tube was placed completely inside the oven. The temperatures used to attain degradation ranged between 180 and 500°C.

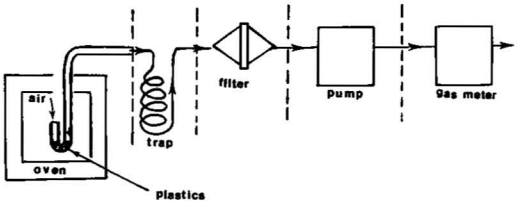


Fig 13. Arrangement for the development of thermal degradation products.

An air pump (Sipin SP 15 personal sampler, Anatole Sipin Co, USA) was used to conduct the air through the degradation tube at the rate of 0.5 l/min. The duration of air conduction was 15 min. The decomposition products were collected from the air flow after the air had passed through the tube.

Degradation products were also generated in a dynamic system (see fig 21) (109). The purpose of this procedure was to test the reproducibility of the field sampling methods. The plastics for degradation were placed in glass tubes (lengths 30—150 cm, outer diameter 17 mm). The load of the plastics was 0.1 g/cm. Each tube was passed through a tubular oven (length 10 cm, inner diameter 18 mm). The oven was moved along the tube by a step motor at a rate of 10 cm/h. The degradation products were conducted to a chamber (100 l) by the air flow. The rate of the air flow varied between 0.02 and 0.50 l/min. The degradation tube and the chamber were connected with T-tubing. Another stream of air (5 l/min) was fed into the T-tube in order to dilute the fumes. A cylindrical plastic end-piece with 10 radial side holes was connected to the T-tube to ensure an even distribution of the degradation products within the chamber. The samples were removed from the chamber through 7-mm holes in the side walls.

Sampling

Laboratory sampling. The sampling device consisted of a spiral trap (diameter 4 mm, length 80 cm, wall thickness 1 mm) bathed in liquid nitrogen (—178°C). The vaporized degradation products condensed in the trap. The aerosol, which partly passed through the spiral together with the air flow, was collected on a filter located in front of a suction pump.

After the sampling, the spiral trap was brought to room temperature, and the revaporized gases were conducted into a laminated plastic bag. The degradation products that remained inside the spiral were washed out, first with 2 ml of car-

Table 12. Methods of sampling and analysis.

Compound	Sampling	Analysis	Type of analysis
Very volatile compounds	Plastic laminated bag	Gas chromatography	Total
Volatile compounds	Charcoal tube	Gas chromatography	Total
Fumes	Liquid absorption	Infrared spectroscopy	Total
Fumes	Filter	Weighing	Total
Aldehydes and ketones			
Total concentration	Liquid absorption	Iodometric	Total
Formaldehyde	Liquid absorption	1. Colorimetric	Specific
	Liquid absorption	2. Liquid chromatography	Specific
Acetaldehyde	Liquid absorption	Liquid chromatography	Specific
Acrolein	Liquid absorption	Liquid chromatography	Specific
Benzaldehyde	Liquid absorption	Liquid chromatography	Specific
Acetone	Liquid absorption	Liquid chromatography	Specific
Acetophenone	Liquid absorption	Liquid chromatography	Specific
Organic acids			
Total concentration	Liquid absorption	Potentiometric	Total
Formic acid	Charcoal tube	Liquid chromatography	Specific
Acetic acid	Charcoal tube	Liquid chromatography	Specific
Benzoic acid	Charcoal tube	Liquid chromatography	Specific
Peroxides	Liquid absorption	Iodometric	Total
Radicals	Liquid absorption	Electron spin resonance	Total
Styrene	Charcoal tube	Gas chromatography	Specific
Nitriles	Liquid absorption	Colorimetric	Total
	Tenax tube	Gas chromatography	Specific
Carbon monoxide	Indicator tube (Dräger)	Direct	Specific
Hydrogen cyanide	Liquid absorption	Ion specific	Specific
Ammonia	Indicator tube (Dräger)	Direct	Specific

bon disulfide and then with 2 ml of methanol or acetone. The samples were used to test and develop the analytical methods.

Sampling for field measurements. The sampling methods for the field measurements (table 12) were tested in the laboratory. Thermal degradation products were generated in air at temperatures between 200 and 350°C. The degradation took place in the previously described dynamic system. The sampling media and other details (flow speed, time, volume) are described in the Analytical Methods section.

Analytical methods

Very volatile compounds. The air for the analysis of short-chained aliphatic hydrocarbons and carbon monoxide was sampled into laminated plastic bags. Polyethylene-aluminum foil terephthalate, which was obtained from Euran Paperi Ltd, Finland, was used to make the heat-sealed bags. Injection needles and a portable pump (Sipin SP 15) were used to blow the samples into the completely closed bags.

The analyses were done by gas chromatography. A gas-tight syringe was used to draw a sample through the wall of the bag. A gas sampling loop was then used to inject the sample into the gas chromatograph. The volume of the loop varied between 0.1 and 1.0 ml. The columns used for the analysis of the very volatile compounds were a wide-pore capillary SE 30 column (length 50 m, diameter 0.7 mm) and a packed Tenax column (length 2 m, diameter 2 mm). The temperature of the column oven was 40°C. Flame ionization detection was used. n-Butane was used for calibration. Because some of the sample was lost from the bag (5 % in 5 d), the samples had to be analyzed within 5 d after the sampling.

Volatile compounds. Samples for the analysis of volatile compounds were absorbed on activated charcoal (PCB, Chemviron, Pittsburgh, United Kingdom) (50). The charcoal was first sieved (corn size between 0.4 and 0.8 mm) and then washed with distilled water and dried at 350°C overnight in a flow of nitrogen. Glass tubes (length 10 cm, inner diameter 4 mm) were filled with 200 mg of the charcoal. Both ends of the tubes were closed with glass-fiber stoppers. The flow resistance of the charcoal tubes was 1.1 ± 0.1 kPa. Air samples were sucked through the tubes with Sipin pumps.

The duration of the sampling was 1 h at a flow rate of 0.2 l/min. After the sampling, both ends of the tubes were sealed with plastic stoppers. The collected impurities were eluted from the charcoal overnight by 2 ml of carbon disulfide. Gas chromatography was used for the analysis. The gas chromatograph was equipped with an SE 30 capillary column (length 50 m, diameter 0.7 mm) and a flame ionization detector. A hydrocarbon solvent of the "white spirit" type (boiling point 150—200°C; Shell) was used for calibration in the analysis of samples collected during the processing of PE. When the samples collected during the processing of the styrene-containing thermoplastics were analyzed, styrene was used for the calibration. Two hundred milligrams of charcoal from the same batch used for the sampling was added to 2 ml of each calibration liquid.

Fumes. The fumes from the samples were absorbed in tetrachloroethylene. Twenty-five milliliters of tetrachloroethylene was placed in the bubblers used for absorption. The two bubblers, which were in series, were embedded in ice when the samples were taken. The air sample was sucked in by a DuPont constant flow sampler (model P 2500, El DuPont de Nemours and Co Inc, Canada) at a flow rate of 1 l/min. The volume of air used was 150 l. After the sampling, a rotating evaporator was used to evaporate the tetrachloroethylene gently to dryness. The residue was washed out with tetrachloroethylene and diluted to 1 ml. The fume samples collected during the processing of the plastics were analyzed by infrared spectrophotometry. Liquid cuvettes (pathlength 0.1 mm) were used for the analysis. The quantitative measurements of the PE fume samples were performed on the basis of carbon-hydrogen stretching bands in the wave number region of 2,800—3,000 cm^{-1} (36). Paraffin oil meeting Scandinavian pharmaceutical standards was used for the calibration. The fumes from the styrene-containing thermo-

plastics were analyzed in the wave number region of 700 cm^{-1}. The same plastic used in the process was used for the calibration. Acetonitrile was used as the solvent for ABS and SAN because they were insoluble in tetrachloroethylene.

After the measurement by infrared spectrophotometry, the sample was transferred to an evaporating dish. The solvent was left to evaporate at room temperature under a slight flow of pure nitrogen, and the residue was weighed.

The fumes were also collected on glass-fiber filters (Sartorius, type 13400, diameter 37 mm). Before use the filters were washed with cyclohexane and dried in an exsiccator overnight. Reciprotor pumps (model 506 R, Reciprotor AG, Denmark) coupled to a gas meter were used to suck air through the fourfold filter at a flow rate of 20 l/min. The minimum sampling time was 4 h. After the sampling, the filters were again dried overnight and weighed. A qualitative analysis of the samples was made by infrared spectrophotometry.

In addition a mass spectrometer (Varian MAT 112S-SS) equipped with a Varian data system 166 and a capillary gas chromatograph (Varian 1400) was used for the qualitative identification of the compounds present in the fumes when the styrene-containing thermoplastics were processed (37).

The fumes were also collected on a Nuclepore filter with a pore size of 0.2 μm (obtained from the Nuclepore Corp, USA). The DuPont constant flow sampler was used for the sampling. A flow rate of 2 l/min and a sampling time of 4 h were used. The size and shape of the fume particles were studied with an electron microscope (Jeol JEM 100 CX).

Total aldehydes. Aldehydes react with sodium hydrogensulfite, forming insoluble compounds that are stable in acidic and neutral solutions (32). Air samples were absorbed in 1 % sodium hydrogensulfite (prepared by dissolving 4.6 g of sodium hydrogensulfite in 500 ml of water). Two bubblers were used in series. The bubblers were equipped with capillaries. Each bubbler contained 25 ml of the absorption liquid. A flow rate of 1 l/min (DuPont sampler) and a duration of 1 h were used for the sampling. After the sampling, the absorption liquid was divided into three parts: 10 ml for the determination of total aldehydes, 5 ml for the determination of acrolein, and 5 ml for the determination of formaldehyde.

Ten milliliters of the absorption solution was titrated with 0.01 N iodine with starch as the indicator. Ten milliliters of sodium carbonate buffer (80 g of sodium carbonate and 20 ml of concentrated acetic acid in 500 ml of water) was added, and the solution was titrated again until a light blue color appeared.

Volatile aldehydes and ketones. The samples were absorbed directly into a reagent solution and analyzed by high-performance liquid chromatography (25, 53). The absorption liquid was made by dissolving 0.5 g of recrystallized 2,4-dinitrophenylhydrazine in 500 ml of 2 N hydrochloric acid. The liquid was washed by shaking five times with 5 ml of methylene chloride. The sampling was done by bubbling 12 l of air (0.2 l/min, Sipin pump) through two capillary bubblers, which were in series. Each bubbler contained 25 ml of the absorption liquid. The sampling solutions from the two bubblers were combined and extracted twice with 5 ml of methylene chloride. The extracts were combined, washed twice with 20 ml of 2 N hydrochloric acid, washed twice with 20 ml of distilled water, and finally evaporated to dryness in a rotating evaporator. The dried sample was dissolved in 2 ml of acetonitrile. This solution was used for the high-performance liquid chromatography. The column used was a reversed phase C_{18} column (length 25 cm, particle size 10 μm), and the elution liquid was a mixture of acetonitrile and water (62 : 38) in an isocratic analysis. The detection was done by ultraviolet spectrophotometry at 340 nm. The standards were prepared from synthesized and recrystallized 2,4-dinitrophenylhydrazones of aldehydes and ketones. Formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, benzaldehyde, acetophenone, and acetone were analyzed in this way.

Acrolein. The sampling of acrolein was carried out in the same manner as the analysis for total aldehydes. For the ana-

lysis of acrolein, 1 ml of a reagent solution (5 mg of mercuric chloride and 2.5 g of 4-hexylresorcinol in ethanol) and 5 ml of trichloroacetic acid solution (4.5 g of trichloroacetic acid in a mixture of water and ethanol, 1 : 1) were added to 5 ml of the absorption liquid and mixed well. The mixture was heated in a bath of boiling water for 5 min and then left to stand at room temperature for 45 min, after which it was spun in a centrifuge at 3,500—4,000 r/min for 5 min. The intensity of the color of the supernatant was measured with a spectrophotometer and glass cuvettes at 605 nm against a reagent blank (21).

