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Waterborne paints

A review of their chemistry and toxicology and the results of determinations made during their use

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HANSEN MK, LARSEN M, COHR K-H. Waterborne paints: A review of their chemistry and toxicology and the results of determinations made during their use. Scand J Work Environ Health 13 (1987) 473-485. This work presents information on the composition of waterborne construction paints used in Denmark, data from determinations of chemicals evaporating from paints applied with a brush or roller, and the toxicology of these chemicals. Seven product types were selected to illustrate the composition of the paints. Measurements at two workplaces were used as models for the work environment during painting. Evaporating chemicals were collected on Tenax TA™ and analyzed with capillary column gas chromatography after thermal desorption. In smudging work, waterborne paints may result in skin irritation and/or sensitization when safety precautions are not taken. Irritation of the mucous membranes may be expected if airing is not sufficient. This irritation may lead to headache mediated by trigeminal nerve stimulation. No other health hazards (e.g., brain damage) are expected. The available information indicates that waterborne paints are a clear improvement over traditional paints which use white spirit as the main solvent.

Key terms: biocides, headache, irritation, latex paint, monomers, sensitizers, siccatives, solvents, surface active compounds, trigeminal nerve.

In the 1970s there was a substantial change in the consumption of construction paints in Denmark. Before this time, most paints were formulated with white spirit as the main solvent. Today more than 90% of construction paints are waterborne. The reasons for this change may have been the public discussion of the possibility of brain damage due to solvent exposure, the technological developments, the information campaigns of the trade unions, and the regulation by the Danish Labour Inspectorate. The change has resulted in some further advantages, e.g., fewer risks of fire or explosion and a decreased emission of solvents to the environment.

The present review was initiated as part of an investigation of whether or not health problems might be expected from work with waterborne construction paints. It is a compilation of a Danish report (21), and it deals with (i) the composition of waterborne paints according to specifications from the Danish manufacturers, (ii) the toxicology of the chemicals contained in these paints, with the main emphasis on effects related to exposure to these types of products, and (iii) analysis of chemicals evaporating from waterborne paints under work conditions.

Review of the chemistry and the toxicology of waterborne paints

Chemistry of waterborne paints

The following seven waterborne product types were examined: acrylic latex paint (flat), acrylic latex paint (semi-gloss), heavy-bodied latex wall paint, latex enamel, latex primer (micro disperse), latex wall paint, and sealing waterborne paint (for ceilings). They were chosen from the Danish market in collaboration with, among others, the Danish Painters’ Union, representatives of the Danish paint industry, and the Danish National Institute of Occupational Health. These product types represent 90% of the waterborne paint used in Denmark when binders, gloss, consumption, and technical properties are considered.

Acrylic latex paints are high in quality. The binders are acrylic copolymers. They may be used on both interior or exterior surfaces. Latex wall paints are of lower quality. The binder may be acrylic copolymers, but many products use other binders, e.g., vinyl acetate copolymers. They are only used on interior surfaces. Heavy-bodied latex wall paints have a high content of pigments. The latex enamels are high in quality, with acrylic copolymers as binders. They usually have a high gloss. The latex primers are not pigmented. The sealing waterborne paints use alkydys as the binder, possibly combined with an acrylic copolymer.

Special product types with, e.g., epoxy and aziridine hardeners have been excluded from this review.

With the aid of the Danish Paint, Varnish and Lacquer Industry’s Association, specifications for paints of the seven product types were retrieved from...
the firms in this association. A total of 34 specifications were collected. Raw material manufacturers and suppliers reported the chemical composition of the 34 products. All products examined had code numbers 00-1 or 0-1 (13).

The general composition of the seven product types is given in Table 1. Many of the zeros shown in the table are due to the latex primers, which do not usually contain, eg, pigments, plasticizers, and driers. The six other product types contain most of the chemical compounds mentioned. Eight paints were selected for the chemical analyses, which were carried out at the Scandinavian Paint and Printing Ink Research Institute. Only minor deviations were found between the contents reported in the specifications and the results obtained in the analyses. The chemicals/raw materials reported in the specifications are listed in Table 2—7. The content found in the paints and the chemical abstract service number (CAS-No) are also given, when known.

The biocides (fungicides, preservatives) are used for in-can preservation, and they are listed in Table 2. Biocides are normally used as commercial formulations, which may contain up to four of the mentioned compounds.

Surfactants include antifoaming agents and protective colloids/thickeners. We were not able to list all information on this type of compound because, eg, the latex producers were not willing to disclose the content of the surfactants used in their latices.

### Table 1. Minimum and maximum concentrations of the raw materials in the paints. (% w/w = percentage by weight)

| Chemical compound | Content (% w/w) |
|-------------------|-----------------|
| Water             | 26—86           |
| Biocides          | 0—1.1           |
| Surfactants       | 0.7—5           |
| Pigments/extender pigments | 0—54         |
| Binders           |                 |
| Latex (dry weight)| 6—27            |
| Alkyds (dry weight)| 6—14           |
| Coalescing agents/cosolvents | 0—15          |
| Amines            | 0—0.5           |
| Plasticizers      | 0—2.2           |
| Driers (siccatives)| 0—0.6          |
| Others            | 0—4             |

