2. Production and Use of Paint Products

2.1 Production

(a) Production processes

The modern manufacture of paints, which are generally made in batches, involves three major steps: (i) mixing and grinding of raw materials; (ii) tinting (shading) and thinning; and (iii) filling operations (US Environmental Protection Agency, 1979), as illustrated in Figure 1.

To produce a batch of paints, manufacturers first load an appropriate amount of pigment, resin and various liquid chemicals into a roller mill, which is a large, hollow, rotating steel cylinder. Mills for grinding primer or dark pigments are partly filled with steel balls that measure about 1–2 cm in diameter. Mills for grinding light colours usually contain flattened ceramic spheres (pebbles) that measure about 3–4 cm in diameter. Depending on the type of mill used, the grinding process lasts about 24 h or until the pigment has been ground to a sufficiently fine paste. After the pigment has been ground, more resin and solvent are added to the paste in the mill and the paste is 'let down', that is, pumped out of the mill through a strainer which removes the grinding media to a holding tank.

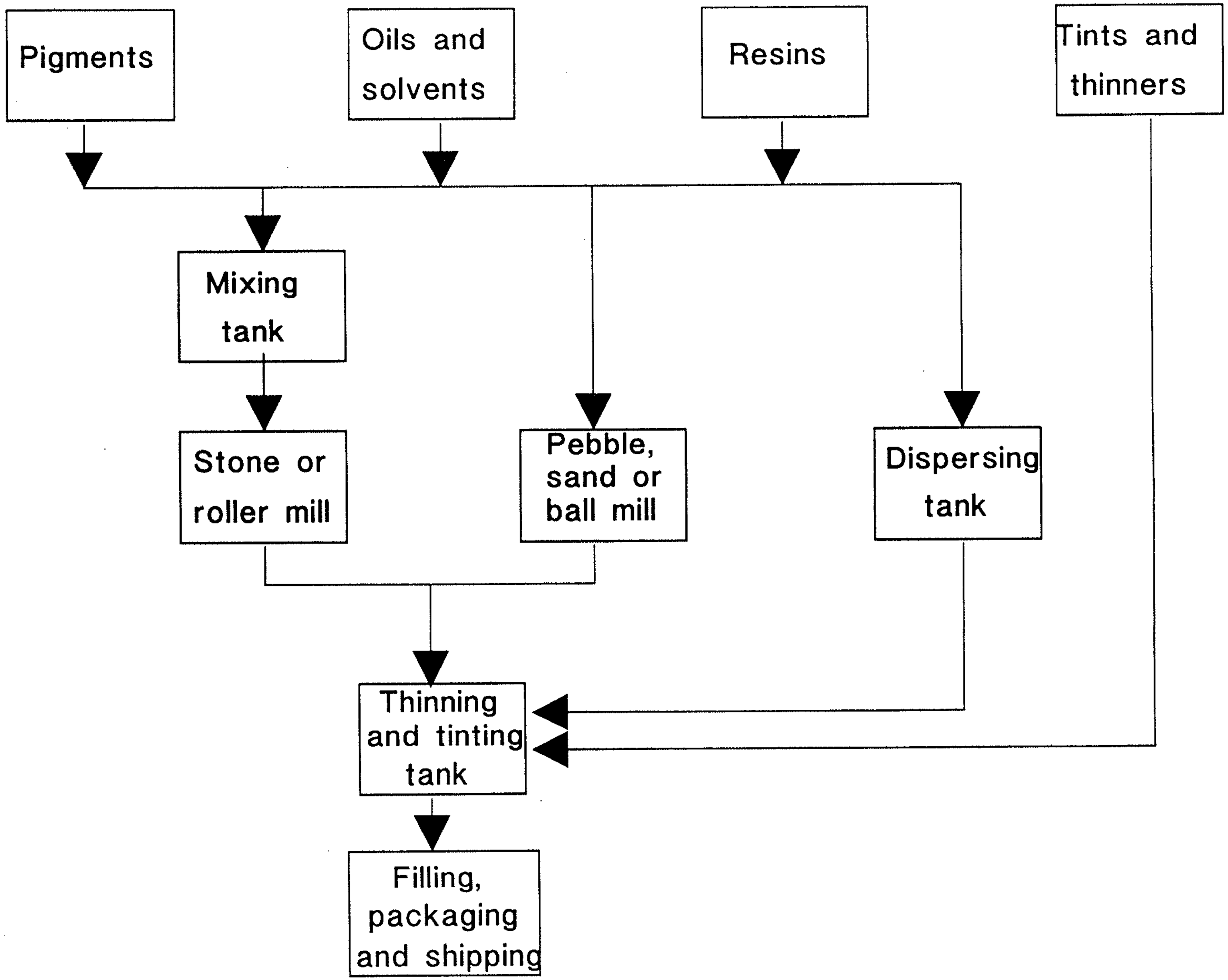
Until the 1930s, drying vegetable oils, primarily linseed oil, were used as binders in paints and as liquids for grinding. Since these oils were relatively poor pigment wetters, considerable energy was required for the grinding (dispersion) steps. Earlier dispersion techniques which involved pebble, steel ball or roller mills were replaced during the 1960s by high-speed equipment which was first used to dissolve large chips of pigment dispersed in solid binders. As pigment production and wetting characteristics improved, pigments were dispersed satisfactorily in high-speed dissolvers (Schurr, 1981).

The 'tinting' step involves comparing samples in the holding tank with colour standards. Small amounts of shading pastes, which are highly concentrated blends of ground pigments, and a vehicle are added as required to match the standard. After the batch has been shaded to specifications, it is thinned to the desired viscosity by the addition of solvent, filtered and poured into containers for shipment (Schurr, 1981).

The complexity of paint technology is indicated by the numerous types and number of raw materials required. A plant that produces a broad line of trade, maintenance and industrial paints requires over 500 different raw materials and purchased intermediates, including oils, pigments, extenders, resins, solvents, plasticizers, surfactants, metallic driers and other materials (Federation of Societies for Paint Technology, 1973).

The modern manufacture of unpigmented lacquers is generally a cold-cutting or simple mixing operation. For example, cellulose nitrate solutions are made by adding the nitrated cellulose from alcohol-wet cotton to the solvent mixture and agitating for 1–2 h in a paddle or turbine blade mixer. Alkyd resins, which are supplied in solution, can be added directly to the cotton-based solution. Hard resins may be dissolved separately, usually in toluene, and added as solutions, or the lumps may be dissolved directly in the cotton-based

Fig. 1. Process for manufacturing solvent-based paints[a]



[a] From US Environmental Protection Agency (1979)

solution by stirring. Liquid plasticizers are then simply poured or pumped into the mixing tank (Hamilton & Early, 1972).

In pigmented lacquer manufacture, the pigments are first dispersed in ball mills with plasticizers, such as dibutyl phthalate, after which natural or synthetic resins are added. Cellulose nitrate (or cellulose acetate) is then added and all the components are mixed in a vertical mixer or churn before the finished product is run off into containers (Browne, 1983).

Modern manufacture of varnish is carried out in jacketed and enclosed kettles or set pots, and the required high temperature is achieved by different methods, including the use of heat-transfer media (Browne, 1983).

(*b*) *Production figures*

Traditionally, two distinct types of coatings are produced – trade sale paints and industrial product finishes (Kline & Co., 1975).

Trade sale paints are sold through a variety of distribution channels to builders, contractors, industrial and commercial users and government units, as well as to the general public. These products are primarily for exterior and interior coatings for houses and buildings, although sizeable amounts of automobile and machinery refinishes, traffic paints and marine shelf-goods are also dispensed through trade sales outlets (Kline & Co., 1975).

Industrial product finishes or chemical coatings are produced to user specification and sold to other manufacturers for factory applications on such items as automobiles, aircraft, appliances, furniture and metal containers. They also include the category of industrial maintenance coatings, which are specially formulated and are used to maintain industrial plants and equipment (e.g,. as resistance to corrosion). Within these major product lines, the paint industry produces thousands of different products for a broad spectrum of substrates, applications and customers (Kline & Co., 1975).

World production in 1971 of surface coatings by selected countries or regions is given in Table 6. North America was the largest producer and manufactured 4.5 million tonnes (31.6%), while western Europe produced 4.2 million tonnes (29.3%) and eastern Europe produced slightly over 3 million tonnes (21.6%; Kline & Co., 1975).

A more recent listing of paint production in the USA, Japan and western Europe is presented in Table 7. Japan is now the largest paint producer outside of the USA, followed by the Federal Republic of Germany, France, the UK and Italy. In 1986, US paint production was 967 million gallons [approximately 4340 thousand tonnes] (Reisch, 1987).

Estimated consumption of various resins, pigments and solvents in the USA in 1975, 1980 and 1985 is shown in Tables 8, 9 and 10. The major resins used in the production of paints are alkyd, acrylic and vinyl resins, which account for over 60% of total resin use in the USA. The main pigment was titanium dioxide and the major solvents aliphatic hydrocarbons, toluene and xylenes (see monographs, p. 125).

The number of paint manufacturers in the USA has declined steadily from about 1500 in 1963, to about 1300 in 1972 and 1000 in 1987 (Kline & Co., 1975; Layman, 1985; Reisch, 1987). In the UK, there have been similar reductions from about 500 paint manufacturers in the 1950s to only about 250–300 in 1985 (Layman, 1985).