Formaldehyde. The sampling of formaldehyde was carried out in the same manner as the analysis for total aldehydes. For the analysis of formaldehyde, 5 ml of 3 M sodium disulfite (30 g of sodium disulfite in 100 ml of water) was added to 5 ml of the absorption liquid, and the mixture was evaporated to dryness. The residue was dissolved in 5 ml of water. Five milliliters of chromotropic acid (1 g of chromotropic acid in 20 ml of water) was added to 2 ml of the sodium disulfite solution, which was then cooled under running water. The intensity of the color was measured with a spectrophotometer at 580 nm against a reagent blank (77).

Total acids. The air samples were obtained by bubbling 12 l of air through an absorption liquid, and the acidic groups were titrated potentiometrically with 0.01 M sodium hydroxide. The sampling equipment consisted of two bubblers equipped with fritted glass. The bubblers were in series. Each bubbler contained 25 ml of a mixture of ethanol and water (1 : 1). During the sampling, the bubblers were in an ice bath. The air flow (Sipin pumps) did not exceed 0.2 l/min. The sample was titrated with 0.01 M sodium hydroxide. A dropper was used to add the base, and the resulting pH value was recorded after each drop (0.02 ml). A titration curve was drawn where the change in pH was plotted against the amount of added 0.01 M sodium hydroxide. A blank was made by bubbling 12 l of pure air through the absorption liquid, which was then titrated with 0.01 M sodium hydroxide.

Volatile organic acids. The volatile organic acids were converted to p-bromophenacyl esters, which were then analyzed by high-performance liquid chromatography (49). The samples were collected by charcoal tube sampling. The duration of the sampling was 1 h, the flow rate was 0.2 l/min, and a Sipin pump was used. The collected acidic impurities were eluted overnight from the charcoal by 2 ml of dimethyl formamide. One milliliter of the clear elution solution was transferred to another tube. Anhydrous sodium sulfate was added to the tubes to remove moisture, and 0.1 ml of a bromophenacyl bromide solution (277.8 mg/10 ml of acetonitrile) and 1 μl of diisopropylethylamine were added to the tubes. The tubes were stored for 2 h at 60°C, and then overnight at room temperature. The samples were analyzed the next day by high-performance liquid chromatography in a reversed-phase C^{18} column. The elution was performed with acetonitrile and water (45 : 55) in an isocratic analysis with a flow rate of 1.5 ml/min. The detection was made in the ultraviolet region at 254 nm. The standards, which were dissolved in acetonitrile, were treated in the same manner.

Hydrogen cyanide. Thermoplastics which contain nitrogen (ABS & SAN) generate hydrogen cyanide during thermal degradation. Air samples were sucked through two fritted bubblers, which were in series. Each bubbler contained 25 ml of 0.01 N sodium hydroxide. An ion specific electrode (cyanide activity electrode, model 94—06, Orion Research, USA) was used to analyze the samples (78).

Peroxides. Peroxides were sampled by liquid absorption and assayed iodometrically (61). Absorption liquid A contained a mixture of 15 ml of acetic acid and 10 ml of acetanhydride in 200 ml of isopropanol. Absorption liquid B consisted of 50 ml of isopropanol saturated with sodium iodide (about 10 g/50 ml). Solution A was poured into solution B just before use. The mixed solution was carefully saturated with carbon dioxide. Since organic impurities had to be avoided, well-cleaned glassware was used, and particular care was taken to avoid the use of plastic material (bottles, tubes, etc). All the so-

lutions were freshly prepared. The absorption liquid was stored in a cold, dark place. Two bubblers of dark glass in series were used for the sampling. Each bubbler contained 25 ml of the absorption liquid. The bubblers were kept in an ice bath during the sampling. The rate of the sampling flow did not exceed 0.1 l/min (Sipin pump), and the duration of the sampling was restricted to 1 h. After the samples had been collected, dry ice was immediately added to the bubblers to saturate the liquid. The majority of the organic peroxides was readily reduced by the iodide ions in the reagent solution. The liberated iodine could be measured photometrically at 360 nm with glass cuvettes. The measurements, which were made immediately after the sampling, were taken with a portable photometer (Hach, spectrophotometer, model 2504—00, Hach Chemical Co, USA). Blank measurements were carried out simultaneously with the determinations of the samples. One blank consisted of pure air drawn through the absorption liquid at the same speed and for the same duration as used for the sampling. The second blank was unused absorption liquid.

Free radicals. The sampling of air for the trapping and detection of airborne free radicals was performed by liquid absorption in a toluene solution, which contained a nitrone compound as a spin trap, and the measurements were made by electron-spin resonance spectrometry (30, 46, 90, 107) (fig 14). The air sample, which was pumped by a Sipin pump, was first fed through an absorption tube (Merck 1562, Merck AG, Federal Republic of Germany) to remove carbon dioxide. The sample was then pumped through a bubbler-type trapping cell of glass designed to serve also as a sample cell for the electron-spin resonance instrument. The volume of air sampled (0.1 l) was sucked through 0.3 ml of absorption liquid at the sampling rate

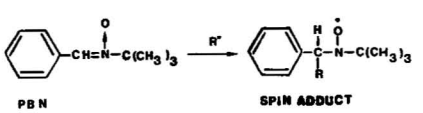


Fig 14. Spin trapping reaction.

of 10 ml/min. The absorption liquid was 0.05 M phenyl-N-tert.butyl-nitrone (Aldrich Chemical Co, USA) in redistilled toluene, which was deoxygenated with pure nitrogen. The samples in the trapping cells were stored and transported in liquid nitrogen to suppress the reactivity of the spin adducts of the collected radicals. The measurements for paramagnetic activity were made with a Varian E-109 electron-spin resonance spectrophotometer operating at a frequency of 9.5 GHz and with a magnetic field modulation of 100 kHz. The cavity (Varian E-231-2) operated in the TE_{102} rectangular mode. The samples were recorded at 0 °C in a variable temperature accessory (Varian E-257). The signals could be seen at this temperature for about 15 min. Quantitative assays of the samples were made with the free radical, 2,2,6,6-tetramethyl piperidinooxy (Aldrich Chemical Co, USA) as the absolute spin standard. This compound was dissolved in redistilled and deoxygenated toluene in different concentrations. These diluted standards, which decomposed slowly, were usable for two weeks when stored at 5 °C. The samples and the standards were measured consecutively with equal spectrophotometer settings, and the heights of the first derivative spectra were compared. This procedure yielded the spin density of the sample. For the calculation of the concentration of free radicals in the air samples, a standard atmosphere with the numerical density of 2.5×10^{25} molecules/m^3 was used. The relative concentrations of the samples were obtained in parts per million (volume : volume).

Nitriles. Organic nitrile groups in the absorption samples were oxidized to amides by 3 ml of 30 % hydrogen peroxide and then converted by alkaline hydrolysis (5 ml of 5 N sodium hydroxide) to ammonia, which was analyzed colorimetrically after distillation (51, 108). The ammonia was allowed to react with 2 ml of 45 % phenol and 2 ml of 3.7 % alkaline sodium hypochlorite. This procedure yielded indophenol. The blue color of the indophenol was measured photometrically at 630 nm. The reaction was accelerated by the addition of 0.1 ml sodium nitroprusside. Two capillary bubblers in series, each containing 25 ml of 0.01 N sulfuric

acid, were used for the sampling. A Sipin pump was used for flow, the rate of which was 0.2 l/min. The duration of the sampling was 1 h. The water used as the solvent was distilled from a mixture of 15 ml of 0.5 N sodium hydroxide and 1 g of potassium pyrosulfate.

The volatile organic nitriles were also analyzed by gas chromatography. A Varian gas chromatograph (model 3700), which was equipped with a thermionic specific detector (sensitive for nitrogen compounds) and an SP 1000 capillary column (length 30 m, diameter 0.2 mm), was used.

Direct measurements. "Dräger" tubes (Dräger Werk AG, Federal Republic of Germany) were used for direct measurements of carbon monoxide and ammonia, sometimes also for measurements of hydrogen cyanide, formic acid, and formaldehyde.

Industrial hygiene measurements

The thermal degradation products were measured in factories under normal processing conditions. The types of processes were the extrusion of films and coatings, injection molding, blow molding, and packing with plastic film. The temperatures in the machines used in the processes ranged from 140 to 250°C. On four separate occasions the thermoplastics being processed was only PE; on two occasions the thermoplastics was PS only. IPS was the sole component of the plastics on four occasions, and twice the plastics being processed was ABS. On three occasions, the plastics being processed were composed of both PE and other thermoplastics.

The samples were taken at stationary sampling points located between 50 cm and 1 m away from the processing machines, at the height of the workers' breathing zones. Parallel double sampling continued for about 6 h at each sampling point.

Results

Methods of sampling and analysis

The methods for the sampling and analysis of the air impurities were tested at the same low concentration levels found in the preparatory hygienic measurements made during processes involving the machining of PE and styrene-containing thermoplastics. In measurements of compound groups, at concentrations between 0.5 and 10 mg/m³, coefficients of variation ranging from 0.1 to 0.7 were reached. At concentrations between 0.06 and 0.6 mg/m³, in measurements of single compounds, the coefficients of variation were between 0.2 and 0.3, including both the sampling and the analysis. The lowest detection limit varied from 0.02 to 1.0 mg/m³ for the compound groups, and from 0.02 to 0.05 mg/m³ for the single compounds measured (table 13).

Polyethylene

During the processing of PE, the main thermal degradation products were hydrocarbons. The first group of compounds (very volatile compounds) in table 14 represents very vaporizable hydrocarbons. The analysis was made from gaseous samples by gas chromatography. n-Butane was used as the reference substance. The average concentration in the samples was 6.4 (SD 1.3) mg/m³. The second group of compounds (volatile compounds) in table 14 was analyzed from charcoal tube samples by gas chromatography. White spirit was used as the reference. The group represents hydrocarbons with higher boiling points than the first group mentioned in the table. The average concentration was 31.2 (SD 14.7) mg/m³.

The third and fourth groups presented in table 14 represent compounds with high boiling points. Such compounds appeared in the air mostly as fumes. The concentration of fumes collected by liquid absorption and measured by infrared spectroscopy averaged 3.5 (SD 1.5) mg/m³. The average concentration of fumes collected on filters and analyzed by weighing was 1.2 (SD 0.6) mg/m³. The scanning electron micrographs of the Nuclepore filters (fig 15) showed that the aerosol consisted of very tiny particles partly joined into aggregates. The size of the particles was smaller than 0.2 μm, which was the diameter of the pore in the Nuclepore filter.

Oxidized compounds were also detected in the air during the processing of PE (table 15). The concentrations of single

compounds with low molecular weights, eg, formaldehyde, acetaldehyde, formic acid and acetic acid, were low. The average concentration of each compound found in the samples was less than 1 mg/m³. The average concentration of total aldehydes, calculated as aldehyde groups, was 2.2 (SD 0.6) mg/m³ when aldehydes were measured as a group. The average concentration of total acids analyzed as a group was 15.4 (SD 1.4) mg/m³, calculated as acid groups. The concentrations of reactive intermediates, peroxides, and radicals (table 16) were also low. The average concentration was 0.7 (SD 0.3) mg/m³ for peroxides, calculated as hydroperoxide groups, and 0.25 (SD 0.01) ppm for radicals, calculated as free active units.

Table 13. Evaluation of the methods (including both sampling and analysis).[a]

Compound	Lowest detection limit (mg/m³)	Coefficient of variation (CV = SD/mean)	Concentration level at which the coefficient of variation was examined (mg/m³)
Very volatile compounds	1.0	0.5	10.0
Volatile compounds	0.5	0.4	10.0
Fumes			
Liquid absorption	0.5	0.1	7.0
Filter	0.2	0.2	1.0
Total aldehydes	0.1	0.7	1.0
Formaldehyde	0.02	0.2	0.06
Acetaldehyde	0.02	0.3	0.1
Benzaldehyde	0.02	0.2	0.1
Acrolein	0.02	0.2	0.1
Total acids	1.0	0.7	10.0
Formic acid	0.02	0.2	0.1
Acetic acid	0.05	0.2	0.2
Benzoic acid	0.02	0.3	0.2
Peroxides	0.2	0.1	0.5
Radicals	0.01 ppm	0.3	0.05 ppm
Styrene	0.04	0.2	0.6
Total nitriles	0.05	—	—
Acrylonitrile	0.02	—	—
Hydrogen cyanide	1.0	—	—
Carbon monoxide	2.5	—	—

[a] Number of samples was six or more in each case.