### Table 2. Biocides used in waterborne paints for in-can preservation. Each biocide formulation may contain up to four of the chemicals (confidential). (% w/w = percentage by weight, CAS-No = chemical abstract service number)

| Chemical compound | Maximum content (% w/w) | CAS-No |
|-------------------|-------------------------|--------|
| Aliphatic nitrogen-containing and heterocyclic sulfur-containing compounds (isothiazoliones?) |                       |        |
| 1,2-Benzisothiazolin-3-one | 0.05 | 2534-33-5 |
| Benzyl alcohol monoo(poly)-hemiformal | 0.3 | 14548-60-8 |
| Carbazidam | 0.1 | 10605-21-7 |
| 1-(3-Chlorallyl)-tetraazaadamanant hydrochloride | 0.2 | 4080-31-3 |
| 5-Chlor-2-methyl-4-isothiazolin-3-one | 0.003 | 26172-55-4 |
| Didecyl dimethyl ammonium chloride | 0.01 | 7173-51-5 |
| Formaldehyde | about 0.1 | 50-00-0 |
| 5,8,11,13,16,19-Hexaoxaxicosane | 0.15 | 143-29-3 |
| 3-Iodo propynyl butyl carbamate | 0.16 | 55406-53-6 |
| 2-Methyl-4-isothiazolin-3-one | 0.003 | 2682-20-4 |
| Sodium benzoate | 0.2 | 532-32-1 |
| Sodium nitrite | 0.1 | 7632-00-0 |

a Other numbers exist.

b Also used as anticorrosion compounds.

### Table 3. Surfactants used in waterborne paints, as, eg, surfactants, antifoaming agents, protective colloids, and thickeners. (% w/w = percentage by weight, CAS-No = chemical abstract service number)

| Chemical compound | Maximum content (% w/w) | CAS-No |
|-------------------|-------------------------|--------|
| Aluminum stearate | 0.01 | 637-12-7 |
| Cellulose ethers (eg, hydroxyethyl cellulose) | 1.1 | 9004-62-0 |
| Copolymers of different carboxylic acids (eg, acrylic acid), 2,5-furanione, isobutylene and/or acrylamide (may be sodium or ammonium salts) | 0.1 |        |
| Disodium phosphate | . | 1330-43-4 |
| Poly(dimethylsiloxanes) | 1 | 9016-00-0 |
| Polyethylene | 4 | 9002-88-4 |
| Poly(oxyethylene) nonyl phenyl ethers | 1 | 9016-45-9 |
| Potassium and/or sodium pyrophosphates | 0.5 | 7722-88-5 |
| Sodium diocyl sulfosuccinate | 0.2 | 577-11-7 |
| Sodium hexametaphosphate | 0.2 | 10124-56-8 |

### Table 4. White pigments/extender pigments in waterborne paints. (% w/w = percentage by weight, CAS-No = chemical abstract service number)

| Chemical compound | Maximum content (% w/w) | CAS-No |
|-------------------|-------------------------|--------|
| Bentonite (magnesium aluminum silicate) | 1 | 1302-78-9 |
| Calcium carbonate | >30 | 4713-34-1 |
| Diatomite (silicon oxide) | 8 | 7631-86-9 |
| Dolomite (calcium magnesium carbonate) | 20 | . |
| Kaolin (aluminum silicate) | 8 | 12141-46-7 |
| Mica (potassium aluminum silicate) | 8 | 1327-44-2 |
| Talc (magnesium silicate) | 16 | 14807-96-6 |
| Titanium dioxide | 27 | 13463-67-7 |
| Zinc oxide | 2 | 1314-13-2 |

a Other numbers exist.
surfactants given in Table 3 are mainly those added by the paint manufacturers.

To be able to compare different products, we only collected specifications for white paints. Table 4 lists the white pigments used.

Most of the binders in the examined paints were of the latex type. Latices are made by emulsion polymerization of the monomers dispersed in water as droplets. The polymerization takes place within these droplets. The polymerization is initiated by free-radical generators (e.g., benzoyl peroxide) (32). According to the producers, the molecular weight of the polymers is approximately 1,000,000. Several different monomers are used for the polymerization (Table 5). The latices may contain ammonia [e.g., 0.3 percent by weight (% w/w)], formaldehyde (e.g., 0.06 % w/w) or other biocides (e.g., mixture of isothiazolines), and surfactants. They may also contain a small amount of a polymerization inhibitor or initiator [e.g., p-methoxyphenol (CAS-No 150-76-5), hydroquinone (CAS-No 123-31-9), or benzoyl peroxide (CAS-No 522-66-7)].

Alkyls are oil-modified polyester resins. They are polymers formed by the reaction of polybasic acids, polyhydric alcohols, and monobasic fatty acids (32). The polybasic acid may be phthalic acid, the alcohol may be pentaerythritol, and the fatty acids may come from tall oil. However, many other substances are used (32). The examined alkyls were emulsions, except for one, which had an alkyl solubilized with triethylamine (CAS-No 121-44-8).

Solvents are added to the paints for many reasons, e.g., to aid in film formation (32). Table 6 lists the coalescing solvents/cosolvents used.