Table 6. World production (in thousands of tonnes) of surface coatings by selected country or region in 1971[a]

Region	Production	% Distribution
North America		
USA	4155	29.0
Canada	379	2.6
Total	4534	31.6
Europe		
Germany, Federal Republic of	1192	8.3
France	744	5.2
UK	614	4.3
Italy	420	2.9
Spain	207	1.4
Netherlands	192	1.3
Sweden	160	1.1
Belgium/Luxembourg	130	0.9
Austria	101	0.7
Denmark	84	0.6
Yugoslavia	80	0.5
Switzerland	68	0.5
Norway	66	0.5
Finland	46	0.3
Portugal	32	0.2
Turkey	27	0.2
Greece	20	0.1
Ireland	17	0.1
Total	4200	29.3
Eastern Europe (total)	3094	21.6
Asia		
Japan	1140	7.9
India	67	0.5
Israel	49	0.3
Hong Kong	26	0.2
Other[b]	304	2.1
Total	1586	11.1
Latin America[c]	484	3.4
Oceania		
Australia	179	1.2
New Zealand	45	0.3
Other	4	<0.1
Total	228	1.6

Table 6 (contd)

Region	Production	% Distribution
Africa		
South Africa	81	0.6
Other	138	1.0
Total	219	1.5
TOTAL	14 345	100.0

[a]From Kline & Co. (1975)

[b]Includes the Philippines and the Republic of Korea

[c]Includes Mexico

Table 7. Paint production (in thousands of tonnes) in selected countries in 1984[a]

Country	Prodution
USA[b]	4432
Japan[c]	1803
Germany, Federal Republic of	1321
France	809
UK[d]	670
Italy	625
Spain	278
Netherlands	253
Sweden	189
Denmark	133
Belgium	131
Austria	126
Portugal	92
Finland	82
Switzerland	82
Norway	75

[a]From Layman (1985), unless otherwise specified

[b]From Connolly *et al.* (1986)

[c]From Kikukawa (1986)

[d]Production in millions of litres

Table 8. Estimated consumption (in thousands of tonnes) of resins in paints and coatings in the USA[a]

Resin	1975	1980	1985
Alkyd[b]	315	295	300
Acrylic	158	203	223
Vinyl	166	183	191
Epoxy[c]	38	70	87
Urethane	33	54	58
Amino	29	33	41
Cellulosic	24	27	24
Polyester[b]	11	33	62
Phenolic	11	11	12
Chlorinated rubber	6	8	8
Styrene-butadiene	11	7	6
Natural	9	8	7
Linseed oil	23	35	36
Other resins	77	61	66
Plasticizers	20	19	17
Total	931	1047	1138

[a] From Connolly *et al.* (1986)

[b] Data for 1985 are not comparable to those for previous years, since it is probable that some of the resins reported as alkyds in previous years were actually polyesters.

[c] Includes unmodified epoxy resins plus hybrids (e.g., acrylate enhancement)

Table 9. Estimated consumption (in thousands of tonnes) of pigments in paints and coatings in the USA[a]

Use and pigment	1975	1980	1985
Colours			
Titanium dioxide	323	354	393
Chrome	29	33	33
Iron oxide	43	53	57
Carbon black	8	8	9
Other coloured inorganic	7	5	5
Phthalocyanine	1	2	2
Other organic	7	7	8
Aluminium	10	11	11
Fillers			
Calcium carbonate	175	175	213
Talc	136	150	136
Clay	154	159	199

Table 9 (contd)

Use and pigment	1975	1980	1985
Fillers (contd)			
Silica	59	71	83
Barytes	34	33	34
Nepheline syenite and feldspar	19	34	35
Other extenders and fillers	17	20	26
Other			
Zinc oxide	10	12	12
Zinc dust	24	32	24
Lead (corrosion inhibiting)	11	8	5
Cuprous oxide	2	4	3
Other	3	6	6
Total	1072	1177	1294

[a] From Connolly *et al.* (1986)

Table 10. Estimated consumption (in thousands of tonnes) of solvents in paints and coatings in the USA[a]

Solvent	1975	1980	1985
Aliphatic hydrocarbons	533	456	433
Toluene	281	265	277
Xylenes	240	213	211
Other aromatic compounds	91	79	84
Butyl alcohols	50	59	68
Ethyl alcohol	82	84	95
Isopropyl alcohol	48	53	41
Other alcohols	25	26	29
Acetone	79	79	89
Methyl ethyl ketone	145	154	152
Methyl isobutyl ketone	47	48	50
Ethyl acetate	31	35	36
Butyl acetates	55	62	71
Propyl acetates	8	8	9
Other ketones and esters	61	68	75
Ethylene glycol	23	29	34
Propylene glycol	14	12	14
Glycol ethers and ether esters	109	120	136
Chlorinated solvents	6	10	21
Miscellaneous	16	16	15
Total	1944	1876	1940

[a] From Connolly *et al.* (1986)

2.2 Use

(*a*) *Uses and application methods*

The various uses of paint products are described by type of resin in Table 11.

Paints are applied by direct contact or by deposition by atomization processes. The direct-contact category includes the familiar brushing and roller techniques, dipping, flow coating and electrodeposition. Deposition by atomization processes includes conventional spray, hot spray and electrostatic spray. Machine roller coating is used in the industrial application of paint to paper, plywood and metal sheets, as well as continuous coating of metal coils. Dip coating is used in large industrial operations (Browne, 1983; Lowell, 1984)

Probably the greatest advance made during the early 1900s in the field of paint technology was the introduction of the spray gun. Its advent helped in the introduction of cellulose nitrate lacquers and their application to automobile assembly line production. Electrostatic spraying was first introduced in the USA in the 1940s and later in the UK. Electrodeposition of paint, introduced during the 1960s, is an important milestone in industrial painting and has proven especially advantageous for painting automobile bodies and other parts because of its superior corrosion resistance. In this technique, the coating is an aqueous dispersion of low solid content. The binder particles carry ionized functional groups which may be positive or negative, thus having either anodic or cathodic deposition. The anodic type typically uses amino- or alkali-solubilized polycarboxylic resins and the cathodic type, salts of amine-treated resins, such as epoxy resins (Brewer, 1984; Lowell, 1984).

(*b*) *Use patterns*

Use of paints in the major markets in the USA in 1985 is presented in Table 12. Distribution of use of resins and the other main components of paints in the USA in 1985 is shown in Table 13.

2.3 Exposures in the workplace

(*a*) *Introduction*

No data on the numbers of paint production workers or painters worldwide were available to the Working Group. According to a 5% census sample of the US population in 1970 (National Institute for Occupational Safety and Health, 1970), paint manufacturers employed approximately 62 000 workers. Extrapolating from the proportion of world production of surface coatings contributed by the USA (see Table 6), it can be estimated that the total number of paint production workers in the world is approximately 200 000. According to the same US census survey, there were 362 000 construction/maintenance painters and 106 000 painters/paperhangers/decorators in the USA. On the basis of these figures, it can be similarly estimated that the number of painters worldwide must be at least several million.

Table 11. Uses of polymer systems in industrial coatings[a]

Polymer systems	Coil	Metal	Appliance	Furniture	Hardboard	Lumber and plywood	Marine	Maintenance	Automobile manufacture	Automobile refinish	Tins	Paperboard
Natural and modified polymers												
Drying oils				+	+	+	+	+			+	
Cellulose esters		+		+		+			+	+		+
Cellulose ethers				+						+		
Condensation systems												
Alkyd resins	+	+	+	+	+	+	+	+	+	+	+	+
Polyesters, high molecular weight	+	+	+		+	+						
Amino resins	+	+	+	+	+	+			+	+		
Phenolic resins	+	+	+				+	+	+	+	+	
Polyamides		+					+	+			+	+
Polyurethanes				+	+		+	+	+		+	+
Epoxy resins	+	+	+	+	+		+	+	+		+	
Silicones		+	+				+	+			+	
Vinyl polymers and copolymers based on:												
Butadiene								+			+	
Acrylic or methacrylic ester	+	+	+	+	+		+	+	+	+	+	+
Vinyl acetate				+	+	+	+	+				
Vinyl chloride	+	+	+	+	+	+	+	+	+		+	
Vinylidene chloride							+	+				+
Styrene		+	+		+			+	+	+	+	+
Vinyl acetal or butyral	+	+		+				+			+	
Fluorocarbons	+											
Resin combinations												
Acrylic and amino	+	+	+	+	+				+		+	+
Acrylic and epoxy		+	+						+		+	
Acrylic and silicone	+	+						+				
Alkyd and amino	+	+	+	+	+				+	+	+	+
Alkyd and acrylic		+	+	+				+	+	+	+	
Alkyd and epoxy		+	+					+	+			
Alkyd and silicone	+	+	+									
Polyester and epoxy		+	+					+	+		+	+
Polyester and silicone	+	+			+							
Cellulose ester and urethane				+								
Alkyd, acrylic and amino					+							
Polyester and amino											+	+
Phenolic and epoxy							+	+			+	
Epoxy and amino											+	
Phenolic and amino											+	
Alkyd and vinyl chloride polymers							+	+				

[a] From Lowell (1984)

Table 12. Consumption of paints and coatings by major market in the USA, 1985[a]

Paints and coatings	%	% of total
Architectural coatings		46
Water-based	73	
Solvent-based	27	
Product finishes		38
Miscellaneous[b]	32	
Containers	15	
Wooden furniture	14	
Automotive	12	
Machinery	10	
Metal furniture	7	
Coils	5	
Wood flat stock	4	
Special purpose coatings		16
Traffic	28	
Auto refinishes	25	
Special maintenance	19	
Aerosols	10	
Other[c]	18	

[a] From Connolly *et al.* (1986)

[b] Includes appliances, other transportation, marine, paper and foil, and other

[c] Includes paints for roofs, bridges, marine shelf goods, metals and others

A wide range of potential occupational health hazards is present in relation to the manufacture and use of paints, varnishes and lacquers. Coatings are complex mixtures containing a variety of groups of substances, such as organic solvents, organic and inorganic pigments, extenders, resins and additives such as catalysts, surfactants, driers, plasticizers and biocides. Each of these categories covers a range of tens or hundreds of individual chemical compounds (Connolly *et al.*, 1986). It has been reported that over 3000 individual paint components are used worldwide.