Table 14. PE — Groups of air impurities according to volatility.

	Concentration (mg/m³)		Number of processes studied	Number of measurements	Highest concentration measured (mg/m³)
	Mean	SEM [a]			
Very volatile compounds, calculated as n-butane	6.4	1.3	7	20	74.0
Volatile compounds, calculated as "white spirit"	31.2	14.7	12	133	160.0
Fumes					
Liquid absorption, calculated as paraffin oil	3.5	0.5	4	12	4.6
Filter, weighed	1.2	0.6	9	44	4.3

[a] SEM = standard error of the mean of the number of processes.

The average concentrations of both single compounds and compound groups in air were relatively low, but at times some high peak concentrations were found for the concentrations of the total aldehydes, total acids, and fumes shown in tables 14 and 15.

Carbon monoxide could not be clearly detected during the PE process.

Styrene-containing thermoplastics

Samples collected during the processing of PS had only trace concentrations of very volatile hydrocarbons (table 17). Even the average concentration of styrene was 0.4 (SD 0.2) mg/m³ for PS and 0.1 (SD 0.04) mg/m³ for IPS. The average concentration of oxidized compounds detected in the samples was at the same level. The qualitative composition of the oxidized products of the PS samples differed from the qualitative composition of the oxidized products of the PE samples in that the aldehyde group contained, in addition to formaldehyde and acetaldehyde, trace amounts of benzaldehyde and acetophenone. The acid group contained formic acid and acetic acid, but also slight amounts of benzoic acid.

When either SAN or ABS was processed, the concentrations of styrene were still lower than when the process involved PS and IPS. The concentration of styrene

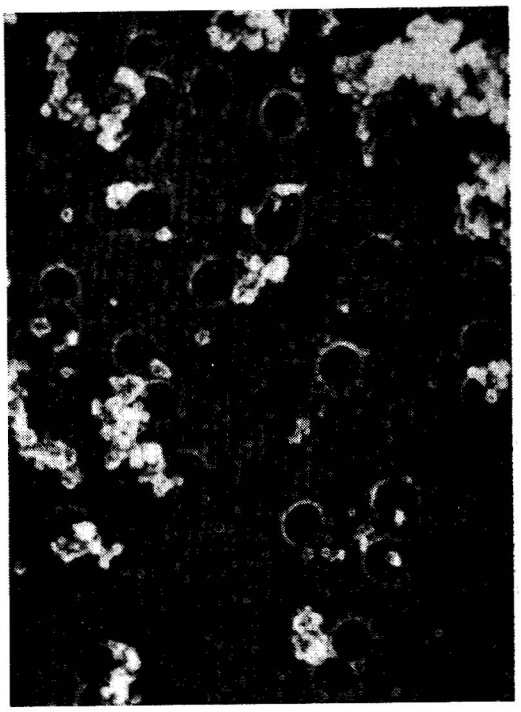


Fig 15. Scanning electron micrograph — PE fume on a Nuclepore filter (0.2 μm pore). (20,000 ×)

Table 15. PE — Oxidized thermal degradation products in the air during processing.

	Concentration (mg/m³)		Number of processes studied	Number of measurements	Highest concentration measured (mg/m³)
	Mean	SEM [a]			
Aldehydes					
Total concentration, calculated as aldehyde groups in the air	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 concentration, calculated as acid groups in the air	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

[a] SEM = standard error of the mean of the number of processes.

from either SAN or ABS was less than 0.06 mg/m³. Only small traces of oxidized compounds could be detected. Organic nitriles were detected during the processing of thermoplastics containing acrylonitrile, but only at the low concentration of 0.06 mg/m³, calculated as nitrile groups. The presence of acrylonitrile could not be detected in these samples.

Only small traces of peroxides could be detected during the processing of styrene-containing thermoplastics, and the amount of free radicals was only one-fifth of the concentration found during the processing of PE (table 16).

The average amounts of fumes generated from styrene-containing thermoplastics and collected by liquid absorption were between 1.2 and 2.4 mg/m³ (table 18). When the fumes were collected on glass-fiber filters, the gravimetric analyses yielded concentrations between 0.3 and

Table 16. Reaction intermediates in the air during the processing of thermoplastics.

	Concentration		Number of processes studied	Number of samples	Highest concentration measured
	Mean	SEM [a]			
Peroxides (mg/m³), calculated as the hydroperoxide in the air					
PE processing	0.7	0.3	6	20	1.9
PS processing	—	—	—	—	—
ABS processing	—	—	—	—	—
Alkoxy radicals (ppm), calculated as the free active units in the air					
PE processing	0.25	0.01	4	8	0.26
PS processing	0.06	0.03	3	8	0.09
ABS processing	0.05	0.02	3	6	0.07

[a] SEM = standard error of the mean of the number of processes.

Table 17. Styrene-containing thermoplastics — Thermal degradation products in the air during processing.

Product	PS processing			IPS processing			ABS processing		
	Concentration (mg/m³)		Number of processes studied	Concentration (mg/m³)		Number of processes studied	Concentration (mg/m³)		Number of processes studied
	Mean	SEM[a]		Mean	SEM[a]		Mean	SEM[a]	
Aldehydes (mg/m³)									
Total concentration, calculated aldehyde groups in the air	0.2	0.1	3	0.4	0.2	3	0.7	0.2	3
Formaldehyde	0.1	0.1	3	0.06	0.02	2	0.04	0.04	2
Acetaldehyde	Not detected		2	Trace amounts		2	Trace amounts		2
Acrolein	Not detected		3	Not detected		2	Not detected		2
Benzaldehyde	Trace amounts		2	Trace amounts		2	Trace amounts		2
Ketones									
Acetophenone	Trace amounts		2	Trace amounts		2	Not detected		2
Organic acids									
Total concentration, calculated as acid groups in the air	8.1	—	1	5.8	—	1	0.2	0.1	2
Formic acid	1.0	0.2	2	0.6	0.4	4	0.1	0.6	4
Acetic acid	0.3	0.2	2	0.5	0.2	4	0.06	0.02	4
Benzoic acid	Trace amounts		2	Trace amounts		4	Trace amounts		4
Very volatile hydrocarbons	Trace amounts		2	Trace amounts		4	Trace amounts		4
Styrene	0.4	0.2	2	0.1	0.04	4	0.06	0.01	3
Nitriles, calculated as nitrile groups	—	—	2	—	—	4	0.06	0.01	3

[a] SEM = standard error of the mean of the number of processes.

0.7 mg/m³. The scanning electron micrographs of Nuclepore filters (fig 16 & 17) showed that the size of the particles in these fumes, which developed from PS and ABS, was less than 0.2 μm, the diameter of the filter pores.

No hydrogen cyanide, ammonia, or carbon monoxide could be detected during the processing of styrene-containing thermoplastics.

Table 18. Styrene-containing thermoplastics — Concentrations of fumes in the air during processing.

Thermoplastics	Concentration mg/m³		Number of processes studied	Number of measurements	Highest concentration measured (mg/m³)
	Mean	SEM [a]			
PS					
Liquid absorption	2.4	0.1	3	16	21.0
Filter	0.3	0.2	2	3	0.5
IPS					
Liquid absorption	2.2	1.0	5	12	4.5
Filter	0.7	0.4	5	11	2.6
ABS					
Liquid absorption	1.2	0.6	2	15	37.0
Filter	0.6	0.4	3	8	1.2

[a] SEM = standard error of the mean of the number of processes.

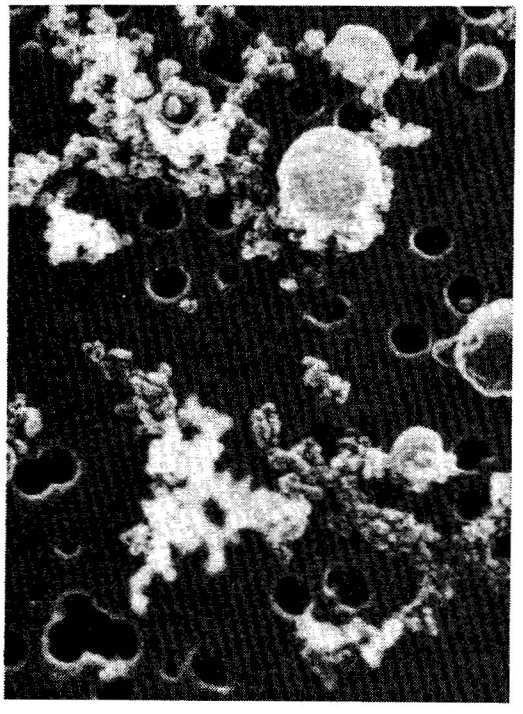


Fig 16. Scanning electron micrograph — PS fume on a Nuclepore filter (0.2 μm pore) (20,000 ×).

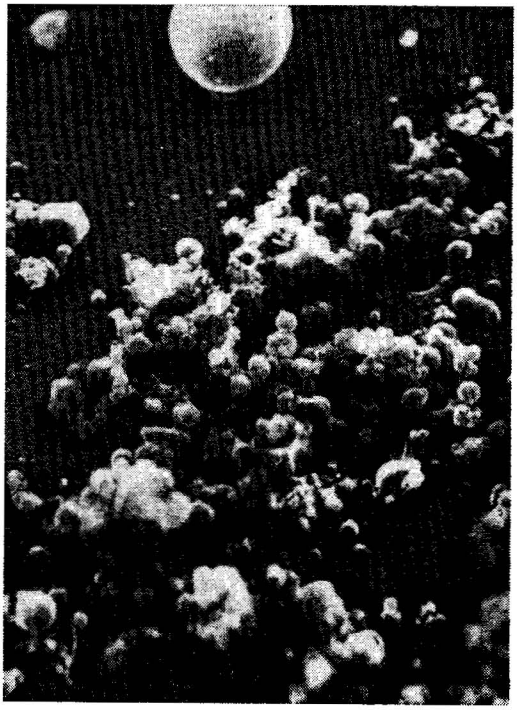


Fig 17. Scanning electron micrograph — ABS fume on a Nuclepore filter (0.2 μm pore) (15,000 ×).

Discussion

Sampling and analysis

The development of the methods for the hygienic measurement of the thermal degradation products of PE and styrene-containing thermoplastics was based on laboratory experiments with these plastics (Part II) and preparatory measurements during actual industrial processes. The laboratory experiments proved that the products of the thermal degradation of PE included mainly aliphatic hydrocarbons. The hydrocarbons were fragments of PE chains broken randomly at high temperatures (58). The thermal degradation products of the styrene-containing thermoplastics were mainly aromatic hydrocarbons composed of various multiples of styrene (dimers, trimers, tetramers, etc). The molecular weights of both types of hydrocarbons varied greatly. Therefore, their vapor pressures and boiling points also differed greatly. Thus these thermal degradation products appeared in the air in different physical states, ie, as gases, vapors and fumes. The fumes consisted of particles and oily hydrocarbons.

The laboratory experiments also showed that the hydrocarbons released from PE and styrene-containing thermoplastics are easily oxidized at high temperatures in the presence of air. Their derivatives that contained oxygen were alcohols, aldehydes, ketones, and organic acids. Aldehydes and acids were the most abundant groups among the oxidized compounds. It was also presumed that the oxidation reactions could lead to the appearance of radicals and peroxides as oxidation intermediates of hydrocarbons (90).

It was difficult to find sampling media and equipment which would trap all the impurities, gases, vapors, and fumes which appear in the air during the processing of thermoplastics. Cool trapping with liquid nitrogen (— 178 °C) was an effective method in the laboratory but would not have been usable under field conditions. Therefore, a set of methods (table 12) was used to sample and analyze the air impurities in the workplace. Methods were developed for the measurement of air impurities as groups. Such sampling made it possible to distinguish between substances with different functional groups; for instance, samples from the workplace air were collected and the concentrations of total aldehydes, total acids, peroxides, or radicals were measured. In addition, since it was considered important to measure the concentrations of compounds suspected of being particularly detrimental to human health, the concentrations of volatile compounds such as formaldehyde, acrolein, acrylonitrile, and formic acid were analyzed separately.