Most latex paints are adjusted to a pH of 8—9 with ammonia (CAS-No 7644-41-7). Ammonia may also come from the raw materials. As has already been mentioned, triethylamine was used to solubilize a water-

Table 5. Monomers used for latex production. The typical amount of monomers in the latices according to the manufacturers. (% w/w = percentage by weight, CAS-No = chemical abstract number)

| Chemical compound               | Typical amount (% w/w) | CAS-No   |
|----------------------------------|------------------------|----------|
| Acrylamide                       | ...                    | 79-06-1  |
| Acrylonitrile                    | 0.001                  | 107-13-1 |
| Acrylic acid                     | ...                    | 79-10-7  |
| Butyl acrylate                   | 0.02—0.06              | 141-32-2 |
| Butyl methacrylate               | ...                    | 97-88-1  |
| 2-Ethylhexyl acrylate            | 0.01                   | 103-11-7 |
| Methacrylic acid                 | ...                    | 79-41-4  |
| Methyl methacrylate              | 0.01                   | 80-62-6  |
| Styrene                          | 0.01—0.04              | 100-42-5 |
| Vinyl acetate                    | ...                    | 108-05-4 |
| Vinyl ester of Versatic 5%       | ...                    | 59965-62-3 |

a Versatic 5% is a mixture of branched acids with nine carbon atoms.

| Chemical compound               | Maximum content (% w/w) | CAS-No |
|----------------------------------|-------------------------|--------|
| Hydrocarbon mixtures             |                         |        |
| Turpentine                       | 0.3                     | 8006-64-2 |
| White spirit                     | 2                       | 8030-30-6 |
| Xylene                           | 0.01                    | 95-47-6 |
| Alcohols                         |                         |        |
| Ethanol                          | 0.1                     | 64-17-5 |
| 2-Propanol                       | 0.01                    | 67-63-0 |
| 1-Butanol                        | 0.01                    | 71-36-3 |
| Esters                           |                         |        |
| "Isobutanol esters of dicarboxylic acids" | 1                  |        |
| Glycols                          |                         |        |
| Ethylene glycol                  | 2                       | 107-21-1 |
| Propylene glycol                 | 10                      | 57-55-6 |
| Hexylene glycol                  | 5                       | 107-41-5 |
| Oxybispropanol                   | 0.1                     | 25265-71-8 |
| Polypropylene glycol             | 1                       | 25322-69-4 |
| Glycol ethers/esters             |                         |        |
| Ethylene glycol ethyl ether      | 1.1                     | 110-80-5 |
| Ethylene glycol butyl ether      | 1.4                     | 111-76-2 |
| Ethylene glycol phenyl ether     | 5                       | 122-99-6 |
| Diethylene glycol methyl ether   | 4                       | 111-77-3 |
| Diethylene glycol ethyl ether    | 1                       | 111-90-0 |
| Diethylene glycol butyl ether    | 1.5                     | 112-34-5 |
| Dipropylene glycol methyl ether  | 4                       | 34590-94-8 |
| Ethylene glycol ethyl ether      | 0.02                    | 111-15-9 |
| 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (Kodaflex TXIB) | 6                | 6846-50-0 |
| 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (Texanol) | 5                | 25265-77-4 |

a Present as one of the raw materials.

Table 7. Driers (siccalives) used in waterborne paints to accelerate the curing. (% w/w = percentage by weight, CAS-No = chemical abstract service number)

| Chemical compound               | Maximum content (% w/w) | CAS-No |
|----------------------------------|-------------------------|--------|
| Barium octoate                   | 0.3                     | 4696-54-2 |
| Calcium naphthenate              | 0.8                     | 61789-36-4 |
| Cobalt octoate                   | 0.3                     | 136-62-7 |
| Cobalt naphthenate               | 0.4                     | 61789-51-3 |
| 1,10-Phenanthroline              | 0.02                    | 66-71-7 |
| Zirconium octoate                | 0.4                     | 5206-47-3 |

a Other numbers exist.

redducible alkyl (max 0.5 % w/w). Dimethylamino-methylpropanol (CAS-No 7005-47-2) and 2-aminopropanol (CAS-No 78-91-1) were also present in some raw materials (max 0.01 % w/w).

In a few instances dibutylphthalate (CAS-No 84-74-2) was used as a plasticizer (max 2.2 % w/w).
Driers (siccatives) are used in unsaturated polymers, eg, alkyds, to accelerate the curing (32). Table 7 lists the driers used.

In one product, butanone oxime (CAS-No 96-29-7) was used as an antiskinning agent (0.25 % w/w). Sodium benzoate and sodium nitrite were used in a few paints as corrosion inhibitors and as biocides. In one product sodium nitrite was added as a salt with triethanol amine ("triethanol nitrite") (0.25 % w/w) as a corrosion inhibitor (CAS-No unknown).

Toxicology of chemicals in waterborne paints

The toxicologic evaluation of waterborne paints was based on a review of more than 1 500 references, of which 686 were determined to be valuable and were included in the Danish report (21). In the present review, only the most important references are included. Because of difficulties in determining a no-effect level for, eg, carcinogens and teratogens, chronic effects, with the exception of allergy, have been considered in the Discussion.

Biocides. Most of the biocides (table 2) are skin sensitizers (2, 11, 28, 30, 33). Only one of the biocides (mixture of chloromethylisothiazolinone and methylisothiazolinone) proved capable of causing sensitization in the concentrations used (approximately 0.003 % w/w) (10). These chemicals have been described in detail elsewhere (22). Formaldehyde is absorbed in the upper respiratory tract during inhalation, and possibly also through the skin (30). A few of the other biocides may be absorbed through the skin (20, 40).

Surfactants. Among the surfactants, polyphosphates (1, 31), poly(oxyethylene)monyl phenyl ethers (19, 31), and sodium dioctyl sulfosuccinate may contribute to irritation of the skin (14, 26). Sodium dioctyl sulfosuccinate is a sensitizer (18). No other health hazards have been found for these compounds (table 3).

Pigments/extender pigments. Pigments and extender pigments (table 4) probably do not involve a health hazard when paints are brushed and rolled on.