Occupational exposure results predominantly from the inhalation of gases and vapours, mainly organic, from solvents, binders and additives, of mainly inorganic pigment dusts and of complex inorganic and organic mixtures such as dusts from dried coatings and mists generated during the spraying of paint. The other major route of occupational exposure is through cutaneous contact with the various paint compounds, many of which can be absorbed through the skin. Ingestion related to personal work habits constitutes another potential route of entry.

Table 13. Distribution of use of components of paints in the USA in 1985[a]

Use	Proportion by use (wt% of total)					Total
	Resins	Pigments	Additives	Solvents	Water	(wt% of grand total)
Product finishes						
Wood furniture and fixtures	25.7	2.9	0.1	66	5.3	4.4
Wood mat stock	38	20	0.6	24	17	1.7
Metal furniture and fixtures	32	25	0.1	36	6.7	2.8
Containers and closures	38	6.2	0.3	43	13	4.8
Sheet, strip and coil	32	26	0.1	33	8.1	2.3
Major appliances	37	24	0.1	33	5.4	1.4
Other applicances	39	22	0.1	35	3.5	0.8
Automobile						
Topcoat	32	16	0.05	46	5.7	1.7
Primer	23	24	0.3	29	23	1.7
Underbody components and parts	26	18	0.2	35	21	1.1
Trucks and buses	31	16	0.1	27	25	1.2
Railroad	25	25	0.1	33	17	0.4
Other transportation	38	25	neg	38	neg	0.4
Machinery and equipment	30	27	0.2	38	5	4.2
Electrical insulation	51	0.0	0.0	49	neg	1.1
Paper, film and foil	39	2	0.1	43	17	1.0
Other product finishes	27	17	0.2	40	16	5.2
Total	31	17	0.2	41	11	36.8
Architectural coatings						
Interior water-based						
Mat	14	40	2	1.6	43	16.5
Semigloss and gloss	18	23	2	9.5	48	4.5
Other	18	21	1.5	0.2	57	1.3
Interior solvent-based						
Mat	21	58	0.2	30	0.0	1.1
Semigloss and gloss	27	41	0.1	32	0.0	2.6
Varnish	33	1.4	0.2	27	0.0	0.7
Other	26	21	0.2	43	0.0	0.7
Exterior water-based						
Mat (house paints)	19	35	25	4.2	39	11.2
Trim	20	23	2.6	3.3	51	0.9
Stains	17	19	1.5	3.5	59	1.4
Other	17	24	1.7	5	52	0.8
Exterior solvent-based						
Mat (house paints)	28	38	0.5	33	0.0	2.1
Enamel	42	26	0.3	32	0.0	2.4
Primer	25	37	0.7	37	0.0	0.7
Varnish	58	0.0	0.4	42	0.0	0.3
Stains	41	0.0	0.4	59	0.0	1.2
Other	24	40	0.5	36	0.0	0.3
Total	20	33	1.7	12	33	48.5

Table 13 (contd)

Use	Proportion by use (wt% of total)					Total (wt% of grand total)
	Resins	Pigments	Additives	Solvents	Water	
Special-purpose coatings						
Maintenance	36	23	0.2	33	8.2	2.8
Marine						
Pleasure	50	0.0	0.5	50	0.0	0.04
Commercial and maintenance	35	29	0.1	35	0.5	1.1
Automobile refinishing	23	22	0.2	55	neg	3.2
Traffic paints	15	59	0.1	26	0.9	5.6
Aerosol	15	5.5	0.1	80	neg	1.1
Other	21	46	0.2	32	0.1	3.2
Total	23	38	0.1	37	1.8	16.4
Grand total (thousands of tonnes)	1138	1294	42	1217	884	4536

[a] From Connolly *et al.* (1986); neg, negligible

Workers in the painting trades may also be exposed to a number of chemical agents originating from other operations that they or fellow workers are involved in, such as cleaning and preparing by chemical or mechanical means the object to be painted or cleaning themselves and the painting equipment.

The main substances to which workers may be exposed are listed in Table 14. The main occupational agents for which quantitative exposure data are available are presented in the following sections, covering the major paint trades.

Exposure to solvent mixtures is often described in the following sections using a summary measure, the cumulative exposure index (CEI), i.e., the sum of ratios of various measured levels to the respective occupational exposure limits. If this index exceeds unity, the combined exposure to different components of a solvent mixture is considered to exceed the recommended exposure limit. The values of the CEI are not always comparable because the exposure limits may vary with country and time.

In some painting operations, personal protective equipment is worn. However, it is common industrial hygiene practice to determine potential exposure by monitoring the breathing zone outside such protective gear. The results reported are thus not necessarily actual personal exposures.

Table 14. Main substances (and classes of substances) to which workers may be exposed in the painting trades[a]

Material	Principal uses or sources of emissions	*IARC Monographs*[b]
Acrylates (e.g., ethyl acrylate, methyl methacrylate)	Acrylic resins, ultraviolet curing paints	IARC (1979c)
Acrylic resins	Binders	IARC (1979c)
Alcohols, aliphatic (e.g., methanol, isopropanol, *n*-butanol)	Solvents (lacquers), paint removers	
Alkalis (e..g. sodium hydroxide, potassium hydroxide	Paint removers	
Alkyd resins	Binders	
Aluminium, powder	Pigment	
Amides, aliphatic (e.g., dimethylformamide)	Solvents	This volume
Amines (mono), aliphatic (e.g., diethylamine) and alkanolamines (e.g., 2-amino-2-methyl-l-propanol)	Water-based paints	
Amines (poly), aliphatic (e.g., diethylenetriamine)	Curing agents (epoxy resins)	
Amines, aromatic (e.g., *meta*-phenylenediamine, 4,4-methylenedianiline)	Curing agents (epoxy resins)	IARC (1978b) IARC (1986d)
Amino resins (e.g., urea-formaldehyde resins, melamine-formaldehyde resins)	Binders	IARC (1982a)
Ammonia	Water-based paints	
Anhydrides, organic (e.g., maleic anhydride, phthalic anhydride, trimellitic anhydride)	Alkyd resin synthesis, curing agents (epoxy resins)	
Antimony compounds (e.g., antimony trioxide)	Pigments, fire retardant pigments	This volume
Arsenic compounds (e.g., copper aceto-arsenate)	Antifouling agents	IARC (1980c)
Asbestos	Filler, spackling and taping compounds, talc	IARC (1977b)
Barium compounds (e.g., barium sulfate, barium carbonate)	Pigments	
Benzoyl peroxide	Catalyst	IARC (1985c)
Bisphenol A	Epoxy resins	
Cadmium compounds (e.g., cadmium sulfide, cadmium sulfoselenide)	Pigments	IARC (1976c)
Calcium compounds (e.g., calcium sulfate, calcium carbonate)	Fillers	
Camphor	Plasticizer	
Carbon black	Pigment	IARC (1984)
Cellulose ester resins (e.g., cellulose nitrate, cellulose acetate)	Binders	
Chloracetamide	Fungicide (water-based paints)	
Chromium compounds (e.g., chromic oxide, chromates)	Pigments	IARC (1980a)
Chlorofluorocarbons	Spray-can paint propellants	IARC (1986e)
Clays (e.g., bentonite)	Fillers	

Table 14 (contd)

Material	Principal uses or sources of emissions	*IARC Monographs*[b]
Coal-tar and asphalt	Special waterproof coatings (ships, tanks, pipes)	IARC (1985b)
Cobalt compounds	Pigments, driers	
Copper and copper compounds (e.g., bronze powder, cuprous oxide)	Pigments, antifouling agents	
Dyes and pigments, organic (e.g., aromatic azo dyes, phthalocyanines, rhodamine)	Pigments	IARC (1974b, 1978a)
Epichlorohydrin	Epoxy resins	IARC (1976b)
Epoxy resins	Binders	IARC (1976a)
Esters, aliphatic (e.g., ethyl acetate, isopropyl acetate)	Solvents	
Ethers, aliphatic (e.g., isopropyl ether, tetrahydrofuran) and glycol ethers (e.g., methylcellosolve)	Solvents	
Formaldehyde	Amino resin varnishes, biocide (water-based paints)	IARC (1982a)
Gasoline	Solvent	IARC (1989a)
Glycidyl ethers (e.g., *n*-butyl glycidyl ether and bisphenol A diglycidyl ether)	Epoxy resin diluents and constituents	This volume
Glycols (e.g., ethylene glycol)	Polyester resins, water-based paints	
Hydrocarbons, aliphatic (e.g., hexanes, heptanes)	Solvents (naphthas, white spirits)	
Hydrocarbons, aromatic (e.g., benzene, toluene, xylenes, trimethylbenzene)	Solvents (naphthas, white spirits), paint removers	IARC (1982b); this volume
Hydrocarbons, chlorinated (e.g., dichloromethane, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene)	Solvents, paint removers, metal degreasers	IARC (1979g,h,i; 1986c)
Hydrochloric acid (hydrogen chloride)	Catalyst (amino resins)	
Iron compounds (e.g., iron oxides, ferric ferrocyanide)	Pigments	IARC (1972)
Isocyanates (e.g., 1,6-hexamethylene diisocyanate, toluene diisocyanate)	Two-component polyurethane resins	IARC (1986b)
Isothiazolones (e.g., 1,2-benzisothiazolin-3-one)	Biocides in tinned foods	
Kerosene	Solvent	IARC (1989b)
Ketones, aliphatic (e.g., acetone, methyl ethyl ketone, cyclohexanone, isophorone, diacetone alcohol)	Solvents, lacquers, paint removers	
Lead compounds (e.g., lead chromate, lead oxides, basic lead carbonate, lead naphthenate)	Primers, pigments, driers	IARC (1980a)
Magnesium compounds (e.g., magnesium carbonate)	Fillers	
Manganese naphthenate	Drier	
Mercury compounds (e.g., mercuric oxide, phenyl mercuric acetate)	Fungicides (water-based paints)	
Methyl cellulose	Thickener (water-based paints)	

Table 14 (contd)