Principally, the sampling and analytical methods were based on the conventional methods used in industrial hygiene. The specific purpose of revising the methods was to increase their sensitivity and specificity. Increased sensitivity and specificity were needed because concentrations of impurities, especially of single compounds, were expected to be very low in the air during the processing of thermoplastics, and the air was expected to contain very complicated mixtures of impurities. Derivatives of the compounds in the samples were made and then analyzed by chromatography. For instance, aldehydes were analyzed by high-performance liquid chromatography after they had been converted into 2,4-dinitrobydrazones, and acids were analyzed in the same way after they had been converted into p-bromophenacyl esters. The oxidation of hydrocarbons is a chain reaction in which radicals and peroxides are the intermediates. Only a few attempts have been made earlier to detect radicals among the thermal degradation products of plastics (105) and in industrial air (107). These intermediate compounds proved very unstable and ready to react further. Thus, the conditions of sampling and analysis had to be checked and standardized very carefully. The methods were developed so that parallel measurements of radicals from the experimental atmosphere generated in the dynamic system reached a coefficient of variation of 0.3 at the concentration level of 0.05 ppm (calculated as active units) and measurements of peroxides reached a coefficient of variation of 0.1 at the concentration level of 0.5 mg/m^3. The radical and peroxide concentrations measured from the air samples have, however, only semiquantitative value because no standard atmosphere of these compounds could be

arranged for the evaluation of the sampling efficiency.

The fumes were collected by liquid absorption because the size of the particles was so small (fig 15, 16 & 17) that the fumes were thought to permeate filters conventionally used for dust collection. The amounts of fumes collected on glass-fiber filters, even on fourfold ones, were smaller than the amounts of the fumes collected in liquid. Thus some permeation seemed to take place through the filters. The analyses of filter samples were made by weighing. Infrared spectrometry served as a method for the measurement of PE fumes collected in liquid. Evaporation of the absorption liquid and weighing of the residue was used as a reference method for the infrared measurement.

Industrial hygiene measurements

The vaporized single compounds detected during thermooxidative degradations in the laboratory (Part II) in high concentrations were also detected in the workplace air when thermoplastics were processed. Such vaporizable single compounds included formaldehyde, acetaldehyde, formic acid, and acetic acid. Those compounds revealed only in minor concentrations in the laboratory were not detected in the air of the factory. The probable reason was that the concentrations present in the air were below the detection limit of the available methods (table 13). Such compounds included acrolein, acrylonitrile, hydrogen cyanide, and carbon monoxide. In general, the average concentrations of single vaporizable compounds were low in comparison to the available hygienic standards (5, 37). Nevertheless, the concentrations of impurities measured as groups were sometimes high.

Air impurities during the processing of polyethylene. Of the measured oxidized products, the total acid concentrations during the PE process were the highest. With the exception of formic and acetic acid, however, the acidic effect (value of the dissociation constant) of these acids is probably weak, like the acidic effect of organic acids in general. The concentrations of aldehydes present in the air samples were low, lower than the concentrations of acidic compounds.

Other groups of oxidized compounds detected in the air were radicals and peroxides. The trapped radicals collected from the worksites yielded the same qualitative results by electron-spin resonance spectroscopy as those generated in the laboratory experiments (30, 105, 107). The collected radicals were trapped by an aromatic nitroso compound (fig 14). The nitrogen-coupling constant of the trapped species was 2.5 mT. No hydrogen splitting could be detected. The g values and the hyperfine splitting constants indicated that the detected radicals were alkoxy radicals formed from the decomposing polymer and oxygen.

The peroxides reacted immediately after they had been trapped in the reagent solution, and no more color development had occurred 10 min later. This result may indicate that the trapped peroxides were mainly hydroperoxides (61).

The results of the measurements of radicals and peroxides showed that their concentrations in the air were at roughly the same level as the concentrations of aldehydes. The aldehydes may also be considered intermediates in the oxidation reaction; the acids, on the other hand, were final products of the oxidation (90).

It was difficult to stabilize the sampling and the analysis of radicals and peroxides at this low concentration level. However, the measurements indicated that, while the results were semiquantitative, they do show that plastic processing gives rise to free radicals and peroxides with lifetimes long enough to reach the breathing zone of workers. The real significance of these measurements for industrial hygiene is not yet clear. But since radicals and peroxides are highly reactive compounds, they may present a health hazard in the occupational environment.

Fume samples were collected in liquid during the processing of PE, and the samples were analyzed by infrared spectrometry (fig 18) (42). The qualitative composition of the spectra showed that the samples had strong absorption maximums in the wave number region from 2,890 cm^{-1} to 2,980 cm^{-1}, which indicates carbon-hydrogen stretching bands. A saturated hydrocarbon fraction, paraffin oil, had strong bands in the same region. The fume samples differed, however, from the

paraffin oil in that the samples showed bands in the region of 1,660 cm^{-1}, which points to unsaturated carbon-carbon bands. Also in the region from 2,890 cm^{-1} to 2,980 cm^{-1} there were differences between the samples and paraffin oil; these were probably due to different chain lengths and branchings of the molecules of the

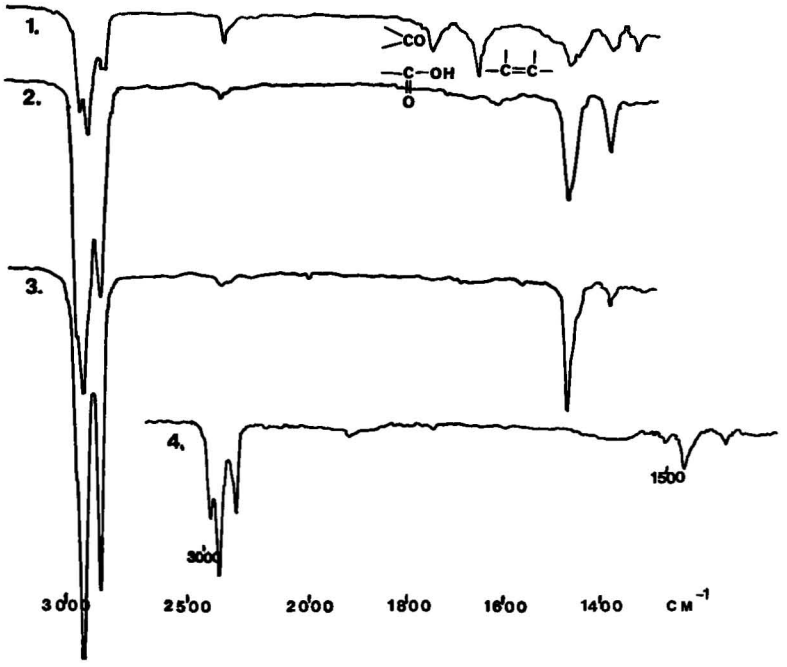
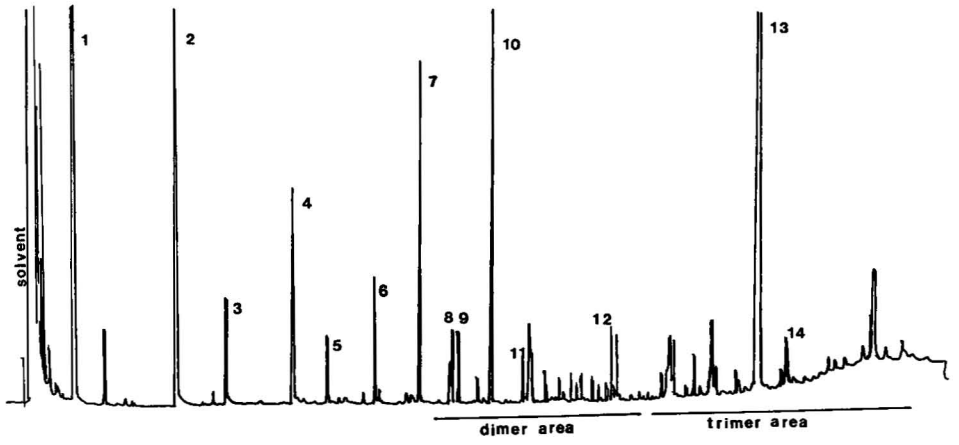


Fig 18. Infrared spectra. [1 = a workplace sample of PE fume, 2 = paraffin oil, 3 = paraffin wax, 4 = saturated hydrocarbon, n-decane ($C_{10}H_{22}$)]



1. C_8H_8
2. C_7H_7O
3. C_8H_8O
4. C_9H_8O
5. C_7H_8O
6. C_6H_6O
7. $C_9H_{10}O$
8. $C_{15}H_{16}$
9. $C_{17}H_{18}$
10. $C_{16}H_{16}$ (dimer)
11. $C_{15}H_{14}$
12. $C_{15}H_{14}O$
13. $C_{24}H_{24}$ (trimer)
14. $C_{25}H_{26}$

Fig 19. A gas chromatogram of IPS degradation products collected in dichloromethane (column FFAP, 30 m/0.3 mm, temperature 40°—260°C/2.5°C/min).

samples and the paraffin oil. In addition, the band from around 1,720 cm^{-1} to 1,750 cm^{-1} indicated the presence of oxidized products in the samples. Thus there were qualitative differences between the fume samples and paraffin oil. Despite these differences the quantity of the samples was measured against paraffin oil in the wave number region which indicated hydrocarbons (2,890—2,980 cm^{-1}).

The scanning electron micrographs of the PE fumes which had been collected on Nuclepore filters (fig 15) showed that the particles were so small (the diameter was smaller than 0.2 μm) that they could be compared to respirable dusts; the American threshold limit value for respirable dust is 5 mg/m^3 (5). On one hand the fume resembled paraffin oil and paraffin wax (fig 18); on the other it differed from these pure paraffin substances by containing oxidized substances. These oxidized compounds were aldehydes and acids, possibly also peroxides, which were partly dissolved in the hydrocarbons of the fumes and partly chemically bound to the fume particles. This evidence may allow the comparison of PE fumes with paraffin wax fumes with respect to health effects. Paraffin wax fumes have a threshold limit value of 2 mg/m^3 in the list of the American Conference of Governmental Industrial Hygienists (5) and a hygienic standard of 1 mg/m^3 in Finland (75).

Carbon monoxide could be detected during the PE process in only a few cases. The detection limit for Dräger tubes, which were used for the measurements, is about 2 ppm (2.5 mg/m^3). The minor amounts which were sometimes detected could just as well have been emitted by the fork-lifts driving through the work area.

The field samples collected during the processing of LDPE did not clearly differ from the samples collected during the processing of HDPE.

Air impurities during the processing of styrene-containing thermoplastics. The concentration of styrene in the air was low during the processing of styrene-containing thermoplastics. Aliphatic hydrocarbons could be detected only in trace amounts. Also the amounts of oxidized compounds were low. In the case of styrene-containing thermoplastics, the concentration of fumes in the air gave a rough indication of the total amount of impurities in the air. The qualitative analysis of the fume samples by gas chromatography-mass spectrometry showed that the fumes contained different styrene oligomer isomers (dimers, trimers, tetramers, etc). According to an unpublished work of A Hesso the analysis also showed chemically bonded oxygen on the oligomer molecules found in the fumes (fig 19 & 20).

The scanning electron micrographs of PS and ABS fumes collected on Nuclepore filters (fig 16 & 17) showed that also these fume particles were small. The diameter was smaller than 0.2 μm. Therefore the fumes generated from styrene-containing thermoplastics could be compared to respirable dust.