Binders. The latex binders are copolymers of two to five monomers, eg, butyl acrylate, acrylic acid, and styrene. The contents of monomers in latices are usually stated to be less than 0.3 %. Some producers of latices have given more detailed information. (See table 5.) The contents listed agree with the results of the determinations made in two workplaces in that butyl acrylate was the only monomer determined in the air of the workplaces. (See workplaces 1 and 2 in the section Representative Workplaces.) Styrene was determined in a workplace not mentioned in this paper.

Most of the monomers have a pungent smell, and they may contribute to irritation of the mucous membranes (25, 44). Some monomers, eg, butyl acrylate and 2-ethylhexyl acrylate, are skin sensitizers in concentrations as low as 0.1 % (27). The monomers are absorbed through the lungs and through the skin (44).

The latices may contain biocides (eg, 0.06 % formaldehyde or isothiazolinones), surface active ingredients, and ammonia. The corresponding effects are listed in the following sections.

Polymerization initiators and inhibitors are presumably found in very low concentrations. They are not expected to present health hazards in these paints. However, they are irritating to the skin and the mucous membranes, and they are sensitizers (1, 37, 38, 48).

Coalescing solvents/cosolvents. The solvents (table 6) may smell (24, 44, 47), and they may contribute to irritation (9, 41, 42, 43) in cooperation with, eg, formaldehyde and ammonia. Turpentine is a known sensitizer (49). Most of the solvents are absorbed through the lungs and/or through the skin (41, 44). Most of these solvents are central nervous depressants (1).

Amines. The amines used in the seven product types may smell (47), and they may irritate the skin and the mucous membranes (1, 36, 45). Triethylamine is a sensitizer (8). The amines may be absorbed through the skin, as well as through inhalation (1, 8, 50).

Plasticizers. Dibutyl phthalate may smell (17). Health hazards may not be expected from this compound.

Driers (siccatives). Salts of cobalt and zirconium may sensitize (46, 51). No other health hazards are expected from the siccatives (table 7).

Determination of air contaminants during the use of waterborne paints

Measurements of the various substances in the ambient air during the use of the aforementioned waterborne paints were made under normal work conditions.

Air sampling and analysis

Organic vapors. The organic vapors were adsorbed on polymer in cartridges of stainless steel [150 ± 1 mg of Tenax TA, 60—80 mesh (Chrompack)]. The sampling time was 20 min, corresponding to a sampling volume of 0.9 l. An automatic pump (SKC Universal sampler, model 224-035) was used. Duplicate samples were taken with the use of a split.
The analyses of the organic vapors were performed with a gas chromatograph (Hewlett-Packard 5711) with a flame ionization detector. Two capillary columns were used (Chrompack SIL 19CB and CP 57CB). The column temperature was 30°C for 2 min, followed by an increase (4°C/min) to 200°C. This temperature was held for 16 min. The gas chromatograph was coupled to an automatic thermal desorber unit (Perkin-Elmer ATD-50). This method will be described in detail elsewhere (Wolkoff et al, unpublished results).

The compounds were identified by a central computer (Hewlett-Packard 1000) using a library containing more than 300 compounds occurring in indoor air or in workplaces. The identification was based on retention time indices on the two columns.

If white spirit was present in the paint, all unidentified peaks were classified as white spirit components. As no universal absorbent or universal detector exists, the concentration of the very volatile organic compounds (eg, acetone), the nitrogen-containing compounds (eg, the amines), and the halogen-containing compounds must be accepted as minimum values.

**Ammonia.** Ammonia was determined with indicator tubes (Dräger ammonia 5/a). Depending on the concentration of ammonia, 10 to 50 strokes with a Dräger gas detector pump were used.

**Formaldehyde.** Formaldehyde was collected in two impinger absorbers connected in series, each containing 10 ml of distilled water. A Dupont pump model P-2500 with a flow rate of 1 l/min was used. The sampling time was 30 min. Immediately after the sampling, 10 ml of Hantzsch reagent was added to each impinger. The samples were then stored in the cold. They were analyzed within one week with the acetyl acetone method (7). No attempts were made to analyze other aldehydes. A small amount of hexanal was found once by gas chromatography (0.1 mg/m³) in the apartment mentioned later in relation to workplace 2.

**Temperature and relative humidity.** Temperature and relative humidity were determined with a Bacharach sling psychrometer.

**Representative workplaces.** Measurements of the substances in question were made in a total of 15 workplaces (21). Table 8 presents the results. Two representative workplaces were chosen to illustrate the composition of the organic vapor phase of the air in the work area during and after the application of the waterborne paints. Thus the first example (workplace 1) describes the application of a latex wall paint in one room. The second example (workplace 2) describes the application of four different paints in one room over 3 d in one apartment, where the other rooms were also painted. The volatile chemicals in the canned products of the applied paints can be found in table 9.

In **workplace 1** the walls in a corridor with a ground area of 35 m² and a volume of 54 m³ were painted twice with a total of 15 l of latex wall paint during 3.25 h. Heavy-bodied latex wall paint had been applied a few days earlier in adjoining rooms. Some acrylic latex paint I (semi-gloss) was also applied at the end of the day, and it thus contributed to the measured air concentration. The work was repair work.

**Workplace 1** was characterized by a high level of formaldehyde. The concentration increased during the painting from 40 to 133 % of the Danish occupational exposure limit of 0.4 mg/m³ (ceiling value). Formaldehyde may have originated from the formaldehyde releaser 1-(3-chlorally1)-tetraazaadamantan hydrochloride or from the binder. After 4.5 h of painting, ammonia, white spirit, and butyl acrylate contributed with 16, 13, and 4 %, respectively, of the Danish occupational exposure limits, which are 18, 600, and 55 mg/m³, respectively. Figure 1 describes the volatile chemicals during and after the application of the latex wall paint. A more detailed description of workplace 1 is given in the appendix.