Material	Principal uses or sources of emissions	*IARC Monographs*[b]
Mica	Filler	
Molybdenum compounds (e.g., lead molybdate)	Pigments	
Nickel, metal powder	Pigment	IARC (1976c)
Nitroparaffins (e.g., nitroethane, 2-nitropropane)	Solvents	IARC (1982e)
Oils, vegetable (e.g., linseed oil, tung oil)	Binders	
Oximes (e.g., methyl ethyl ketoxime)	Anti-oxidants, anti-skinning agents	
Petroleum solvents (e.g., Stoddard solvent, VM & P naphtha)	Solvents, paint removers	This volume
Phenol	Phenol-formaldehyde resins, paint remover (formerly)	This volume
Phenol-formaldehyde resins	Binders	
Phenols, chlorinated (e.g., pentachlorophenol)	Fungicides (water-based paints)	IARC (1979j)
Phosphates, organic (e.g., tricresyl-*ortho*-phosphate, tributyl phosphate)	Plasticizers	
Phthalate esters (e.g., dibutyl phthalate, dioctyl phthalate)	Plasticizers	IARC (1982c)
Polychlorinated biphenyls	Plasticizers	IARC (1978c)
Polycyclic aromatic hydrocarbons	Special waterproof coatings (ships, tanks, pipes)	IARC (1983b)
Polyester resins	Binders	
Polyurethane resins	Binders	IARC (1979k)
Polyvinylacetate resins	Binders	IARC (1979b)
Pyrolysis fumes	Removal of paint by burning; heat-curing operations	
Rosin	Binder	
Rubber, synthetic (e.g., butyl rubber, styrene-butadiene rubber)	Binders (special paints, water-based paints)	IARC (1982f)
Shellac resin	Binder	
Silica, amorphous (e.g., diatomaceous earth)	Filler	IARC (1987b)
Silica, crystalline (e.g., quartz)	Filler, sand-blasting operation	IARC (1987b)
Silicates (e.g., sodium silicate, aluminium silicate)	Fillers	
Stearates (e.g., aluminium, zinc stearates)	Soaps, flattening agents	
Strontium compounds (e.g., strontium chromate, strontium sulfide)	Pigments	IARC (1980b)
Styrene	Polyester resins	IARC (1979d)
Styrene oxide	Diluent (epoxy resins)	IARC (1985d)
Sulfuric acid	Metal cleaner	
Talc	Filler	IARC (1987c)
Tin, metal powder	Lacquers (tinplate containers)	
Tin, organic compounds (e.g., tri-*n*-butyltin oxide, dibutyltin laurate)	Antifouling agents, catalysts	
Titanium dioxide	Pigment	This volume
para-Toluenesulfonic acid	Catalyst (amino resins)	
Turpentine	Solvent	

Table 14 (contd)

Material	Principal uses or sources of emissions	*IARC Monographs*[b]
Vinyl acetate	Polyvinylacetate resins	IARC (1986a)
Zinc and compounds (e.g., zinc metal powder, zinc oxide, zinc chromate)	Pigments, catalysts, bodying agents	IARC (1980b)

[a]From Sterner (1941); Piper (1965); Phillips (1976); O'Brien & Hurley (1981); O'Neill (1981); Dufva (1982); Krivanek (1982); Ringen (1982); Adams (1983); Selikoff (1983); National Institute for Occupational Safety and Health (1984); Swedish Work Environment Fund (1987) and previous sections

[b]See also *IARC Monographs* Supplement 7

(*b*) *Manufacture of paints and related products*

The manufacture of paints and related products such as varnishes, lacquers, enamels and paint removers involves the handling and processing of a complex array of raw materials, e.g., pigments, extenders, solvents, binders and additives, described in section 1, implying overall potential worker exposure to hundreds of chemicals (National Institute for Occupational Safety and Health, 1984). Furthermore, raw materials are often subjected to chemical changes such as during polymerization and cooking, thus creating a variety of new hazards.

The potential for occupational exposure depends largely on the basic types of products being manufactured, the degree of automation of the manufacturing process, the availability of exposure control measures and the nature of the specific job held. Various job classification systems have been developed for the paint manufacturing industry. Workers have thus been regrouped according to the basic product made - water-based paints, solvent-based paints, lacquer and vehicle - and to functions - pre-batch assembler, mixer, tinter, filler, tank and tub cleaner, reactor operator, varnish cooker, filter press operator (Morgan *et al.*, 1981). Additional functions are raw materials handler, laboratory personnel and others such as packagers, maintenance personnel, shippers and warehouse workers (National Institute for Occupational Safety and Health, 1984).

Heavy exposures, both by inhalation and skin contact, occur specifically in operations that can involve manual handling procedures such as weighing dry ingredients (pigments, extenders, resins, additives), loading them into mixing equipment, adding solvents to mills, and cleaning equipment (mixers, mills, reactors, kettles, tanks, filters). Additional exposure to solvents occurs in thinning, tinting and shading procedures, filling operations and filtering of varnishes. The cooking of varnishes may produce emissions of various aldehydes such as acrolein, of phenol, ketones, glycerine and fatty acids as well as dusts or vapours of maleic, phthalic and fumaric anhydrides during the loading of kettles. The production of powder coatings can be associated with significant exposure to dust from resin powders, pigments, curing agents and other additives. In the manufacture of radiation-curable coatings, exposures may occur to monomers such as ethyl acrylate, other acrylates and photoinitiators. Caustic solutions may be used in the cleaning of dispersion equipment (National Institute for Occupational Safety and Health, 1984). In general, important opportunities for exposure result from the presence of spills and the continuous spattering from machines (Adams, 1983).

(i) *Exposure to solvents*

Because of their volatility, solvents are ubiquitous air contaminants in paint manufacturing industries.

Exposure levels measured for various categories of workers in nine Swedish companies and reported as the sums of standardized concentrations are summarized in Table 15. High concentrations of solvents were found in all operations, the worst situation being manual cleaning of equipment with solvents. Local exhaust ventilation was common, and respirators were not often used. Of the 14 types of solvents monitored, the most common were xylene, toluene, butanol and esters (Ulfvarson, 1977).

Exposure to organic solvents was measured in the breathing zone of 17 Swedish male paint industry workers presumed to have the highest exposure of 47 workers employed in seven factories in Sweden, by collecting air with battery-driven syringes and analysing with two portable gas chromatographs. The median exposure values were (mg/m^3): xylene, 111 (16 persons); toluene, 11 (16 persons); isobutanol, 5 (15 persons); ethylacetate, 20 (14 persons); *n*-butylacetate, 14 (13 persons); ethanol, 13 (13 persons); *n*-butanol, 7 (13 persons); methylacetate, 12 (eight persons); dichloromethane, 719 (three persons); white spirits, 45 (three persons); and isopropanol, 129 (one person) (Haglund *et al.*, 1980).

Overall solvent exposure of workers known to be exposed to toluene was measured in seven paint manufacturing companies in New Zealand. Mean total levels of solvents ranged from 19 ppm in one company (five workers sampled) to 130 ppm in another one (three workers sampled), with individual values ranging from 7 to 297 ppm. Toluene, xylene and ethylbenzene were found in the atmosphere of all seven plants; the frequencies of other solvents were as follows: heptane, 6/7; *n*-hexane and methylethylketone, 5/7; acetone, 4/7; pentane, methylisobutylketone, ethanol and *n*-butylacetate, 3/7; and isopropanol, 1/7 (Winchester & Madjar, 1986).

In another study in Sweden, 47 employees of seven paint manufacturing industries, known to be exposed to solvents and including nine manual cleaners of paint mixing equipment, were surveyed for exposure to 12 solvents. The results are summarized in Table 16. The main exposures with regard to both frequency and weight were to xylene and toluene. Outstandingly high exposures occurred during the manual cleaning of equipment (Lundberg & Håkansson, 1985).

In a study on the effects of long-term exposure to solvents in the paint industry in Sweden, overall solvent exposure in a large paint manufacturing company was estimated for various work tasks over three historical periods. The results are presented in Table 17 in terms of the CEI, i.e., the sum of the ratios of the various exposure levels to the respective Swedish occupational standards in 1982 for the various solvents (Ørbaek *et al.*, 1985).

Table 15. Exposure levels (personal breathing-zone samples) to combined organic solvents during various paint manufacturing operations[a]

Operation	Sampling condition		Combined exposure[b]		Main solvents[c]	No. of samples in which solvent found
	No. of samples	Sampling time (min)	Mean	Range		
Charging solvents	33	4-43	2.0	0.2-16	Xylene	16
					Mesitylene	4
					Toluene	4
					Styrene	2
					Butanol	9
Pigment dispersion	18	9-66	1.5	0.2-4.4	Xylene	13
					Butanol	4
Tinting, thinning	14	15-32	0.9	0.1-2.0	Xylene	11
					Butanol	3
Can filling, paints	39	11-32	1.3	0.02-6.6	Xylene	23
					Alkanes	4
					Butanol	7
					Benzene	4
					Toluene	6
Can filling, thinners	14	9-20	1.8	0.1-7.4	Toluene	3
					Xylene	5
					Trichloroethylene	3
					Esters	2
					Acetone	1
Manual cleaning of equipment with solvents	51	3-28	5.7	0.5-30	Xylene	33
					Butanol	8
					Toluene	13
					Dichloromethane	9
					Esters	7
					Ketones	4

[a] From Ulfvarson (1977)

[b] Sum of ratios of individual solvent levels to their occupational exposure limits

[c] Solvents constituting at least one-fifth of individual combined exposure levels

The overall improvement in exposure levels over time has been attributed in large part to better control measures and to the increasing production of water-based paints. These results are corroborated by other estimates of the evolution of average solvent exposures in the Swedish paint manufacturing industry with the following values for the overall CEI: 2 in 1950-69, 1.5 in 1970-74, 0.7 in 1975-79 and 0.3 since 1980 (Lundberg, 1986). Heavy naphthas, toluene and benzene are reported to have been the most commonly used solvents during the 1930s, presumably with high exposure levels. Substitutes for aromatic hydrocarbons,