It seemed evident that styrene-containing thermoplastics emitted less air impurities during processing than PE did. Some exceptions occurred however. The

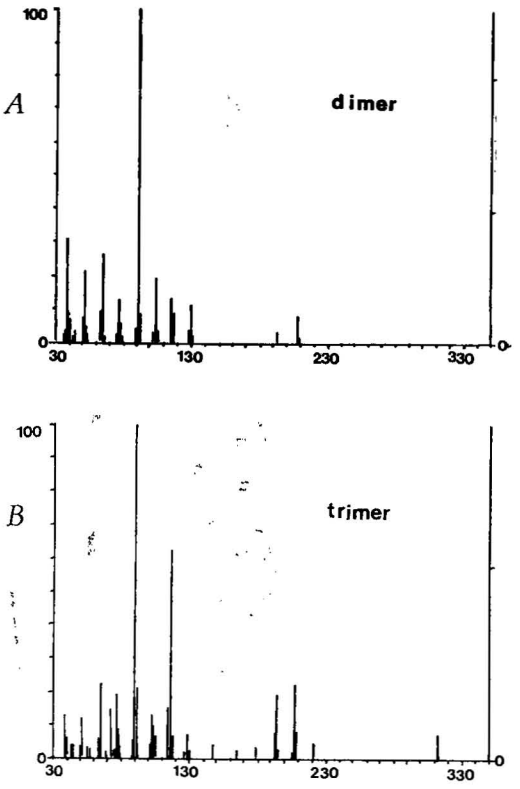


Fig 20. Mass spectra of peaks number 10 and 13 of the gas chromatogram in fig 19.

greatest average fume concentration [37 (SD 13) mg/m^3, N = 3] was measured in a workplace where ABS was processed.

Evaluation of industrial hygiene measurements

Industrial hygiene measurements were carried out during normal work processes with PE or styrene-containing thermoplastics. The results thus represent the level of impurities normally occurring in ambient air during industrial processes involving these plastics. The measured concentrations of both single compounds and compound groups were fairly low, with the exception of the fume concentrations, which could be interpreted as being fairly high in some cases.

The fumes (aerosols) seemed to constitute the foremost hygienic problem during the processing of PE and styrene-containing thermoplastics. The fume particles contained the same elements as the plastics itself in the form of different-sized fragments of the original polymer chain. Thus the PE fumes were long-chain aliphatic hydrocarbons. In the case of styrene-containing thermoplastics, the fumes appeared in the form of oligomers; in other words, the polymer was depolymerized. In addition to chemically bonded oxidized functional groups, the fumes may also act as carriers or solvents for the vaporized, low-molecular, oxidized compounds, eg, formaldehyde or formic acid, simultaneously present in the air. For this reason the fumes are probably physiologically more active than they otherwise would be. The significance of such polymer fumes to worker health is not yet known. On the whole, it must also be remembered that such processes result in exposure to mixtures of air impurities containing many components with unclear physiological activity.

Calculation of the added relative concentration [5] of air impurities was difficult because for several compounds or compound groups there were no hygienic standards available for comparison. Examples of such groups are peroxides, radicals, nitriles, total aldehydes, and total acids. The fumes could be compared to the hygienic standard for respirable dust [5 mg/m^3 (5)] because, as already mentioned, the electron micrographs of the samples collected on filters proved that the fumes were present in the form of very small particles. The application of the hygienic standard for respirable dust gave a relative added concentration of about 1 for PE fumes and a relative added concentration of about 0.5 for styrene-containing thermoplastics. The added relative concentration in the case of PE fumes was about 2 when the hygienic standard for paraffin wax fumes [2 mg/m^3 (5)] was used for comparison.

In a similar manner, a lower hygienic standard should be used for the fumes developing from styrene-containing thermoplastics than for respirable dust because these fumes also contain irritating oxidized groups. When the added relative concentrations of the air impurities were calculated so that fumes were not included, the resulting hygienic effect was only 0.2 for the PE process and only 0.1 for the processing of styrene-containing thermoplastics. Thus the role of fumes among the air impurities during the processing of these plastics is very important.

The concentrations of air impurities varied according to different ventilation arrangements, the quantity of thermoplastics, the types of processes, process variables, and interruptions in the processes. For instance, film extrusion and coating involved the exposure of large, hot plastic surfaces to air. During such work phases degradation products were set free more easily and in greater amounts than during other types of processes, eg, injection molding in which processing takes place in nearly closed systems. Ventilation, other than general ventilation, seemed difficult to arrange — for instance, in film extrusion processes where large surfaces of the hot plastics material are exposed to ambient air. The concentrations of air impurities also depended on the temperatures used in the process, the

[5] The added relative concentrations of air impurities were calculated with a formula in which the measured amounts of air impurities were compared to the respective hygienic standards. The resulting "hygienic effect" should not be higher than 1 (5):

$(c_1/g_1) + (c_2/g_2) \ldots (c_n/g_n) - 1$,

where $c_{1,2 \ldots n}$ = measured concentration in air and $g_{1,2 \ldots n}$ = respective hygienic standard.

speed of the process, and the size and shape of the products. Interruptions occurred in all the processes. They sometimes caused peak concentrations of impurities in the air. These peaks occurred, eg, when large amounts of hot plastics fell on the floor during a malfunction in the film extrusion process or when some of the plastics got stuck in the machinery and started smoldering.

Because of the high number of airborne impurities during the processing of plastics, it is difficult to measure all the substances present in the workplace air routinely. It is thus practical to choose some typical degradation products for each type of plastics. The chosen degradation products can be used as indicator substances in hygienic measurements. The results of this study indicate that the measuring of formaldehyde, formic acid, and fumes is sufficient to give a hygienic picture of the processing of PE plastics. In the processing of PS and other styrene-containing thermoplastics, styrene and fumes are the primary indicators. In addition, group measurements of aldehydes and acids provide information on the total amounts of oxidized substances in the air. These measurements reveal irritating impurities in the air during the processes. The measurement of the concentration of nitriles in the air may be valuable for the hygienic evaluation of the processes involving nitrile-containing plastics (ABS & SAN).

IV. Biochemical effects

by Antti Zitting

Materials and methods

Chemicals

Table 19 shows the thermoplastics used in the toxicologic studies. 7-Ethoxycoumarin was synthetized by the ethylation of 7-hydroxycoumarin (umbelliferone, Fluka AG, Switzerland) in aqueous sodium hydroxide with diethylsulfate. The product was extracted from the reaction mixture into chloroform and washed with dilute sodium hydroxide and water. After the chloroform was evaporated to dryness, the residue was recrystallized three times from 45 % methanol.

7-Ethoxyresorufin was prepared from resorufin (Eastman Kodak, USA) by similar ethylation. The chloroform extract was washed with dilute sodium hydroxide and water and evaporated. The residue was chromatographed on preparative Silica gel G thin-layer plates (2 mm × 20 cm × 20 cm; chloroform-acetonitrile, 9 : 1). The orange band ($R_f = 0.3$) was scraped off, and the product was extracted with chloroform.

Styrene, acrolein, and acrylonitrile were distilled just before the use in hepatocyte incubations.

All the other chemicals were of commercial reagent grade.

Animal exposure

Male Wistar rats (200—250 g) or male Naval Medical Research Institute mice (20—25 g) were used throughout the study. During the periods of exposure, no food was offered so that adsorption on the pellets could be avoided, but water was given ad libitum. The rats were exposed at night, and a daylight rhythm of 12 h was maintained throughout the studies. The mice were exposed during the day.

The plastics pellets were placed in a quartz tube (150 × 1.7 cm) in an even layer (0.17 g/cm). The tube was heated by a ring oven (10 × 1.8 cm), which was moved

Table 19. Thermoplastics used in the toxicologic studies.

Thermoplastics	Tradename	Manufacturer
Hepatocyte exposures		
LDPE	Polyten LD 990	Dow Chemical, United States
PS	PS 634	Dow Chemical, United States
IPS	Polystron 180-C	Sveriges Plastfabrik, Sweden
SAN	Luran 368 R 004	BASF, Federal Republic of Germany
ABS	Cycolac T 10000 Nat	Borg-Warner, The Netherlands
Animal exposures		
LDPE	DFDS 0152	Unifos Kemi AB, Sweden
PS	PS-RH	Stymer Oy, Finland
ABS	Cycolac T 10000 Nat	Borg-Warner, The Netherlands

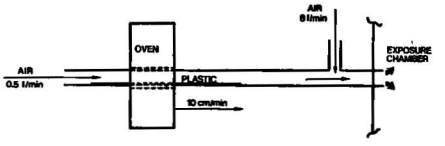


Fig 21. Scheme of the exposure system.

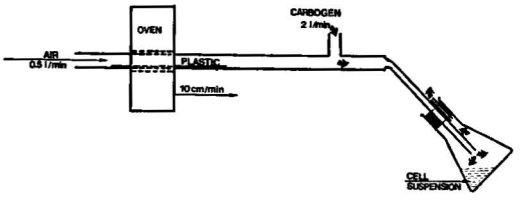


Fig 22. Scheme of the hepatocyte exposures.

along the tube at a speed of 10 cm/h. The oven temperatures were set so that the degradation temperatures of the thermoplastics corresponded to those given in the Results section. The oven was programmed by a timer which switched the exposure equipment on and off automatically. The degradation products were conducted to the exposure chamber (polymethylmethacrylate, 32 × 50 × 70 cm) with dry air (0.5 l/min). Fresh air was mixed with this stream at the rate of 8 l/min immediately before the chamber inlet so that the exposure air would cool off and be diluted (fig 21). The temperature of the air just before the inlet never exceeded 28°C. The control animals were sham-exposed in a similar manner but with no thermoplastics in the tube. The tube was cleaned after the exposures by the burning of the charred plastics at 900°C.

The nondynamic PS degradation product exposures of mice have been described elsewhere (109).

Hepatocyte exposure

The hepatocytes were isolated from the Wistar rats by the method of Moldeus et al (71). Only preparations containing less than 10 % dead cells (tested by trypan blue staining) were accepted for the experiments. The concentration of cells in the exposure incubations was 2×10^6 cells/ml. The incubations were conducted in a complete medium (Medium 199, Gibco Bio-Cult, United Kingdom) supplemented with 10 % newborn calf serum (Microbiological Associates, USA), heparin (10 units/ml), penicillin G (500 units/ml), and N-2-hydroxyethylpiperaxine-N'-2-ethanesulfonic acid (25 mM) (Sigma Chemical Co, USA). The medium was oxygenated with carbogen (95 % oxygen, 5 % carbon dioxide) at 37°C and adjusted to pH 7.4 before use.

The exposure system was similar to that used to expose the animals, but carbogen (2 l/min) was used instead of air to dilute the degradation product stream and to ensure an adequate oxygen concentration (80 %) (fig 22).

Thirty-milliliter batches of cell suspension were placed in 250-ml Erlenmeyer flasks in a reciprocating shaker at 37°C. The control cells were exposed to similar quantities of air and carbogen. The medium without the cells was also exposed so that the background levels could be estimated in the lipid peroxidation measurements.

Measurement of exposure levels

The exposure atmospheres were analyzed for different degradation products by the methods described in Part III. Acrylonitrile was measured by indicator tubes (Dräger Werk AG, Federal Republic of Germany).

The oxygen content was monitored with a Beckman oxygen analyzer D2S (Beckman Instruments, USA). The relative humidity in the exposure chamber was monitored by a Humicamp meter (Vaisala Oy, Finland). Continuous monitoring with a semiconductive detector (AVA-unit, type 001, Sensorex Oy, Finland) was used to check that the flow of degradation products was constant throughout each night of exposure. During exposure to the degradation products of PS the exposure levels were monitored by a flame ionization detector, which responded to the total amount of combustible compounds. The exposure levels were expressed as for styrene (109).

Biochemical methods

Hepatocyte exposure. The viability of exposed hepatocytes was periodically checked with the latency test of cytosolic enzymes (71). Thiobarbituric-acid reactive compounds (40), or diene conjugation (13), was measured in the total incubate so that the possible occurrence of lipid peroxidation could be detected. Reduced glutathione was measured in sedimented cells washed with Krebs-Henseleit buffer (pH 7.4) containing 2 % albumin and 12.5 mM N-2-hydroxyethylpiperaxine-N'-2-ethanesulfonic acid; the method of Saville (92) was used.

Animal exposure. The animals were decapitated 3 h after the end of the last exposure unless otherwise specified in the Results section.

The tissue homogenates were analyzed for their reduced glutathione content (actually nonprotein sulfhydryl groups). For liver, lung, or kidney tissue the method of Saville (92) was used. The method of Hissin & Hilf (38) was used for brain tissue.