In **workplace 2** four different paints were applied during 3 d in one room (sitting room) in an apartment, in which four adjacent rooms were also painted. The work was repair work. The applied paints were (i) sealing waterborne paint (for ceilings), 4 l (day 1); (ii) latex primer, micro disperse, 1.8 l (day 1); (iii) latex

| Table 8. Data on the vapors measured by personal sampling during the application of waterborne paints in 15 workplaces (21). (% w/w = percentage by weight) |
|-----------------------------------------------|
| **Chemical** | **Content in paint (w/w)** | **Concentration in air of work area (mg/m³)** | **Occupational exposure limit** |
|-----------------|---------------------|---------------------|---------------------|
| Ammonia         | 0.01-0.15          | 2-12                | 18                 |
| Butyl acrylate  | 0.02              | 0-2                 | 55                 |
| Diethylene glycol butyl ether | 1.5        | 4-5                  | -                   |
| Diethylene glycol methyl ether | 4        | 8-32                 | -                   |
| Dipropylene glycol methyl ether | 1        | 30-40                | 600                |
| Ethylene glycol butyl ether | 0-1.4c       | 2-60                 | 120                |
| Ethylene glycol phenyl ether | 1.7        | 0-0.7                | -                   |
| Formaldehyde    | 0.4-8              | 2-70                 | 0.4                |
| Texanol<sup>a</sup> | 1-5             | 0.5-12               | -                   |
| Triethylamine    | 0.5                | 4-6                  | 100                |
| White spirit     | 0.9                | 40-75                | 600                |

<sup>a</sup> Danish limits in 1984 (4).
<sup>b</sup> According to producers the concentration in the binders was probably in the range of 0.02-0.06 %.
<sup>c</sup> In one of the list of ingredients, the chemical was not mentioned, but it was found in the air.
<sup>d</sup> The value, as a rule, is unknown. The chemical may come from formaldehyde and formaldehyde-releasing compounds used as biocides or from other raw materials.
<sup>e</sup> 2,2,4-Trimethyl pentane-1,3-diol monoisobutyrate.
wall paint, 3.5 l (day 2); and (iv) acrylic latex paint II, semi-gloss, 0.85 l (day 3). A small amount of acrylic latex paint III (0.1 l) was also applied in the room on the third day.

Among the applied paints, the sealing waterborne paint seemed to contribute the most to the level of contaminants in the workplace air. The main reason was the evaporation of ethylene glycol butyl ether. This compound was measured in concentrations of up to 40% of the Danish occupational exposure limit (120 mg/m³). Triethylamine, dipropylene glycol methyl ether, and ammonia reached 5–10% of their respective limits (100, 600, and 18 mg/m³, respectively). The hygienic load (ie, the percentage of the occupational exposure limit for mixtures) was 85% (60% when formaldehyde was not included). The latex wall paint resulted in an increase of the hygienic load from 43 to 72% (from 16 to 48% when formaldehyde was not included). Formaldehyde and ammonia were the main contributors. The latex primer (micro disperse) and acrylic latex paint II (semi-gloss) mainly contributed with compounds for which an exposure limit had not been established. Figure 2 describes the volatile chemicals in the work environment during the 3 d. A more detailed description of workplace 2 is given in the appendix.

### Discussion

#### Effects on the skin and mucous membranes

**Irritation of the skin due to direct contact with the paint.** All of the evaluated paints contained several chemicals that have been shown to irritate the skin. Although none of these chemicals occurred in concentrations high enough for the individual substances to cause irritation to the skin, the possibility of irritation due to a mixture of the chemicals cannot be excluded. Some examples of the skin-irritating chemicals are monomers from binders [eg, butyl acrylate (44)], coalescing solvents/cosolvents [eg, white spirit (23)], biocides [eg, formaldehyde (30)], surfactants [eg, polyphosphates (1, 31)], and ammonia (1, 36). According to Danish legislation (13) protectors for the hands, face and/or body are not obligatory when these types of products are applied with a brush or roller. All of the paints had code numbers 00-1 or 0-1. Since paints tend to splash when a roller is used, gloves, and possibly facial protection, should always be used during this type of work.

**Irritation of the mucous membranes.** Irritation to the mucous membranes may result either from contact with the paint or from chemicals evaporating from the drying paint. Irritation due to contact with the paint is comparable to the conditions mentioned for irritation of the skin. During drying, all of the evaluated paints released one or more chemicals that were irritating to the mucous membranes.

During painting work only ammonia and formaldehyde were found in the air in concentrations high enough to lead to irritation of the mucous membranes. None of the other chemicals individually cause irritation. However, irritation due to a combined action of the chemicals cannot be excluded.

Irritation of the mucous membranes may result in headache, through irritation of the trigeminal nerve, and may be prevented or reduced through ventilation/airing or the lowering of the concentration of chemicals irritating to the mucous membranes. As