Table 16. Exposure levels (8–h time–weighted average) to organic solvents of 47 paint manufacturing workers[a]

Solvent	No. exposed	Exposure (mg/m^3)	
		Median	Range
Xylene	44	82	1–6070
Toluene	43	10	1–1260
Isobutanol	36	4	1–1040
n–Butanol	35	6	1–1540
Ethanol	33	12	1–1090
Ethyl acetate	32	26	1–767
n–Butyl acetate	31	9	1–1680
White spirits	18	44	5–74
Methyl acetate	11	13	3–169
Dichloromethane	5	719	10–2420
Methyl ethyl ketone	5	39	8–124
Isopropanol	3	129	6–258

[a] From Lundberg & Håkansson (1985)

Table 17. Average combined organic solvent exposure[a] of paint industry workers in various work areas over three periods[b]

Work area	Period		
	1969 and earlier	1970–75	1976 and later
Industrial paint section			
Mixing	2	1.3	0.7
Grinding	3	1.8	0.9
Tinting–finishing	2.2	1.5	0.6
Tapping	2.2	1.2	0.6
Cleaning of vessels	4.5	3	1.5
Alkyd paint section (mixing, tinting, tapping)			0.1–0.2
Small batch manufacturing		1.4	0.7
Filler manufacturing	0.2	0.15	0.1
Storage	0.2	0.15	0.1
Cellulose paint section	2.5		
Laboratory			
Product development	0.7	0.4	0.15
Control laboratory	1	0.75	0.4
Process engineering	2	1	0.4

[a] Sum of ratios of individual solvent levels to their occupational exposure limits; solvents considered: acetone, butanol, butylacetate, ethanol, ethyl acetate, white spirits, methyl isobutyl ketone, toluene and xylene

[b] From Ørbaek *et al.* (1985)

including turpentine, decaline and tetraline, would have been used during the Second World War and immediately after. From 1950 until today, the most commonly used solvents would have been xylene, toluene, white spirits, ethanol, butanol, ethyl acetate and butyl acetate. While operations were largely manual before the late 1960s, improvements such as local exhaust ventilation were gradually introduced in the mid-1960s.

(ii) *Exposure to dusts*

In a Swedish investigation covering ten factories manufacturing paint and industrial coatings, dust was found during tinting, handling of bags, compressing empty bags, floor cleaning and emptying air-cleaner filters. The principal exposure to dust, however, was found during charging of raw materials. Sixty-one breathing-zone samples taken over durations of 5 min to 8 h indicated total dust exposure levels of 1.7–70 mg/m^3. Raw materials charged included inorganic and organic pigments and fillers, chromium and lead compounds, talc and silica. The highest total dust levels (range, 7.7–70 mg/m^3; four samples) were found in a powder coatings factory. Local exhaust ventilation was widely used, but fewer than half of the workers wore respirators. A few air samples were obtained to evaluate exposure to specific dusts during charging operation in some of the companies. Quartz was measured in five factories, with levels ranging from 0.01 to 0.9 mg/m^3. Asbestos levels ranged from 0.3 to 5 fibres/cm^3 (four factories). Chromium levels (as CrO_3) ranged from 0.003 to 1.6 mg/m^3 (seven factories), while lead levels ranged from 0.006 to 4 mg/m^3 (three factories; Ulfvarson, 1977). Blood lead concentrations monitored in 80 workers in 12 paint manufacturing companies in Finland were 5–72 μg/100 ml. The highest value was found in a spray painter (Tola *et al.*, 1976).

(iii) *Other exposures*

Exposure to ammonia was reported while charging it for use in water-based paints in the Swedish paint industry, at average levels of 50–80 ppm (35–56 mg/m^3). In one case, more than 700 ppm (490 mg/m^3) was measured. The levels of pentachlorophenol and phthalic anhydride were below the standards of 0.5 mg/m^3 and 2 ppm (12 mg/m^3), respectively (Ulfvarson, 1977). The concentration of diethylene triamine was below the detection limit (0.01 mg/m^3) in the breathing zone of two workers canning epoxy paint curing agents in a Finnish paint factory (Bäck & Saarinen, 1986).

In a US paint manufacturing company, the 8-h time-weighted average (TWA) concentration of vinyl acetate ranged from 1.0 to 8.4 ppm (3.6–30.6 mg/m^3; four samples). Personal and area air samples indicated concentrations of ethyl acrylate ranging from below the limit of detection to 5.8 ppm (23.8 mg/m^3); concentrations of butyl acetate were all below the limit of detection (16 samples), except one sample at 0.9 ppm (4.7 mg/m^3; Belanger & Coye, 1980).

(c) *Construction painting and lacquering*

Usual painters' work in the construction industry involves the use of a rather limited number of types of coatings – mainly decorative water- or solvent-based paints and wood lacquers and varnishes. The potential for exposure to a variety of substances (mainly solvents and pigments) is high, however: painting performed inside buildings, where poor ventilation opportunities, especially in confined spaces such as small rooms, cupboards, bathrooms, can lead to very high levels of contaminants; whereas when painting the outside of buildings (facades, windows, roofs), natural ventilation is usually effective. Painting of new buildings usually involves mainly water-based paints and spraying equipment; however, during renovation or maintenance, solvent-based paints are still widely used and work is usually performed by hand with a brush or roller.

Surfaces to be coated can be made of plaster- or gypsum-based wall-board composite materials, concrete, wood such as for windows, doors and flooring, and more rarely metal. Construction painters may spend a good proportion of their time in preparatory or accessory work. In a Finnish study on construction painters, 92 of 231 (40%) painters estimated that they spent more time on such work than actually painting (Riala *et al.*, 1984). Removing old paint and preparing surfaces in general may involve the use of paint strippers containing solvents such as dichloromethane, of gas-operated blow torch units or hot air guns which may generate organic pyrolysis fumes, metallic fumes and dusts from pigments containing *inter alia* chromium, lead and arsenic compounds. Other accessory tasks may be polishing, sanding or sandblasting operations, which generate old paint, quartz, concrete, plaster, wood and metal dusts. Acid or alkali washing solutions may be used, as well as steam generators for removing wallpaper, which release carbon monoxide-containing exhaust gases. Preparing surfaces also often involves filling cracks and holes using plaster, cement, sealers, spackling, taping and dry wall materials, putties and wood fillers, implying possible additional exposure to inorganic dusts and fibres (including asbestos) and solvents. Further exposure stems from the use of solvents during the cleaning of equipment as well as for personal cleaning (Ringen, 1982; Huré, 1986; Swedish Work Environment Fund, 1987).

The use of solvents in construction paints, and thus painters' exposures, has evolved radically with time. Early whitewashes and distempers contained no organic solvent, and oil paints contained only about 10% turpentine or, later, white spirits. Alkyd paints introduced in the 1960s required approximately 50% of a solvent such as white spirits. With the introduction of epoxy paints for special surfaces such as floors, other solvents such as alcohols, esters and aromatic hydrocarbons became more widely used. Water-based latex paints were introduced in the 1950s but were more widely accepted in the 1960s and 1970s, to become predominant in the 1980s; now, an estimated 60–80% of building trade coatings are water-based (Dufva, 1982; Hansen, 1982; Riala *et al.*, 1984). Vinylic and acrylic water-based paints are the most common, and these contain only a small percentage of organic solvents, mainly alcohols or glycol ethers.

The 8-h TWA exposure to solvents of 45 Dutch maintenance painters working on 12 different projects has been measured. Summed air concentrations averaged 101 mg/m^3 (geometric mean) for the whole group and 59 mg/m^3 for a subgroup of 20 house painters who applied only alkyd resins by brush and roller. Benzene was detected at only two of the sites and at low concentrations (up to 0.2 mg/m^3). Toluene concentrations were below 4 mg/m^3, except at one site where it reached 43 mg/m^3. C_2- and C_3-substituted benzenes and C_8–C_{11} alkanes were found at most sites, originating mainly from the use of white spirits. Workers using chlororubber paint in a pumping station were exposed to carbon tetrachloride at levels ranging from 10 to 17 mg/m^3; the highest level of toluene was also found at this site (Scheffers *et al.*, 1985).

The exposure of Danish house painters to 13 solvents was investigated in 1974. Overall exposure, standardized to relevant occupational exposure limits, was above the permissible limit for five of 11 maximal values, reaching up to 34 times the permissible limit. Individual solvent average exposure levels were especially elevated for benzene (55 ppm [175 mg/m^3]; 41 samples), believed to originate from thinners, and for trichloroethylene (91 ppm [490 mg/m^3]; 33 samples). The origin of the trichloroethylene was not specified (Mølhave & Lajer, 1976).

In Finland, concentrations of Stoddard solvent during application of solvent-containing alkyd paints were 22–65 ppm (seven samples) and those during application of wood preservatives or alkyd varnishes, 68–280 (four samples). The overall solvent CEI during parquet floor varnishing using cellulose nitrate lacquers and urea–formaldehyde varnish ranged from 0.6 to 2.3, according to Finnish occupational exposure limits. Acetone, ethanol, isobutanol and butyl acetate were the main solvents used. Exposure to formaldehyde during varnishing averaged 2.8–4.5 ppm (3.4–5.5 mg/m^3; Riala, 1982). The risk of formation of bis(chloromethyl)ether (see IARC, 1987s) from the reaction between formaldehyde and hydrochloric acid (used as a hardener) in urea–formaldehyde varnishes has been evoked (Dufva, 1982), but levels higher than 0.2 ppb (>0.9 μg/m^3) have not been found (O'Neill, 1981).