Bivalent calcium-aggregated microsomes were prepared from the livers (3). From the kidneys, lungs, and brains nonaggregated microsomes were isolated (23). The liver microsomes were analyzed for their cytochrome P-450 content according to Omura & Sato (83), and the kidney microsomes according to Johannesen & DePierre (48). The microsomal enzymes determined were 7-ethoxycoumarin 0-deethylase (2), 7-ethoxyresorufin 0-deethylase (87), diphenyloxazole hydroxylase (16), NADPH cytochrome c reductase (86), epoxide hydratase (103), and UDPglucuronosyltransferase [4.5 mM UDPglucuronic acid, 0.35 mM p-nitrophenol) (44)]. Cytosolic glutathione S-transferase was analyzed with 7-H^3 styrene oxide as the substrate (64).

The cerebral hemispheres were analyzed for their ribonucleic acid content (73), lysosomal acid proteinase (63), in vitro protein glycosylation (82), NADPH diaphorase (28), and glutathione peroxidase (24). The superoxide dismutase of the liver homogenate and the cerebral microsomes was assayed according to the method of Marshall & Worsfold (65). The concentrations of protein were determined by the method of Lowry et al (56). Student's t-test was used for the statistical evaluations.

Results

Hepatocyte exposure

The concentrations of styrene, acrolein, and acrylonitrile in the various exposures are given in table 20.

The cellular levels of glutathione were decreased by exposure to the degradation products of the thermoplastics used in the studies, ie, LDPE, PS, IPS, SAN, and ABS. The extent of the decrease depended on the degradation temperatures (fig 23).

Exposure to styrene, acrolein, and acrylonitrile also decreased the hepatocyte levels of glutathione in a dose-dependent manner (fig 24).

The detection of the possible lipid peroxidation in hepatocytes by the thiobarbituric acid and diene conjugation methods failed because the exposure atmospheres contained compounds which greatly interfered with these tests. In the ABS exposure situations, for instance, even more thiobarbituric-acid reactive compounds were detected in the blank incubations

Table 20. Concentrations of styrene, acrolein, and acrylonitrile in various hepatocyte exposure situations.

Exposure	Styrene (N = 3) (ppm)		Acrolein (N = 3) (ppm)		Acrylonitrile (N = 3) (ppm)	
	Mean	SD	Mean	SD	Mean	SD
LDPE						
200°C	Not detected		0.01		Not detected	
250°C	Not detected		0.05	0.02	Not detected	
300°C	Not detected		0.18	0.08		
PS						
200°C	0.7	0.3	0.01		Not detected	
250°C	2.5	0.4	0.01		Not detected	
300°C	25.4	3.3	0.01		Not detected	
IPS						
200°C	0.9	0.5	0.13	0.04	0.5	0.5
250°C	3.3	1.2	0.52	0.22	0.5	0.5
SAN						
250°C	13.2	1.4	0.01		0.5	0.5
300°C	19.0	1.6	0.01		2	1
350°C	19.0	2.0	0.01		5	1
ABS						
250°C	8.2	1.4	0.01		0.5	
300°C	20.4	1.9	0.09	0.04	2	1
350°C	28.2	3.5	0.22	0.09	4	1

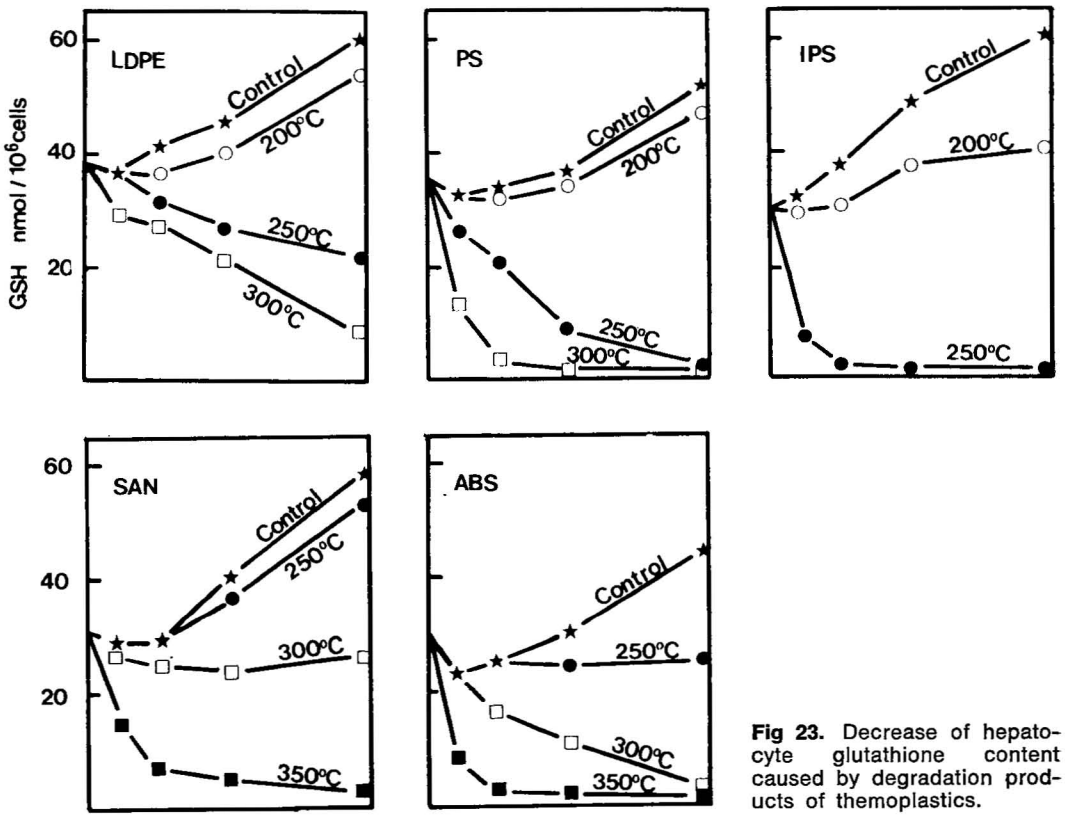


Fig 23. Decrease of hepatocyte glutathione content caused by degradation products of themoplastics.

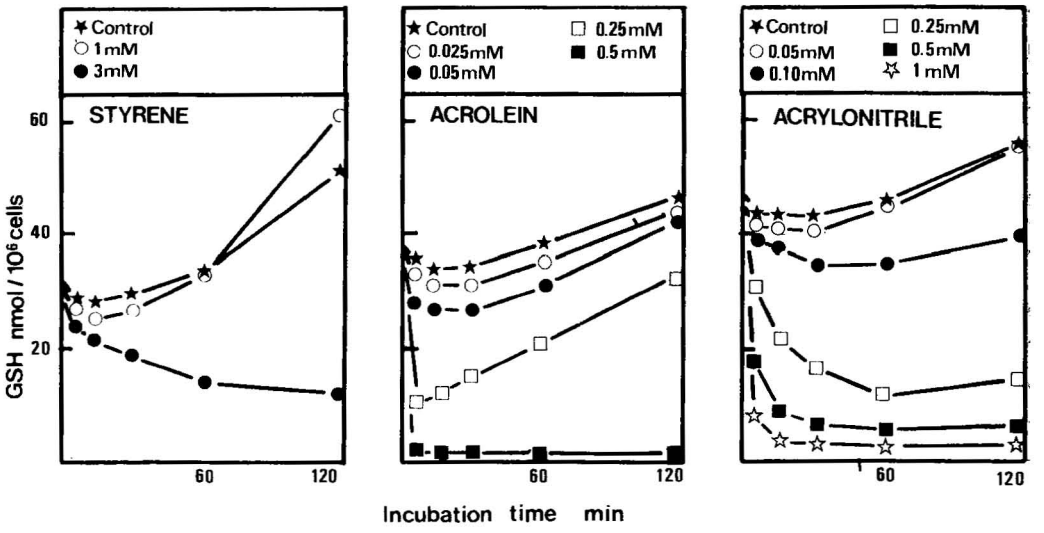


Fig 24. Decrease of hepatocyte glutathione content by styrene, acrolein, and acrylonitrile.

(medium without cells) than during the actual exposure (fig 25).

No lipid peroxidation was detected when the hepatocytes were exposed to styrene or to acrylonitrile, but acrolein induced an increase in thiobarbituric-acid reactive compounds at concentrations of 0.25 mM and 0.5 mM (fig 26). At these concentrations acrolein also impaired the integrity of the cell membranes, an effect that was not detected with styrene or acrylonitrile at the concentrations used in the study.

The degradation products of PS and SAN did not affect membrane integrity during the exposures. LDPE fumes (300°C) affected the latencies of cytosolic enzymes — the latencies were 80 % of the original after 60 min of incubation and 15 % of the original after 120 min of incubation. The fumes from IPS (250°C) also influenced the latency in the 120-min incubation (75 % of the original). ABS degraded at 350°C decreased the latency in 60 min (67 %) and in 120 min (8 %).

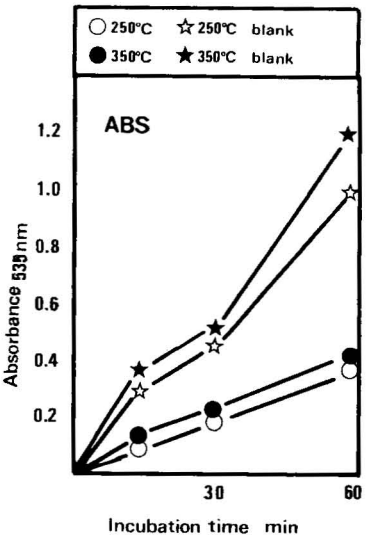


Fig 25. Thiobarbituric-acid reactive compounds in exposure to ABS.

Animal exposure

Low-density polyethylene. The analysis of the atmosphere in the LDPE exposure situations revealed that the concentration of carbon monoxide was below 20 ppm. The concentration of acrolein was 0.54 (SD 0.14) ppm (N = 4), the concentration of formaldehyde was 1.4 (SD 0.3) ppm, and that of total aldehydes (calculated as for formaldehyde) was 19.3 (SD 0.9) ppm. The mean particulate concentration was 9.8 (SD 0.4) mg/m^3, and the oxygen content remained at 20.4 (SD 0.3) %. The relative humidity in the exposure chamber never exceeded 70 %. The temperature in the chamber was 23—27°C.

The 6-h exposures to the LDPE degradation products reduced the levels of glutathione in tissues. A decrease of glutathione was detected in rat liver and kidney (table 21). In the three-week subacute exposures this decrease was compensated for, and the hepatic content of glutathione even exceeded that of the control animals (table 22).

The acute exposures (6 h) increased the level of 7-ethoxycoumarin 0-deethylase in rat kidney (table 21), but no effects on other drug metabolizing enzymes were detected. The subacute exposures had widespread effects however (table 22). The amount of hepatic cytochrome P-450 decreased (table 22). The activity of 7-ethoxycoumarin 0-deethylase increased in rat liver and kidney. The hepatic 7-ethoxyresorufin 0-deethylase activity also increased (table 22).

Neurochemical effects of exposure to degradation products of low-density polyethylene. The concentration of acrolein in the exposure atmosphere was 0.48 (SD

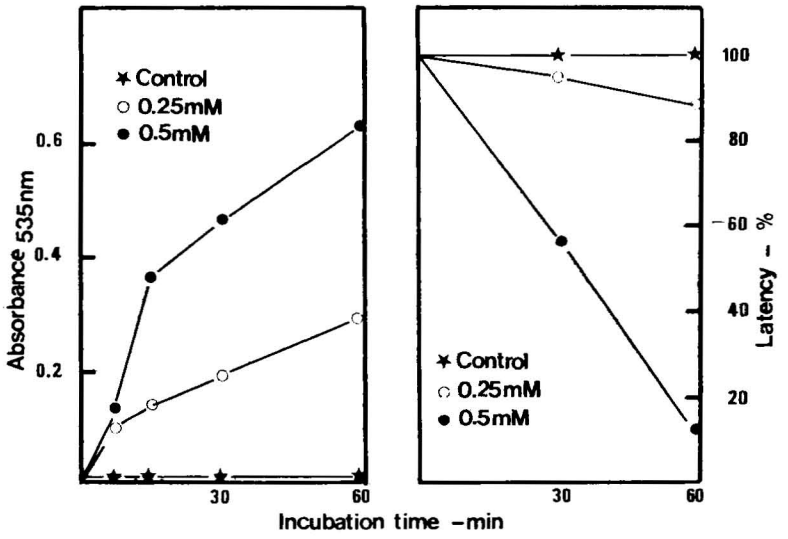


Fig 26. Latencies of cytosolic enzymes and amount of thiobarbituric-acid reactive compounds in the acrolein incubations.