### Table 9. Volatile substances in the applied paints. (% w/w = percentage by weight)

| Substance                                | Content (% w/w) |
|------------------------------------------|-----------------|
| **Acrylic latex paint I, semi-gloss**    |                 |
| Ammonia                                  | 0.05a           |
| Butyl acrylate                           | 0.03a,b         |
| Styrene                                  | 0.1–1a          |
| White spirit                             | 0.5a            |
| Ammonia                                  | 0.04a           |
| Ethylene glycol phenyl ether             | 1.7c            |
| Propylene glycol                         | 1.3c            |
| **Acrylic latex paint II, semi-gloss**   |                 |
| Ammonia                                  | 0.05a           |
| Butyl acrylate                           | 0.03a,b         |
| Ethylene glycol phenyl ether             | 1.7c            |
| Propylene glycol                         | 1.3c            |
| Formaldehyde                             | 0.02d           |
| Ammonia                                  | 0.01a           |
| **Acrylic latex paint III, semi-gloss**  |                 |
| Propylene glycol                         | 0.5a            |
| Styrene                                  | 0.1–1a          |
| Butyl acrylate                           | 0.03a,b         |
| White spirit                             | 0.1–1a          |
| Ammonia                                  | 0.04a           |
| Isobutanol esters of dicarboxylic acids  | 0.1–1a          |
| **Latex primer, micro disperse**         |                 |
| Butyl acrylate                           | 0.03a,b         |
| Styrene                                  | 0.03a,b         |
| Ammonia                                  | 0.03a           |
| **Latex wall paint**                     |                 |
| Butyl acrylate                           | 0.03a,b         |
| Styrene                                  | 0.03a,b         |
| White spirit                             | 0.03a           |
| Ammonia                                  | 0.03a           |
| Isobutanol esters of dicarboxylic acids  | 0.03a           |
| **Sealing waterborne paint (for ceilings)** |             |
| Butyl acrylate                           | 0.1–1a          |
| Styrene                                  | 0.1–1a          |
| Triethylamine                            | 0.04a           |
| Ethylene glycol butyl ether              | 1.5a            |
| Dibutylamine                             | 0.04a           |
| Ethylene glycol butyl ether              | 1.0a            |
| Formaldehyde                             | 0.02d           |

A According to the list of ingredients.

b Only monomers found in the air during the work with the waterborne paints are mentioned.

c Determined by the Scandinavian Paint and Printing Ink Research Institute.

d Determined as expected contribution from formaldehyde releasers and binders.
an example, the formaldehyde exposure could be lowered if the formaldehyde-releasing compounds were substituted with a nonevaporating biocide.

No respiratory protection is required by the Danish authorities for work with these types of products (13).

Allergy. Waterborne paints contain several sensitizing agents, e.g., acrylic monomers (27) and biocides (11, 30). Only a few of these agents are able to sensitize in the concentrations used, but it is not possible to point out "safe" concentrations for sensitizing compounds.

Figure 1. Measured air concentration from latex wall paint in workplace 1. The abscissa shows the time of day. The horizontal bars in the lowest section of the figure indicate the periods when paint was applied or when the room was ventilated. (A = ammonia, ALP = acrylic latex paint (semi-gloss), B = 1-butanol, BA = butyl acrylate, F = formaldehyde, LWP = latex wall paint, PG = propylene glycol, Rel Hum = relative humidity, Temp = temperature, Tex = Texanol*, Vent = ventilation, WS = white spirit)
To protect against sensitization, skin contact with paints should be avoided. (See the section on irritation to the skin.)

Health hazards after absorption

Absorption. Some of the chemicals may be absorbed through the skin, but this possibility can be prevented.
if skin contact is avoided. The absorption of chemicals as vapor through the skin can be considered negligible.

All of the vapors found at the workplaces can be expected to be absorbed when inhaled. The absorption through this route will be reduced if the rooms are aired or if or less volatile chemicals are used.

According to Danish legislation, no respiratory protection is required when these products are applied with brushes or rollers (13).

**Acute health effects.** With the exception of skin irritation, sensitization, and headache (due to irritation), waterborne paints applied with brushes and rollers do not present acute health hazards such as, eg, central nervous depression.

**Irritation and headache.** We carried out two questionnaire surveys (unpublished results). Irritation of the nose and the eyes, as well as headache, were frequently reported symptoms resulting from work with waterborne paints. Waterborne paints contain several chemicals which irritate the mucous membranes, but the cause of headache is less clear. The same has been found at workplaces where related substances have been used. Among 52 male printers in Denmark symptoms including irritation of the nose, the eyes, and the throat and headache were significantly more frequent than among 52 referents not exposed to organic solvents. If the substances have additive effects (eg, toluene, decane, and ethanol), the average hygienic load would have been 0.36, ranging from 0.0 to 1.0 (5). Among 188 workers exposed to trichloroethylene, headache was a frequently reported symptom (6).

The trigeminal nerve is responsible for sensory irritation in the eyes and nose when stimulated by chemicals such as formaldehyde, ammonia, and acrolein (39). The receptor of this sensory irritation is known to some extent. It contains a nucleophilic group, eg, a thiol group (-SH), reacting with chemicals with activated C-C double bonds, eg, the structure $\text{C} = \text{C}-\text{O}$ known from, eg, acrylic monomers. Alpha and beta unsaturated aldehydes and formaldehyde are also highly potent when reacting with this nucleophilic group (39). A group with hydrogen-donor activity in the receptor can account for the adsorption of, eg, alcohols, ketones, and esters. A disulfide bridge in the receptor seems to be the adsorption site for alkylbenzenes (39).

Headache (cluster headache) may be due to axonal reflexes in the trigeminal nerve (3). Cluster headache may be initiated by, eg, kallikrein, 5-hydroxytryptamine, prostaglandins, viral infections (3), trigeminal neuralgia (12), and the release of the substance called P from trigeminovascular neurons to the cerebral blood vessels (34). Chemical irritation of the nasal mucosa (trigeminal nerve) may initiate potent respiratory and cardiovascular reflexes resulting in, eg, slowing of the heart rate and variable changes in blood pressure (16). Drummond & Lance (15) showed that the increase in blood flow to the brain in cluster headache was probably due to vasodilatation mediated through the trigeminal nerve. According to Kohl (29), vasodilating drugs are the most frequent cause of drug-induced headache.