In a study in Finland mainly of maintenance construction workers, the overall average airborne concentration of solvents during alkyd and urethane painting and varnishing, expressed as solvent naphtha exposure, was 132 ppm (77 samples); this was much higher when there was no ventilation, either natural or artificial (197 ppm; 46 samples), than with ventilation (38 ppm; 31 samples). Highest concentrations were observed during painting in small, unventilated rooms (303 ppm) and on large surfaces such as walls and ceilings with no ventilation (206 ppm with roller and brush painting and 243 ppm with spray painting). Taking into account other activities, e.g., use of water-based paints, the overall average 8-h TWA exposure level was 40 ppm (Riala *et al.*, 1984).

Air concentrations (mg/m^3) of organic vapours generated during the application of water-based paints were measured by personal sampling in Denmark, as follows: butyl acrylate, 0–2; diethylene glycol butyl ether, 4–5; diethylene glycol methyl ether, 8–32; dipropylene glycol methyl ether, 30–40; ethylene glycol butyl ether, 2–60; ethylene glycol phenyl ether, 0–0.7; propylene glycol, 2–70; 2,2,4-trimethylpentane-1,3 diol monoisobutyrate, 0.5–12; triethylamine, 4–6; and white spirits, 40–75. Concentrations of two gases, formaldehyde (at 0–0.4 mg/m^3) and ammonia (at 2–12 mg/m^3) were also reported (Hansen *et al.*, 1987).

In a Swedish study of renovation spray painters, very high concentrations of white spirits (1200–1500 ppm) were measured during use of alkyd-type paints and 100–1000-times lower concentrations of solvents during use of acrylate–polyvinyl acetate-based water-borne paints. Dust concentrations, originating from paint mist, were higher during use of water-based paints (77–110 mg/m^3) than solvent-based paints (17–27 mg/m^3). Inorganic substances were found to represent 80% and 70–85% of the dust content, respectively. Exposures to substances such as lead (in solvent-based paints) and zinc (in both types of paints) were 10–23% and 1–2% of their respective exposure limits (Bobjer & Knave, 1977).

The mean blood lead level measured in 1962 for a group of 107 decorative and house painters in the USA was 23 μg/100 g blood, similar to that in control groups (Siegel, 1963).

(*d*) *Painting, varnishing and lacquering in the wood industry*

Application of clear varnish or lacquer finishes on furniture represents the main use of coatings in the wood industry. Paints, varnishes and lacquers are also used in the production of various wooden raw materials (e.g., composite wood boards) and miscellaneous wooden articles (e.g., toys, tableware). Until the mid-1950s, cellulose ester-type lacquers were almost the only ones used in the furniture industry; however, amino resin-based, polyurethane and polyester coatings now constitute the main coatings in the industry (Swedish Work Environment Fund, 1987).

Workers are exposed mainly through inhalation or cutaneous absorption of solvents either from paint mist or from vapours generated by spraying operations, from vapours evolved from finished products or from auxiliary work such as mixing the coatings, cleaning equipment or applying other products such as wood fillers and sealants. The amount of exposure is influenced by the method of applying coatings; the most common are spraying, usually at low pressure, curtain and roller coating and dipping. The main categories of solvents used are aliphatic esters, ketones, alcohols and hydrocarbons as well as aromatic hydrocarbons (O'Brien & Hurley, 1981; Swedish Work Environment Fund, 1987).

Low molecular-weight resin constituents such as formaldehyde and isocyanates may be evolved during application or curing of coatings. Another possible exposure is to wood dust from the general factory environment and from preparatory work such as sanding.

Air monitoring was carried out over a ten-year period (1975–84) in 50 Finnish furniture factories, where the main coatings used were acid-cured amino resin-based paints and varnishes. The most commonly used solvents were xylene, *n*-butanol, toluene, ethanol, butylacetate and ethylacetate, which were present in more than 50% of 394 measurements. Mean concentrations of the solvents present were below 20 ppm, except for white spirits, which occurred at 66 ppm. Arithmetic mean solvent vapour concentrations measured during different work tasks ranged from 0.4 ppm in spray painting to 2.1 ppm during cleaning of a painting machine, with individual values varying from 0.1 to 7.4 ppm. Formaldehyde, derived from the amino resin binder, was the object of 161 short-term measurements (15–30 min) covering different work tasks. The arithmetic mean of the concentrations varied from 0.9 to 1.5 ppm (1.1–1.8 mg/m^3), with individual values ranging from 0.1 to 6.1 ppm (1.2–7.5 mg/m^3; Priha *et al.*, 1986).

The 8-h TWA exposure to formaldehyde of 38 employees in a Swedish light furniture factory applying acid-hardening clear varnishes and paints was found to average 0.4 mg/m^3 (range, 0.1–1.3) with a mean exposure to peak values (15 min) of 0.7 mg/m^3. Mean exposure to solvents was low. The dust concentration was low – usually less than one-tenth of the Swedish threshold limit value of 5 mg/m^3 (Alexandersson & Hedenstierna, 1988).

In a study of a US wood furniture company producing stereo equipment cabinets, the solvent exposure of 27 employees in spray painting and finish wiping operations was measured. In spraying jobs that involved the use of an acrylic base coat, an oil-based glaze or stain and cellulose nitrate lacquers, total exposure to paint mist (8-h TWA) varied from 0.1 to 2.5 mg/m^3 (geometric means). Combined exposure to solvents (CEI) varied from 0.05 to 0.11 in base coat operations (solvents measured: methyl ethyl ketone, isopropyl acetate, xylene, isopropanol, methyl isobutyl ketone, toluene and isobutyl isobutyrate), from 0.06 to 0.10 in glaze operations (toluene, xylene, ethylene glycol monobutyl ether and petroleum distillates) and from 0.08 to 0.24 in lacquer operations (isopropanol, ethanol, isophorone, isobutyl acetate, *n*-butanol, toluene, xylene, ethylene glycol monobutyl ether, methyl ethyl ketone, isobutyl isobutyrate, isopropyl acetate and petroleum distillates). The overall low air concentrations of paint mist and organic solvents were attributed to adequate ventilation in paint booths and good working practices (O'Brien & Hurley, 1981).

Exposure to organic solvent vapours was also measured in 16 small-scale industries in Japan, where synthetic *urushi* lacquer was applied to wooden tableware (bowls), vases and altars, and in two furniture factories. Work involved mainly brush painting, screen painting and hand-spraying operations. Toluene, xylene, ethylbenzene and *n*-hexane were the recorded solvents. Average mixed solvent personal exposure (CEI) was always low (below 0.44), except in the case of an automated spray operation (1.4; Ikeda *et al.*, 1985).

The average 4-h exposure to toluene of 20 workers employed in painting and hand-finishing in an Italian art furniture factory was 27–182 mg/m^3. Toluene was the principal solvent found in the work environment; other major solvents found were acetone, isobutanol, ethanol and ethyl acetate (Apostoli *et al.*, 1982).

In the Finnish plywood industry, solvent concentrations in workroom air were recorded during coating operations involving polyurethane and alkyd paints. The following ranges in ppm (mg/m^3) were obtained from eight to 12 measurements: (i) polyurethane paint: methyl isobutyl ketone, 2–28 (8.2–115); butylacetate, 8–50 (38–238); xylene, 10–25 (43–108); and cyclohexane, 1–28 (3.4–95); (ii) alkyd paint: toluene, 2–3 (7.5–11.3); xylene, 7–12 (30.4–52); isobutanol, 7–11 (21–33); and trimethylbenzene, 1–9 (5–44; Kauppinen, 1986).

In a US plant where paint was stripped from wood and metal, breathing zone TWA concentrations of dichloromethane for three operators ranged from 633 to 1017 mg/m^3 in seven samples (Chrostek, 1980).

(*e*) *Painting in the metal industry*

Protection from corrosion is the primary aim of metal painting. Mild steel is thus almost always subjected to the application of a primer coat containing corrosion inhibitors such as iron and lead oxides or of zinc powder, further covered with a decorative paint. Aluminium may be covered with a zinc chromate-based primer before a decorative coat is applied.

During the preparation of metal parts, painters may be exposed to cleaning and degreasing agents, such as solvents, alkalis and acids, and to abrasive dusts, such as crystalline silica generated during blast cleaning. Depending on the industry, metal painters may be exposed to a variety of dusts, solvents, fumes and gases resulting from operations such as mixing paints, maintaining equipment, applying fillers, sealers or putty, or background metal welding or assembling operations. Most coatings used in the metal industry are solvent-based, and spray painting is the main method of application, leading to potential exposures to paint mist and solvents. Two-component paints, such as those based on epoxy and polyurethane resins, play a major role, implying potential exposure to reactive substances such as isocyanates and epoxides. Air-drying or baking after application results in the evolution of solvents and, possibly, thermal degradation products of resins (Peterson, 1984).

(i) *Exposure to organic solvents*

Exposure of metal spray painters to a variety of solvents has been measured by the US National Institute for Occupational Safety and Health in a number of industries. The results are summarized in Table 18. Except in railroad car painting, overall exposure levels were found to be low. Toluene, xylene and petroleum distillates were among the most common solvents. Analyses of bulk air samples indicated no detectable benzene (0'Brien & Hurley, 1981).

In Finland, solvent concentrations were measured in the breathing zone of 40 car painters at six garages (54 1-h samples). Mean concentrations and the upper limits of various solvents were as follows (ppm) [mg/mg^3]: toluene, 30.6 (249) [115 (940)]; xylene, 5.8 (36) [25 (156)]; butylacetate, 6.8 (128) [32 (608)]; white spirits, 4.9 (150); methyl isobutyl ketone, 1.7 (39) [7 (160)]; isopropanol, 2.9 (85) [7 (209)]; ethyl acetate, 2.6 (14) [9 (50)]; acetone, 3.1 (25) [7 (60)]; and ethanol, 2.9 (27) [6 (51)] (Husman, 1980).