Table 21. Effects of a single 6-h exposure to PE degradation products on rat liver, kidneys, and lungs.

Organ	Control animals (N = 5)		Exposed animals (N = 5)	
	Mean	SD	Mean	SD
Liver				
Glutathione (nmol/g tissue)	6.37	0.39	5.40	0.22 ***
Cytochrome P-450 (nmol/mg protein)	1.29	0.10	1.19	0.12
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	1.50	0.25	1.52	0.31
Epoxide hydratase (nmol/min × mg protein)	14.8	1.5	14.0	1.9
UDPglucuronosyltransferase (nmol/min × mg protein)	1.49	0.19	1.70	0.28
Kidney				
Glutathione (nmol/g tissue)	4.22	0.19	3.58	0.12 ***
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.015	0.003	0.021	0.003 **
Lung				
Glutathione (nmol/g tissue)	1.82	0.43	1.70	0.45
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.057	0.012	0.049	0.015

** $p < 0.01$, *** $p < 0.001$.

0.12) ppm (N = 5), the concentration of formaldehyde 1.36 (SD 0.20) ppm, and that of the total aldehydes (calculated as for formaldehyde) 17.7 (SD 0.6) ppm. The level of carbon monoxide never exceeded 20 ppm, and the mean concentration of oxygen was 20.1 (SD 0.5) %. The particulate concentration was 8.0 (SD 0.6) mg/m^3.

The subacute exposures did not affect either the cerebral concentration of glutathione or the acid proteinase activity (table 23). The ribonucleic acid content of the brain was above the control level after the two-week exposure, but this increase tended to level off when the exposure continued (table 23). NADPH diaphorase activity was below the level of the controls at all times, whereas microsomal superoxide dismutase revealed an increasing trend at later stages of exposure. The glycosylation of cerebral proteins in vitro was increased after the two-week exposure, but the difference diminished later (table 23).

Polystyrene. The total concentration of flame-ionization-detector reactive compounds during the intermittent exposures of the mice to PS was 150 ppm (range 80—200 ppm) when expressed as for styrene. During the dynamic exposures of the rats, the concentration was 140 (SD 10) ppm (N = 15). The relative humidity in the chambers did not exceed 80 %, and the concentration of oxygen was 19.5 (SD 0.6) % (N = 9).

The 3-h exposure decreased the level of hepatic glutathione in mice, but the effect later disappeared; 24 h after the exposure ceased, the levels of glutathione exceeded those of the control animals, and, 48 h after the exposure ceased, the content of glutathione was similar to that of the controls (table 24). Acute exposure decreased the cytochrome P-450 content in mouse liver, but the effect disappeared after 2 d (table 24). 7-Ethoxycoumarin 0-deethylase remained unaffected during the first hours after acute exposure, but with-

Table 22. Effects of the three-week exposure (6 h/night, 5 nights/week) to PE degradation products on rat liver, kidneys, and lungs.

Organ	Control animals (N = 5)		Exposed animals (N = 5)	
	Mean	SD	Mean	SD
Liver				
Glutathione (nmol/g tissue)	7.08	0.35	8.56	0.30 ***
Cytochrome P-450 (nmol/mg protein)	1.29	0.08	1.10	0.06 ***
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	1.51	0.10	1.69	0.15 *
7-Ethoxyresorufin 0-deethylase (nmol/min × mg protein)	0.12	0.02	0.17	0.02 **
Epoxide hydratase (nmol/min × mg protein)	16.9	1.5	12.9	1.9 **
UDPglucuronosyltransferase (nmol/min × mg protein)	1.94	0.32	2.04	0.29
NADPH cytochrome c reductase (nmol/min × mg protein)	117	13	97	18 *
Kidney				
Glutathione (nmol/g tissue)	4.13	0.16	4.11	0.14
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.015	0.002	0.028	0.008 **
Lung				
Glutathione (nmol/g tissue)	1.75	0.10	1.74	0.19
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.013	0.003	0.015	0.003

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Table 23. Neurochemical effects of exposure to PE fumes.

	Control (9 animals)		Duration of exposure (5 animals/exposure period)					
			Two weeks		Three weeks		Five weeks	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Glutathione (nmol/mg protein)	2.20	0.16	2.24	0.16	2.20	0.16	2.24	0.18
Ribonucleic acid (μg/mg protein)	13.3	1.5	15.5	1.9 *	13.7	1.9	14.9	0.6 *
Acid proteinase (nmol/min × mg protein)	2.5	0.3	2.6	0.3	2.6	0.4	2.7	0.3
NADPH diaphorase (nmol/min × mg protein)	101	24	68	16 **	77	11 *	74	18 *
Superoxide dismutase (nmol/min × mg protein)	21.1	6.1	19.0	5.8	19.3	3.2	21.1	6.1+
Protein glycosylation in vitro (fmol/min × mg protein)	18	2	30	9 ***	20	4	21	5

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$ and + differs from the three-week' value at $p < 0.05$.

Table 24. Effects of a 3-h exposure to PS degradation products at different intervals after the termination of exposure.

Hours after exposure	Glutathione (% of controls)	Cytochrome P-450 (N = 5) (nmol/mg protein)		7-Ethoxycoumarin 0-deethylase (N = 5) (nmol/min × mg protein)	
		Mean	SD	Mean	SD
Control	100	1.01	0.07	1.57	0.35
1	70	0.86	0.05 ***	1.48	0.14
4	84	0.87	0.09 **	1.57	0.16
24	113	0.89	0.10 **	2.74	0.31 ***
48	102	1.00	0.13	2.51	0.32 ***

** $p < 0.01$, *** $p < 0.001$.

Table 25. Effects of exposure (3 h/d, 5 d/week) to PS degradation products on mouse liver.

Duration of exposure	Cytochrome P-450 (N = 5) (nmol/mg protein)		7-Ethoxycoumarin 0-deethylase (N = 5) (nmol/min × mg protein)	
	Mean	SD	Mean	SD
Controls	0.58	0.07	1.20	0.24
Two days	0.90	0.04 ***	2.75	0.18 ***
Four days	0.94	0.21 ***	2.00	0.52 **
Two weeks	1.29	0.15 ***	1.92	0.15 ***
Ten weeks	0.90	0.16 ***	1.30	0.14

** $p < 0.01$, *** $p < 0.001$.

in 24 h the activity almost doubled (table 24).

Both the hepatic cytochrome P-450 content and the activity of 7-ethoxycoumarin 0-deethylase were increased about twofold in mouse when the exposures were continued for 2 d (table 25). Cytochrome P-450 remained at an increased level for ten weeks during prolonged exposures, but the enhancement of 0-deethylation gradually diminished (table 25).

The three-week exposure of rats to PS degradation products (6 h/night, 5 nights/week) decreased the level of hepatic glutathione slightly when measured 1 h after the last exposure ceased (table 26), but the concentrations later increased so that, 4 h and 24 h after the exposure ceased, the levels were 133 % ($p < 0.001$) and 121 % ($p < 0.001$) of the control values, respectively. The pulmonary concentration of glutathione also decreased (table 26).

Subacute exposure increased the hepatic concentrations of cytochrome P-450, as well as the hepatic and pulmonary activities of 7-ethoxycoumarin 0-deethylase (table 26). UDPglucuronosyltransferase activities were slightly enhanced in the liver but decreased in the lungs (table 26).

Poly(acrylonitrile-butadiene-styrene). The concentrations of the measured degradation products of ABS in the exposure atmospheres are given in table 27.

The single 6 h exposures at 300°C and 330°C decreased the hepatic concentrations of glutathione (table 28), but the effect disappeared when the exposures were continued for 3 d or 2 weeks (table 29). In the lungs and the kidneys the levels of glutathione decreased later, after the 3-d exposure, but during prolonged exposure the initial levels were recovered (table 29). A decrease in the concentration of glutathione in the brain was observed after the two-week exposure (table 30).

The hepatic cytochrome P-450 content was slightly decreased after the two-week exposure (table 29). The degradation products caused a strong initial inhibition of 7-ethoxycoumarin 0-deethylation in the lungs and the kidneys (table 28), but the control levels were recovered later on (table 29). In the liver a decrease in the activity of 0-deethylation was observed only after the 3-d exposure (table 29). The level of hepatic superoxide dismutase increased after the 3-d exposure but reached the control level later on (table 29). The

Table 26. Effects of a three-week exposure to PS degradation products on rat lungs and liver. (The animals were decapitated 1 h after the last exposure.)

Organ	Control animals (N = 4)		Exposed animals (N = 4)	
	Mean	SD	Mean	SD
Lung				
Glutathione (nmol/mg tissue)	1.86	0.11	1.47	0.07 ***
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.11	0.01	0.15	0.02 **
UDPglucuronosyltransferase (nmol/min × mg protein)	0.95	0.27	0.68	0.18 *
Liver				
Glutathione (nmol/mg tissue)	7.20	0.12	6.80	0.08 ***
Cytochrome P-450 (nmol/mg protein)	0.79	0.11	1.30	0.36 **
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	1.13	0.12	1.52	0.12 ***
Diphenyloxazole hydroxylase (fluorescence units/min × mg protein)	127	15	130	30
Epoxide hydratase (nmol/min × mg protein)	11.5	1.0	13.8	1.6
UDPglucuronosyltransferase (nmol/min × mg protein)	1.87	0.23	2.27	0.31 *
Glutathione S-transferase (nmol/min × mg protein)	236	9	221	23

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

activity of superoxide dismutase in the cerebral microsomes increased after the 3-d exposure, but the value for the two-week exposure was significantly lower than that of the control animals (table 30). The 3-d exposure decreased cerebral acid proteinase, but the control level was later reached in this case too (table 30).

Discussion

The decrease in the cellular contents of glutathione indicates that the thermal degradation products of plastics contain agents which are biologically active. The decrease occurred both in exposed isolated hepatocytes and in in vivo experiments in

Table 27. Exposure concentrations of ABS degradation products.

Product	Degradation temperature			
	300°C (4 measurements)		330°C (4 measurements)	
	Mean	SD	Mean	SD
Aerosols (mg/m^3)	8.4	2.4	26.5	9.6
Acrolein (ppm)	1.4	0.3	1.9	0.4
Acrylonitrile (ppm)	2	1	4	1
Aldehydes, calculated as if formaldehyde (ppm)	6.8	1.0	9.3	1.3
Carbon monoxide (ppm)	4	1	5	1
Formaldehyde (ppm)	0.20	0.08	0.31	0.08
Hydrogen cyanide (ppm)	0.08	0.01	0.67	0.06
Styrene (ppm)	11.8	2.8	2.45	4.2

Table 28. Effects of a single 6-h exposure to ABS degradation products on rat liver, lungs, and kidneys.