In a review describing headache in workplaces, benzene derivatives, organic solvents (eg, trichloroethylene, "paint vapors"), and formaldehyde were mentioned as possible causes of headache (35). Knowledge of the trigeminal nerve functions makes it possible to assume that headache due to work with waterborne paints may be caused by trigeminal stimulation. Thus headache might be caused by many of the evaporating chemicals, eg, formaldehyde, ammonia, acrylic monomers, alcohols (eg, glycols and glycol ethers), esters, and benzene derivatives, eg, as components in white spirit. Further investigation is required to explain the suggested coherence between waterborne paints and headache.

**Chronic health effects.** Knowledge on the development of chronic health effects (eg, cancer, teratogenic effects) as a result of work with waterborne paints is inadequate, but the risk is considered limited. All of the investigated paints contain at least one chemical suspected to cause chronic effects. It is difficult to point out no-effect levels for these chemicals, but lowering the dosage is always expected to lower the risk.

In conclusion, the information regarding the toxicity of the substances in waterborne construction paints indicates that the use of these paints is considered a clear improvement over the use of traditional paints with hydrophobic organic solvents, which in Denmark contain large amounts of white spirit. However, some waterborne products can probably be altered to improve the health characteristics even further. No health hazard (eg, brain damage) seems to be present for the inhalation of volatile chemicals from waterborne paints. Irritation of the mucous membranes may occur however when airing is insufficient.

Headache may be a health problem arising due to waterborne products and may be mediated through the trigeminal nerve.

Gloves, and possibly facial protection, should be used in connection with this work to prevent irritation of the skin and sensitization.

The chronic effects of chemicals in combination have not yet been sufficiently investigated. In this respect waterborne paints do not differ from traditional paints.

Generally speaking, the examined paints seem reasonably formulated with respect to health risks.
(see tables 1—7). However, the health risks could be reduced if the following modifications were made: Formaldehyde should be avoided. The evaporation of formaldehyde from paints should be lowered because of, eg, smell and irritation. Alternatives could be a formaldehyde releaser (for in-can preservation) or nonvolatile biocides. The content of monomers, isothiazolinones, turpentine, cobalt, and zirconium salts should be avoided or minimized to prevent the possibility of sensitization. Ethers of ethylene glycol should not be used in order to avoid effects on reproduction and on blood characteristics. Alternatives could be, eg, ethers of propylene glycol. Corrosion inhibitors with sodium nitrite should be avoided, especially when the possibility exists of a formation of nitrosamines. Surfactants should be chosen critically, and the content of ammonia should be minimized to prevent irritation of the skin and the mucous membranes. The content of white spirit and other volatile solvents should be minimized to reduce the concentrations of solvents in the workplace air.

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Appendix

Detailed description of the representative workplaces

**Workplace 1**

Workplace 1 was being repaired. The walls and the woodwork were painted years before, but no one knew the product types that had been used.

The room was a corridor with 13 doors. The ground area was 34.6 m², the volume of the room was 54 m³, and the painted area was approximately 70 m² (walls). Three adjacent rooms had already been painted with a heavy-bodied latex wall paint during the last few days. The doors to these rooms were closed during the measurements. Eleven doors were usually closed, and two doors were always open. The corresponding rooms behind these doors had volumes of approximately 11 and 20 m³, and these volumes are not included below. The measurements were made on 6 and 7 December 1984. Fifteen liters of latex wall paint were applied with a brush and roller between 0745 and 1200 the first day. This volume corresponds to 0.27 l of paint/m² of air and 0.21 l of paint/m² of wall. Some acrylic latex paint I (semi-gloss) was used on the woodwork. No painting work was done the next day. Before the painting, the temperature was normal (20°C). The relative humidity was 44 %, and ventilation was poor.

Stationary sampling was made in the middle of the room at a height of 1 m.

The chronological data for the measurements are as follows:

6 December 1984

| Time    | Activity                                      |
|---------|----------------------------------------------|
| 0715—0735 | Stationary sampling.                        |
| 0745—0921 | Latex wall paint (8 l) applied to the walls with a brush and roller. Personal sampling 0745—0805 and 0847—0907. At 0845 a draft channel (10 x 10 cm) in an adjoining room (with door open) was opened. |
| 0955—1010 | Good ventilation to remove the humidity (draft). |
| 0958—1200 | Second application of latex wall paint (7 l). Personal sampling 1120—1140. |
| 1150—1244 | Good ventilation to remove humidity (draft). |
| 1230—1400 | Acrylic latex paint I, semi-gloss (1 l) applied to the woodwork with a brush (repair work). Stationary sampling 1306—1326. |
| 1500—1520 | Stationary sampling.                        |

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The room was a sitting room in an apartment with a total of five rooms. The sitting room had a ground area of 15.7 m² and a volume of 39.7 m³, which corresponds to 41 % of the apartment. The sitting room was connected to the hall. The hall was connected to the bedroom, the kitchen, and the bathroom with doors. The measurements were carried out in the sitting room on 25, 26 and 27 September 1984. The first day, 4 l of sealing waterborne paint (for ceilings) was applied to the ceiling (0.10 l/m² room, 0.25 l/m² ceiling). Then the walls were coated with 1.8 l of latex primer (micro disperse) (0.05 l/m² room, 0.11 l/m² wall). The second day the walls were painted with 3.5 l of latex wall paint (0.46 l/m² room, 0.10 l/m² wall). The third day woodwork and a radiator were painted with 0.85 l of acrylic latex paint II (semi-gloss) (0.02 l/m² room). The room was ventilated through a draft channel (10 x 30 cm).