A large study of Swedish car refinishing workshops showed that painters spent only 15% of their time actually spray painting, the rest being occupied with grinding, filling, masking and assembling activities (60%) and colour mixing, degreasing and cleaning activities (25%). The highest overall solvent exposure was observed during spray painting, with a combined exposure of 0.3 (CEI; 106 samples). Toluene, xylene and ethyl acetate were present in all samples, at average levels of 39, 14 and 11 mg/m^3, respectively. Ethanol, butanol and butyl acetate were observed at very low levels in nearly half the samples. Other solvents encountered frequently in other activities, although at low levels, included styrene and white spirits. A reconstitution of working conditions in 1955 indicated that exposure levels to solvents were higher than in 1975, which was considered to be representative of the 1960s and 1970s. In particular, when benzene was used as a solvent in 1975–77, the combined exposure (CEI) reached 0.8 (Elofsson *et al.*, 1980).

Breathing zone samples were taken during short-term spray painting operations in a small autobody repair shop in the USA. Elevated levels of total hydrocarbons (up to 1400 ppm) were measured in winter when the spraybooth fan was turned off to conserve heat. Under these conditions, high concentrations of toluene (590 ppm; 2224 mg/m^3) were seen during lacquer spray painting and of xylene (230 ppm; 1000 mg/m^3) and benzene (11 ppm; 35 mg/m^3) during enamel spray painting. Summer conditions, when the fan was on, resulted in maximal concentrations of 330 ppm total hydrocarbons, 56 ppm (211 mg/m^3) toluene, 44 ppm (191 mg/m^3) xylene and 3.7 ppm (12 mg/m^3) benzene. Other major solvents measured were acetone, cellosolve acetate, methyl isobutyl ketone, *n*-hexane, methyl cellosolve acetate, trimethylbenzene, ethylbenzene and *n*-butyl acetate (Jayjock & Levin, 1984).

Table 18. Painters' time-weighted average exposure levels (personal breathing-zone samples) in various metal spray-painting operations[a]

Operation	Sampling time	No. of samples	Combined exposure[b,c]	Main solvents measured	Concentration (mg/m^3)[c]
Light aircraft finishing, primer spraying	25–41 min	3	0.9 ± 1.5	2-Butanone	42 ± 2.1
				Toluene	60 ± 1.2
				Ethanol	26 ± 1.6
				Isopropanol	19 ± 1.6
Light aircraft finishing, topcoat spraying	27–62 min	7	0.15 ± 1.3	Ethylacetate	77 ± 1.3
				Ethoxyethylacetate	44 ± 1.4
				Aliphatic hydrocarbons	34 ± 1.2
Light aircraft finishing, stripping operations	19–35 min	6	0.13 ± 2.5	Ethylacetate	52 ± 2.5
				Ethoxyethylacetate	30 ± 2.7
				Aliphatic hydrocarbons	73 ± 1.5
Car refinishing	15–45 min	7	0.09 ± 1.5	Toluene	39 ± 1.6
				Xylene	10 ± 1.0
				Petroleum distillates	21–63
				Other solvents	< 10
Railroad car	15–60 min	14	1.3 ± 1.4	Toluene	188 ± 1.5
				Xylene	14 ± 2.6
				Other aromatic compounds	217 ± 1.4
				Aliphatic hydrocarbons	840 ± 1.4
Heavy equipment	60 min	12	0.01–0.05	Refined solvents	21–96
				Other solvents	≤5
Metal furniture, solvent and water-borne paints	8 h	5 painters	0.10–0.46	Toluene	12–61
				Xylene	7–48
				n-Butyl acetate	22–109
				Diisobutyl ketone	< 1–23
				2-Ethoxyethyl acetate	1–14
				Aliphatic hydrocarbons	33–180
Metal furniture, high-solids paints	8 h	6 painters	0.07–0.31	Xylene	6–55
				Aromatic distillates	5–60
				Other solvents	< 10
Appliance finishing	8 h	4 painters	0.38–0.79	Toluene	88–204
				Xylene	112–225

[a] From O'Brien & Hurley (1981)

[b] Cumulative exposure index (see p. 366), based on US Occupational Safety and Health Administration permissible exposure levels

[c] Geometric means ± geometric standard deviation, unless otherwise stated

In Japan, the full-shift TWA concentrations of the following solvents measured for 13 car repair painters (ppm [mg/m^3]; mean ± standard deviation) were: xylene, 8 ± 8 [35 ± 35]; toluene, 19 ± 13 [72 ± 49]; isobutanol, 5 ± 5 [15 ± 15]; and ethyl acetate, 6 ± 4 [22 ± 14]. The overall combined exposure (CEI) was 0.38 ± 0.25. Short-term samples taken during painting showed a higher combined exposure for ten of 14 workers, toluene being the major solvent encountered (Takeuchi *et al.*, 1982). In another Japanese study of car refinishing painters, high toluene concentrations were observed during painting in side-wall ventilated booths (410–660 ppm; 1546–2488 mg/m^3), compared with those in downdraft ventilated booths (28–87 ppm; 106–328 mg/m^3). Short actual painting periods resulted in full-shift TWA concentrations of organic solvents (toluene, xylene, methyl acetate, ethyl acetate and butyl acetate) below the exposure limits. The average hippuric acid concentration in the urine of painters (0.33 mg/ml) was slightly higher than that in controls (0.19 mg/ml; Matsunaga *et al.*, 1983).

Exposure to toluene was investigated in 1940–41 in 106 painters in a large US airplane factory. Eight-hour TWA levels of toluene ranged from 100 to 1100 ppm (377–4147 mg/m^3); approximately 60% of workers were exposed to 200 ppm (754 mg/m^3) or more. Toluene was a major constituent of zinc chromate primers, lacquers, cellulose nitrate dope (lacquer) and brush wash (Greenburg et al., 1942).

An industrial hygiene evaluation was conducted at a commercial airline maintenance facility in the USA. Employees working in and around jet aircraft during the paint stripping process were exposed to levels of dichloromethane in the breathing zone that ranged from 79 to 950 mg/m^3 with a mean of 393 mg/m^3. During application of the prime coat, exposure to solvents was as follows (mg/m^3; mean and range): toluene, 112 (51–179); methyl ethyl ketone, 39 (8–77); butyl acetate, 72 (29–130); *n*-butanol, 25 (9–47); isopropanol, 51 (undetectable to 132); and cyclohexanone 10 (undetectable to 23). During application of the top coat, exposure to the solvents was: ethyl acetate, 333 (undetectable to 857); methyl ethyl ketone, 69 (undetectable to 219); methyl isobutyl ketone, 44 (nondetectable to 117); butyl acetate, 80 (undetectable to 210); xylene, 21 (undetectable to 49) and cellosolve acetate, 18 (undetectable to 46; Okawa & Keith, 1977).

Another study involved workers spray painting large commercial aircraft. Industrial hygiene measurements indicated short-term personal exposures as follows (mg/m^3; mean and range): toluene, 583 (140–1230); methyl ethyl ketone, 1436 (240–3250); ethyl acetate, 1231 (160–3520); naphtha, 44 (20–120); butyl acetate, 64 (20–150); xylene, 318 (60–1330); cellosolve acetate, 4843 (670–25 170); and dichloromethane, 654 (undetectable to 2840). Long-term exposures to the solvents were: ethyl acetate, 264 (10–1100); methyl ethyl ketone, 197 (20–440); toluene, 162 (30–450); butyl acetate, 11 (undetectable to 50); naphtha, 10 (undetectable to 160); xylene, 69 (10–270); cellosolve acetate, 640 (70–2490); and dichloromethane, 100 (undetectable to 760; Hervin & Thoburn, 1975).

Airborne concentrations (CEI) of solvent mixtures for jobs as paint mixer and spray painter ranged from 0.03 to 0.32 at a US plant manufacturing school and general purpose buses. The solvents found at the plant were petroleum naphtha, toluene, xylene, benzene, methyl ethyl ketone and *n*-hexane (Zey & Aw, 1984).

UK shipyard painters working in ships' accommodation and bilges were exposed to various mean TWA levels of organic solvents, depending on their job: 125 mg/m^3 for three painters using a chlorinated rubber paint with white spirits as solvent, 215 mg/m^3 for a worker using paint stripper with dichloromethane as the main solvent and 577 mg/m^3 for four men using white interior paint with white spirits as the main solvent. Other paint solvents used frequently in dockyards are methyl-*n*-butyl ketone, *n*-butanol, trichloroethylene, xylene and cellosolve (Cherry *et al.*, 1985).

In Poland, phenol and hippuric acids were measured in 51 urine samples from shipyard painters working in small spaces of superstructures and in large holds. The average values of phenol in urine were 12.4–66.4 mg/l compared to 7.9 mg/l on average for a control group. Urinary phenol was attributed to benzene: the benzene concentration in air ranged from undetectable to 11 ppm (35 mg/m^3). The average concentrations of hippuric acids in urine (sum of hippuric and methylhippuric acids) were 1812–5500 mg/l compared to 790 mg/l in a control group. Concentrations of toluene and xylene in air were 7–88 ppm (26–332 mg/m^3) and 23–538 ppm (100–2335 mg/m^3), respectively (Mikulski *et al.*, 1972). Elevated values of hippuric (up to 6700 mg/l) and methylhippuric acids (up to 7100 mg/l) were also measured in the urine of shipyard workers in Japan (Ogata *et al.*, 1971).

In a factory producing dump-truck bodies and earth-moving machinery in the UK, full-shift personal exposure levels to xylene and white spirits (two samples) were measured as 52 and 65 ppm (226 and 282 mg/m^3) xylene and 7 and 12 ppm white spirits. After ventilation was properly adjusted, these levels dropped to 9 and 7 ppm (39 and 30 mg/m^3) xylene and < 5 ppm white spirits (Bradley & Bodsworth, 1983). At a US plant where truck bodies and refuse handling equipment were manufactured, breathing zone concentrations of xylene during spray painting operations (eight samples varying from 1 to 3 h) ranged from 5 to 140 ppm (22–608 mg/m^3; Vandervort & Cromer, 1975). Low exposure levels of toluene (3–18 mg/m^3) and isobutyl acetate (2–44 mg/m^3) were observed for Swedish spray painters in a plant manufacturing fireplaces (Hellquist *et al.*, 1983).