Organ	Control (5 animals)		Degradation temperature (5 animals/exposure period)			
			300°C		330°C	
	Mean	SD	Mean	SD	Mean	SD
Liver						
Glutathione (nmol/mg tissue)	7.68	0.45	6.93	0.43 *	6.30	0.32 ***
Cytochrome P-450 (nmol/mg protein)	0.82	0.11	0.85	0.08	0.88	0.06
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	1.10	0.16	0.96	0.09	0.90	0.07
UDPglucuronosyltransferase (nmol/min × mg protein)	2.91	0.57	2.89	0.61	2.48	0.30
Superoxide dismutase (nmol/min × mg protein)	6.6	2.0	6.0	1.4	6.1	1.0
Lungs						
Glutathione (nmol/mg tissue)	1.80	0.07	1.80	0.07	1.81	0.21
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.015	0.002	0.009	0.001 ***	0.008	0.002 ***
Kidneys						
Glutathione (nmol/mg tissue)	4.15	0.39	3.84	0.21	3.71	0.08 *
Cytochrome P-450 (nmol/mg protein)	0.12	0.01	0.12	0.02	0.12	0.01
7-Ethoxycoumarin 0-deethylase (nmol/min × mg protein)	0.012	0.001	0.004	0.001 ***	0.002	0.001 ***

* $p < 0.05$, *** $p < 0.001$.

various organs of the animals. Glutathione plays several biological roles in cells. It is consumed in conjugation reactions during which it reacts both nonenzymically and enzymically (glutathione S-transferases) with potentially toxic electrophilic compounds. This phenomenon usually produces less toxic derivatives. [For reviews, see Chasseaud (19) and Reed & Beatty (88).] The degradation products identified and measured in this study contained many compounds known to be able

Table 29. Effects of 3-d and 2-week exposures to ABS degradation products (300°C) on rat liver, lungs, and kidneys.

Organ	Control (5 animals)		Exposure (5 animals/period)			
			Three days		Two weeks	
	Mean	SD	Mean	SD	Mean	SD
Liver						
Glutathione (nmol/mg tissue)	7.27	0.46	7.50	0.58	7.38	0.38
Cytochrome P-450 (nmol/mg protein)	0.96	0.08	0.92	0.13	0.86	0.07*
NADPH cytochrome c reductase (nmol/min × mg tissue)	94	12	108	18	93	15
7-Ethoxycoumarin 0-deethylase (nmol/min × mg tissue)	0.43	0.07	0.29	0.08***	0.41	0.11
Diphenyloxazole hydroxylase (fluorescence units/min × mg protein)	159	39	191	37	162	13
UDPglucuronosyltransferase (nmol/min × mg tissue)	2.22	0.20	2.30	0.26	2.17	0.65
Superoxide dismutase (nmol/min × mg tissue)	6.2	1.8	10.2	1.8**	6.2	1.0
Lungs						
Glutathione (nmol/mg tissue)	1.77	0.17	1.49	0.10**	1.62	0.15
7-Ethoxycoumarin 0-deethylase (nmol/min × mg tissue)	0.012	0.002	0.013	0.003	0.014	0.003
Kidney						
Glutathione (nmol/mg tissue)	4.36	0.19	3.71	0.16***	4.46	0.22
Cytochrome P-450 (nmol/mg protein)	0.16	0.01	0.14	0.02	0.17	0.02
7-Ethoxycoumarin 0-deethylase (nmol/min × mg tissue)	0.013	0.006	0.011	0.002	0.018	0.003

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Table 30. Neurochemical effects of ABS degradation products (300°C) on rat brain.

	Control (5 animals)		Exposure (5 animals/period)			
			Three days		Two weeks	
	Mean	SD	Mean	SD	Mean	SD
Glutathione (nmol/mg protein)	2.49	0.12	2.31	0.20	2.17	0.12**
Glutathione peroxidase (nmol/min × mg protein)	31	6	32	7	31	6
NADPH diaphorase (nmol/min × mg protein)	97	26	93	15	105	13
Acid proteinase (nmol/min × mg protein)	1.84	0.10	1.63	0.11**	1.83	0.07
Superoxide dismutase (nmol/min × mg protein)	10.6	1.4	18.6	2.0***	8.90	1.4***

** $p < 0.01$, *** $p < 0.001$.

to form glutathione conjugates, eg, styrene and acrylonitrile. Acrolein is also very reactive against the sulfhydryl groups (45). Styrene, acrolein, and acrylonitrile alone depleted hepatocyte glutathione also in this study.

A second toxicologically important role of glutathione is the protection it provides against peroxidative cellular damage by scavenging hydrogen peroxide (20) and by inhibiting the initiation or propagation of lipid peroxidation in glutathione peroxidase-catalyzed reactions (67). The consumption of glutathione induced by lipid peroxidation may also be involved in exposure to these degradation products. The possible contribution of lipid peroxidation in the isolated hepatocyte exposures, however, proved difficult to demonstrate because the degradation products contained agents which greatly interfered with the measurements of thiobarbituric-acid reactive compounds and diene conjugation. This occurrence is obvious because the mechanism of the oxidative thermal degradation of polymers closely resembles that of lipid peroxidation, which involves reactive intermediates like radicals, hydroperoxides, and peroxides. These reactive intermediates may be found in the exposures, as demonstrated by the other phases of this project, and they can cause the observed high backgrounds. The measurements of diene conjugation were also disturbed by the aromatic degradation products with strong ultraviolet absorption. Glutathione may also be consumed in the metabolism of these disturbing degradation products, because in some cases less thiobarbituric-acid reactive compounds were detected in actual exposures than in the exposed medium without cells (fig 25). Lysis was detected in some exposed cells, and lysis has been shown to occur in isolated hepatocytes after lipid peroxidation (7).

Some observations from the animal exposures also suggest that lipid peroxidation might be involved. In addition to the initial decrease in the levels of hepatic glutathione, the cytochrome P-450 levels in the liver also decreased initially during exposure to LDPE and ABS. LDPE fumes also diminished the activity of NADPH cytochrome c reductase. Similar effects have been observed earlier in, eg, peroxidative liver damage induced by carbon tetrachloride (1). Glutathione is also depleted in the liver after the administration of paraquat, a compound causing an increased superoxide anion production and consequent lipid peroxidation (14). The enhancement of superoxide dismutase activity after the 3-d ABS fume exposure can be explained as a reaction to peroxidation. However, if lipid peroxidation took place in the cells after the animals were exposed to the plastics fumes, it was not very extensive because, eg, the activities of UDP glucuronosyltransferase were affected only slightly. In carbon tetrachloride intoxication membrane damage causes considerable enhancement of this lipid-embedded enzyme activity (1).

In the hepatocyte exposures, the most obvious reason for the contribution of possible lipid peroxidation to the decrease in glutathione is the existence of reactive degradation intermediates. But because reactive intermediates can hardly reach the liver, the kidneys, or the brain of the animals exposed via inhalation, other explanations for peroxidation should be sought. For instance, hypoxia can initiate peroxidative damage (62), probably by shunting electrons from the mitochondrial respiratory chain to other chains and thereby causing an increase in the production of reactive oxygen species (31). The exposures contain airborne compounds which may induce hypoxia — for example, formaldehyde is metabolized to formate and nitriles are metabolized to cyanide. Both formate and cyanide inhibit cytochrome-c-oxidase (79, 111). The uncouplers of oxidative phosphorylation may also induce elevated superoxide formation (26).

Lipid peroxidation may also be involved in the cerebral effects resulting from exposure to ABS. The activity of superoxide dismutase initially increased in the brain, but after the two-week exposure a decrease was observed when compared to the level of the control animals. The levels of glutathione were concomitantly decreased. These facts may indicate profound cellular damage. The cerebral effects of exposure to LDPE differed from those caused by exposure to ABS, but because of the longer periods of exposure and different parameters the comparison

is somewhat difficult to evaluate. Prolonged exposure to LDPE led to a trend towards an increasing level of cerebral superoxide dismutase; this enhancement may be a reaction to increased oxidative stress. An increase in the concentration of ribonucleic acid, as well as an initial increase in the glycosylation of cerebral protein, might have resulted from peripheral nervous irritation [for a more-detailed discussion, see Zitting & Savolainen (110)].

Although the complexity of the degradation products in the various exposures makes it impossible to demonstrate the causative agents for the biological effects, it seems that the effects of exposure to PS are mainly due to styrene. The observations closely resemble those obtained from exposure to styrene (102), with similar adaptations to exposure. Although styrene is the most abundant airborne degradation product of ABS, the observed effects differ qualitatively from those obtained with styrene, PS, or PE. The activities of 7-ethoxycoumarin 0-deethylase were initially decreased in the lungs and the kidneys of animals exposed to ABS, but exposure to PE led to an initial increase in renal 0-deethylation and had no effect on the activity of the lungs. These facts either point to different affecting compounds or are due to different interactions.

V. Summary

Plastics are used for many purposes — They serve as materials in building and construction, in the making of car parts, in packing, in the making of electronic equipment, etc. The increase in the annual consumption of plastics varied between 7—13 % during the 1970s. Plastics are high-molecular-weight compounds containing additives.

The techniques used in the processing of plastics depend to a large extent on the type of products required. PE and styrene-containing thermoplastics are generally processed by methods which utilize heat. The processing temperatures usually vary within the range of 200—320°C. Somewhat higher temperatures can also be encountered. Thermoplastics degrade at elevated temperatures. The presence of oxygen augments the process. The degradation during processing can be minimized, but not totally eliminated, as seen in the present investigation since degradation products were also found in factory air when hygienic measurements were made.

The laboratory experiments of the present study proved that linear hydrocarbons are generated during the initial stage of the thermal degradation of LDPE and HDPE. The experiments also revealed that the degradation of PE in the presence of air gives rise to a very complex mixture of oxidated products. More than 44 compounds representing ten classes of organic products were found among the volatile compounds evolving from PE when the plastics was heated in air. The most abundant products were fatty acids, eg, formic acid and acetic acid, followed in abundance by aldehydes, eg, formaldehyde and acetaldehyde.

Thermal degradation of styrene-containing thermoplastics yielded styrene only as a minor product. Thus, a considerable part of the volatiles were compounds with higher boiling points than styrene. The yield of these compounds was much higher from PS and IPS than from ABS and SAN. The products with a high boiling point structurally resembled the original polymer. They were oligomers of styrene (dimers, trimers, etc). The oxidated products formed during the thermooxidative degradation of styrene-containing thermoplastics in the laboratory experiments were benzaldehyde, benzoic acid, and acetophenone, expressed in the sequence of

their yield. Oxidized products of compounds with a high boiling point were also found. The oxidation of polymers is a chain reaction which also produces intermediates, peroxides, and free radicals, with limited stability. These compounds easily react further and form stable oxidized products (acids, aldehydes).

Industrial hygiene measurements were carried out during normal work processes with PE and styrene-containing thermoplastics. The measured concentrations were fairly low, with the exception of the fume (aerosol) concentrations. Thus the fumes, which consisted of degradation products with very high boiling points, seemed to form the main hygienic problem during the processing of these thermoplastics.

The calculation of the added effects, "hygienic effects," of air impurities was difficult because there were no hygienic standards available for several compounds and compound groups, eg, peroxides and free radicals. When available hygienic standards (those of the American Conference of Governmental Industrial Hygienists) were used, the average hygienic effect (concentrations of air impurities relative to the respective hygienic standards) was 1 for the PE processes and 0.5 for the processing of styrene-containing thermoplastics. The concentrations of fumes were compared to the hygienic standard for respirable dust because the electron micrographs showed that the fumes contained tiny particles with a diameter of less than 0.2 μm. These particles were to some extent aggregated. A hygienic standard lower than that for respirable dust could, however, be recommended because, in addition to chemically bonded oxidized groups, the fumes may also act as a solvent or carrier for the low-molecular oxidized compounds, eg, formaldehyde and formic acid, simultaneously present in the air. When the concentrations of the fumes were excluded, the average "hygienic effect" of the vaporized compounds was 0.2 for the PE processes and 0.1 for the processing of styrene-containing thermoplastics.

It seems evident that styrene-containing thermoplastics emit less air impurities than PE. Results vary to some extent due to differences in raw materials, processing, ventilation, etc.

The laboratory experiments, as well as the measurements in industry, showed that the degradation products of PE and styrene-containing thermoplastics contain biologically active compounds. The obtained toxicologic results indicate that the degradation products can cause imbalances in the metabolism and biochemistry of exposed organisms. The effects vary when different thermoplastics are used.

A high number of different airborne contaminants evolves during thermoplastics processing; thus it is practical to choose some typical degradation products for each type of plastics for the evaluation of hygienic conditions in industry. According to the analytical and toxicologic results obtained in this study, suitable indicator compounds would be the following: (i) formaldehyde, formic acid and fumes for PE processing and (ii) styrene and fumes for the processing of PS and other styrene-containing thermoplastics, although other degradation products, eg, acids, aldehydes, and nitriles, may contribute significantly to the biological effects.

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