Stationary sampling was made in a corner 30 cm from the walls and at a height of 1 m. The corner was chosen as it was as far as possible from the window.

The chronological data for the measurements are as follows:

25 September 1984

0710—0730 Stationary sampling.
0740—0834 Sealing waterborne paint (for ceilings) applied by brush in all five rooms.
0834—0852 Same paint (2 l) applied by roller. Personal sampling 0834—approximately 0849, when the pump stopped.
0852—0924 Same paint applied by roller in other four rooms.
0924—1015 Good ventilation (exterior door open) to remove humidity.
1025—1050 Same paint applied by brush in all five rooms.
1055—1258 Back walls of cupboards in kitchen painted with latex wall paint (low consumption).
1258—1314 Sealing waterborne paint (for ceilings) (2 l) applied by roller. Personal sampling 1258—1314. Stationary sampling 1314—1318.
1314—1335 Same paint applied by roller in the other four rooms.
1355—1413 Latex primer, micro disperse (1.8 l) applied to walls with a very big brush. Personal sampling 1355—1413. Stationary sampling 1413—1415.
1413—1430 Same paint applied in kitchen and bedroom. Exterior door open from 1415 to 1425 to remove humidity.
1458—1518 Stationary sampling.

26 September 1984

0700—1015 Grinding and washing of woodwork in all rooms. Stationary sampling 0817—0837.
1015—1045 Latex wall paint applied to walls by brush. Personal sampling 1015—1045.
1045—1102 Same paint (3.5 l) applied by roller. Personal sampling 1045—1102. Stationary sampling 1102—1103.
1230—1320 Latex wall paint applied in bedroom. Stationary sampling 1240—1300.
1320—1355 Latex wall paint applied to cupboards and kitchen walls a second time.
1355—1416 Acrylic latex paint, flat, applied in the hall. Good ventilation started at 1412 (windows open).

27 September 1984

0730 Ventilation stopped.
0730—0950 Acrylic latex paint III, semi-gloss (0.1 l) used on woodwork in the sitting room, bedroom and bathroom. Stationary sampling 0742—0802.
0950—1100 Acrylic latex paint II, semi-gloss (0.75 l) applied to woodwork by brush. Personal sampling 1012—1032.
1417—1437 Stationary sampling.
1500—1600 Same paint (0.1 l) applied to radiator by brush.
Figure 2 in the Air Sampling and Analysis section shows the measured concentrations of contaminants in the air.

The room was poorly ventilated through a draft channel. The temperature was between 19 and 23°C, and the humidity was normal (52 % RH) before the application of the paints started. Before the application only formaldehyde was found in the air (0.07 mg/m³).

The concentration of ammonia fluctuated with the work. The highest concentration (5 mg/m³) was measured during the application of latex wall paint. The concentration of 1-butanol fluctuated with the work. Normally 2 mg/m³ was present during the work, and before and after application it was less than this concentration. Butyl acrylate was a common monomer in all four of the applied paints, but it was only found during and after the application of latex primer (micro disperse) and acrylic latex paint II (semi-gloss). In both cases, approximately 1 mg/m³ was found. Butyl ether may have been a reaction by-product from the manufacture of 2-butoxyethanol. The highest measured concentration was 2.4 mg/m³. Decane was a component of white spirit. The small concentrations (up to 1 mg/m³) measured the first day may have come from latex wall paint used in the kitchen. Diethylene glycol butyl ether was only a component of the sealing waterborne paint (for ceilings). The concentration increased to 5 mg/m³ during the application. The next day, the concentration was still 5 mg/m³, and the third day a decrease to a little over 2 mg/m³ was found. Dipropylene glycol methyl ether was a component of the sealing waterborne paint. The concentration increased during the application to a maximum of 36 mg/m³. The concentration decreased steadily to approximately 16 mg/m³ the next day, and to approximately 4 mg/m³ the third day. Ethylene glycol butyl ether was a component of the sealing waterborne paint. The concentration increased during application to a maximum of 48 mg/m³. The concentration decreased steadily to approximately 10 mg/m³ the next day, and to 2 mg/m³ the third day. Ethylene glycol phenyl ether was a component of the acrylic latex paint II (semi-gloss). This compound evaporated very slowly, and it was found at very low concentrations (0.3 mg/m³) hours after the application of the paint. Formaldehyde may have been released either from the binder or from the formaldehyde-releasing compound (1-(3-chlorallyl)-tetraazaadamantan hydrochloride) in the sealing waterborne paint or from the latex wall paint.

Propylene glycol was a component of the acrylic latex paint II (semi-gloss). The concentration increased during the application to 10.5 mg/m³. The little amount measured in the morning may have come from the acrylic latex paint III (semi-gloss) used in small amounts. Texanol® was found in the latex wall paint. The little amount found the first day may have come from this paint, applied to the cupboards in the kitchen. The application of latex wall paint in the sitting room resulted in an increasing concentration (up to 2.2 mg/m³). The next day the concentration was still around 2 mg/m³. Triethylamine was found in the sealing waterborne paint. The concentration increased during the application to a maximum of 6.1 mg/m³. Then it decreased to 3 mg/m³ the next day and to 0.8 mg/m³ the third day. This concentration is a minimum concentration. Undecane was a component of white spirit. White spirit may have come from the latex wall paint. The concentration increased during the application to more than 50 mg/m³. The next day, the concentration had decreased to 14 mg/m³.