(ii) *Exposure to paint mists, dusts and specific metals*

Exposures of metal spray painters to paint mists, lead and chromium have been measured by the US National Institute for Occupational Safety and Health in a variety of industries. The results are summarized in Table 19. High concentrations of paint mist have been recorded in several operations, often linked with the painting of enclosed spaces and internal cavities, faulty ventilation and work practices. Substantial but short-term lead exposure was encountered in situations where lead-based pigments were used, such as for painting transportation and heavy equipment. Elevated but brief exposures to chromium were noted during the spraying of aircraft with primer. No antimony, arsenic, cadmium or mercury was encountered in these studies. Very low levels of tin (2–7 μg/m^3) were recorded during the spray painting of dibutyltin dilaurate containing enamel on light aircraft (O'Brien & Hurley, 1981).

In a large study of Swedish car refinishing workshops, averages of 7 mg/m^3 mist, 100 μg/m^3 lead and 26 μg/m^3 chromium were measured during spraying activities; during grinding activities, the corresponding values were 3 mg/m^3, 20 μg/m^3 and 6 μg/m^3. The conditions

Table 19. Painters' exposure (personal breathing-zone samples) to paint mists, lead and chromium in various metal spray-painting operations[a]

Operation	Sampling conditions	No. of samples	Exposure level[b]		
			Paint mist (mg/m^3)	Lead (µg/m^3)	Total (µg/m^3)
Light aircraft finishing, primer spraying	25–41 min	3	23.3 ± 1.6	ND	1600 ± 1.6
Light aircraft finishing, topcoat spraying	27–62 min	6	23.3 ± 1.7	ND	-
Light aircraft finishing, stripping operations	19–35 min	6	14.1 ± 2.0	ND–5000	-
Car refinishing	15–45 min	7	8.7 ± 1.6	52 ± 1.5	-
Car refinishing	8 h	7	5.0	30	-
Railroad car	15–60 min	13	43.3 ± 1.4	211 ± 1.7	220 ± 2.2
Heavy equipment	60 min	3	2.0–36.5	230–1300	31–230
Metal furniture	8 h	6 painters	3.7–27.6	ND–1050[c]	-
Metal furniture, high-solids paints	8 h	6 painters	0.5 -6.2	5–26	5–9
Small appliance parts, powder coating, electrostatic spraying	8 h	3	1.3 ± 1.1	-	-
Appliance finishing	8 h	4 painters	21.7–54.5	<6–20	-

[a] From O'Brien & Hurley (1981)

[b] Geometric means ± geometric standard deviation, unless otherwise indicated

[c] Only 2.5-h samples taken one afternoon showed detectable levels (30–1050)

were thought to be representative of those in the 1960s and 1970s. Simulation of work conditions in 1955 showed low concentrations of lead during the use of all colours except red, when the Swedish exposure limit was exceeded by 70-fold. The actual exposure of painters was believed to be reduced by the use of individual protective equipment (Elofsson *et al.*, 1980). Breathing-zone samples were taken during short-term spray painting operations in a small auto-body repair workshop in the USA. Only one of eight samples, corresponding to a red paint formula, contained significant levels of chromium (490 µg/m^3) and lead (210 µg/m^3); in all other measurements, the levels of chromium, lead and cadmium were below the detection limit. The concentration of total dust collected during the sanding or grinding of plastic body filler was 5–40 mg/m^3 and that of respirable dust, 0.3–1.2 mg/m^3 (Jayjock & Levin, 1984). In a factory producing dump-truck bodies and earth-moving machinery in the UK, full-shift personal exposure levels to total paint solids (two samples) were measured as 11.6 and 15.9 mg/m^3. After ventilation was properly adjusted, these levels dropped to 1.4 and 5.2 mg/m^3. The major pigments used were titanium dioxide and iron oxide (Bradley & Bodsworth, 1983). At a US plant where truck bodies and refuse handling equipment were made, breathing zone concentrations of solid contaminants measured during various spray painting operations (seven samples varying from 1 to 3 h) were 4.8–47 mg/m^3 for total particulates, 20–3000 μg/m^3 lead and 10–400 μg/m^3 chromium (Vandervort & Cromer, 1975). Low overall exposure levels were found for Swedish spray painters working in a plant manufacturing fireplaces, with a total dust level of 1.7 mg/m^3, chromium oxide, 5–8 μg/m^3 and zinc oxide, 20–30 μg/m^3 (Hellquist *et al*., 1983).

At a US plant where school and general purpose buses were manufactured, employees working in and around the paint booth were reported to be exposed to hexavalent chromium and lead. The concentrations of hexavalent chromium in five personal air samples were 0.03–0.45 mg/m^3, with a mean of 0.23 mg/m^3; airborne lead concentrations (eight personal samples) ranged from below the laboratory limit of detection (3 μg/filter) to 2.01 mg/m^3, with a mean of 0.78 mg/m^3 (Zey & Aw, 1984).

A US manufacturer of large-scale weapon, electronic and aero-mechanical systems reported exposure of workers to hexavalent chromium while spraying aircraft wheels with yellow lacquer primers containing zinc chromate. In 12 personal breathing zone samples, the level of chromium[VI] ranged from 13.3 to 2900 μg/m^3 with a mean of 606.7 μg/m^3 (Kominsky *et al*., 1978).

In a US plant in which bridge girders were sprayed with lead silico-chromate paint, personal air levels of lead and chromium (as Cr) in five samples were 0.01–0.25 mg/m^3 (mean, 0.08) and 0.01–0.04 mg/m^3 (mean, 0.02), respectively (Rosensteel, 1974). Substantial exposure to airborne lead was demonstrated for US workers involved in scraping old lead-based paint from the metallic structure of a bridge and priming it (24–1017 μg/m^3); recoating with lead-based paint implied lower exposure levels (6–30 μg/m^3). Blood lead levels in these workers were 30–96 μg/100 ml, with 58% above 60 μg/100 ml (Landrigan *et al*., 1982). In the Netherlands, workers involved in flame-torch cutting of a steel structure coated with lead-based paints were shown to be exposed to 2–38 mg/m^3 airborne lead (Spee & Zwennis, 1987).

Blood lead levels have also been measured in workers in various occupations in three Finnish shipyards. Painters were among the most heavily exposed: mean blood levels in a total of 77 painters in the three shipyards were 20–28 μg/100 ml (Tola & Karskela, 1976).

(iii) *Other exposures*

Use of polyurethane type paints can result in exposure to diisocyanate monomers and their oligomers. In Sweden, 43 car repair painters were exposed to a TWA of 115 μg/m^3 hexamethylene diisocyanate (HDI)-biuret oligomer, with a range of 10–385 μg/m^3. Very high exposure peaks (up to 13 500 μg/m^3) were measured. The concentration of HDI was 1.0 μg/m^3 (Alexandersson *et al*., 1987). In Finland, average HDI and HDI-biuret oligomer levels in four car paint shops during spray painting (ten 5–10-min personal samples, outside respirator) were 49 (± 22 SD) and 1440 (± 1130) μg/m^3, respectively. The proper use of a respirator with combined charcoal and particle filters was shown to reduce exposure levels to below detection limits (Rosenberg & Tuomi, 1984). In a US car repainting shop, three short-term air samples (5–13 min) taken in the breathing zone during spray painting operations showed HDI levels of < 130 μg/m^3. Similar measurements taken during various light aircraft finishing operations (7–21 min, eight samples) indicated HDI levels below approximately 70 μg/m³, except for one operation with a level of 250 μg/m³ (O'Brien & Hurley, 1981).

Ambient levels of HDI during the spray application of an enamel top coat at a US airline maintenance facility were < 0.04–3.20 mg/m³, with a mean of 1.1 mg/m³ (Okawa & Keith, 1977).

Epoxy paints are usually applied as reactive mixtures of epoxy resins and curing agents, leading to potential exposure to compounds containing the epoxide group. Total epoxide concentrations have been measured in area samples of aerosols collected during three painting operations involving the use of a bisphenol-A diglycidyl ether type of epoxy resin. In a facility producing military aircraft, the use of an epoxy primer did not result in detectable epoxide levels, and the authors surmised that the epoxy–amine curing reaction had probably consumed most of the epoxide group. Epoxide levels of 2–12 μEq/m³ epoxide functional group were recorded during the painting of a tank with coal-tar epoxy coatings and the painting of a metal ceiling using an epoxy architectural coating (Herrick *et al.*, 1988). In a US company that finished structural steel members and other fabricated steel products, the products are blasted with steel shot or sand and spray-painted with two-component epoxy paints or oil-based paints. Personal air levels of epichlorohydrin were reported to range from 2.4 to 138.9 mg/m³, with a mean TWA of 64.9 mg/m³. Bisphenol A glycidyl ethers were also detected in the workers' breathing zone at levels which ranged from below the limit of detection (0.6 μg) to 28.6 μg/m³, with a mean of 9.8 μg/m³ (Chrostek & Levine, 1981).

The major thermal degradation components of epoxy powder paints were identified as phenol, cresols, bisphenol-A, pyridine, 2,3-dimethylpyrazine and formaldehyde; bisphenol-A glycidyl ether was not observed. Levels in the work environment of painters were not measured (Peltonen, 1986; Peltonen *et al.*, 1986). Diethylene triamine, which is a component of curing agents of epoxy paints, was measured in three samples collected from the breathing zone of a painter during spray painting of paper machine cylinders and pulp tanks at a concentration of 0.02–0.07 mg/m³ (Bäck & Saarinen, 1986).

Operators working in eight plants where coal-tar enamel protective coating was applied to pipelines with heat were exposed to high levels of coal-tar pitch volatiles (see IARC, 1985b) at up to 24 mg/m³ of benzene-soluble matter (full-shift samples). The overall respirable concentration of benzo[*a*]pyrene in the plants averaged 133 μg/m³ (Larson, 1978).