Paints, Lacquers, and Varnishes in Occupational Dermatology

63

Rebecca M. Law and Howard I. Maibach

Contents

Abstract

Although the risks of allergies or irritation are highest for those who are most consistently in contact with paints over a prolonged period, such as painters, people with more acute exposures such as residence dwellers in a newly painted home may also be at higher risk. Even public places where painting is being done could potentially be a health hazard both for the workers and the general public. Water-based paints require important additives (e.g., preservatives) which are often the cause of an irritant or allergic reaction. Minute amounts of an additive may induce a potent allergic reaction. Volatile paint ingredients, including preservatives of the isothiazolinone class and synthetic resins such as epoxy resins and

R. M. Law (✉)
School of Pharmacy and Faculty of Medicine, Memorial University of Newfoundland, St. John's, NL, Canada

Department of Dermatology, University of California San Francisco, San Francisco, CA, USA
e-mail: rlaw@mun.ca

H. I. Maibach
Department of Dermatology, University of California, San Francisco, CA, USA
e-mail: Howard.Maibach@ucsf.edu

S. M. John et al. (eds.), *Kanerva's Occupational Dermatology*, https://doi.org/10.1007/978-3-319-68617-2_61

isocyanates, may cause respiratory and other nondirect contact symptoms of allergic dermatitis. As allergens, the most problematic recent isothiazolinone is methylisothiazolinone (MI); others include methylchloroisothiazolinone (MCI), octylisothiazolinone (OIT), benzisothiazolinone (BIT), and butylbenzisothiazolinone (BBIT). The most problematic recent epoxy resin is diglycidyl ether of bisphenol A resin (DGEBA-R); diglycidyl ether of bisphenol F (DGEBA-F) is also a significant allergen. Both aromatic and aliphatic isocyanates may be volatile, causing asthma, airway irritation, and hypersensitivity pneumonitis; although polyisocyanates based on hexamethylene-1,6-diisocyanate (HDI) are less volatile. Allergic reactions may take repeated exposures over months to years before symptom manifestation. Allergens are also found in other products (e.g., MI is commonly used as a preservative in cosmetics). Cross-sensitization between products within the same class can occur, but co-existing reactions may be due to co-exposure and not cross-sensitization.

Keywords

Paint · Varnish · Lacquer · Isothiazolinones · Methylisothiazolinone · MI · Methylchloroisothiazolinone · MCI · Diglycidyl ether of bisphenol A resin · DGEBA-R · Isocyanates · Hardeners · Curing agents · Biocides · Preservatives · Airborne sensitization · Cross-sensitization

1 Core Messages

- Paint components and formulations change over time.
- Water-based paints have greater complexity and require preservation as well as other paint additives which may be sensitizing.
- Additives are often the cause of an irritant or allergic reaction.
- Minute amounts of an additive may induce a potent allergic reaction.
- The airborne nature of some volatile paint ingredients may cause respiratory and other nondirect contact symptoms of allergic dermatitis.
- Volatile allergens include preservatives of the isothiazolinone class. The most significant recent culprit is methylisothiazolinone (MI). Others include methylchloroisothiazolinone (MCI), octylisothiazolinone (OIT), benzisothiazolinone (BIT), and butylbenzisothiazolinone (BBIT).
- Epoxy resins are also volatile. The most significant recent culprit is diglycidyl ether of bisphenol A resin (DGEBA-R). Diglycidyl ether of bisphenol F (DGEBA-F) is also a significant allergen.
- Both aromatic and aliphatic isocyanates may be volatile, causing asthma, airway irritation, and hypersensitivity pneumonitis. Aliphatic polyisocyanates based on hexamethylene-1,6-diisocyanate (HDI) are less volatile and commonly used in lacquers, coatings, and spray paints.
- Some of the allergic reactions may take repeated exposures over months or even years before manifestation of symptoms.
- Allergic or irritant reactions are not always occupation-related.
- Allergic or irritant reactions are not always from a paint, varnish, or lacquer. Many potential allergens are also found in other products such as cosmetics.
- Cross-sensitization between products within the same class (for example the isothiazolinones) can occur. However, co-existing reactions may also be due to co-exposure and not cross-sensitization.

2 Introduction

Paints and painted surfaces are ubiquitous. They are constantly encountered by persons in all walks of life from the wealthiest to the homeless. Not only are there painted walls and ceilings, we have painted/varnished furniture, floors, decks, and fences. We ride in painted cars, trucks, trains, and airplanes. We use painted appliances and other items such as lacquered bento boxes and

lacquered toilet seats as used in Japan. We live or work with paints and potentially live with freshly painted environments around us. Although the risks of allergies or irritation are highest for those who are most consistently in contact with paints over a prolonged period, such as painters, people with more acute exposures such as residence dwellers in a newly painted home may also be at higher risk. Even public places where painting is being done could potentially be a health hazard both for the workers and the general public.

Paint constituents differ and may change over time. Liquid wall and ceiling paints have evolved from mostly oil and solvent-based to primarily water-based paints which have greater complexity and many more component types in their formulations. Paints may also be in powder form when applied to surfaces. Paint application may be via brush, roller, spray, or other methods.

It should be clarified that paints as discussed in this chapter (as in the Painters chapter) do not include paints used by artists who produce paintings and other works of art. Artistic paints may have entirely different formulations. Issues relating to paints and varnishes as used by artists are not specifically discussed here.

Lacquer refers to a liquid coating typically applied to wood or other materials that dries to a hard and potentially shiny finish. There are natural lacquers and others including synthetic lacquers. Natural lacquer is a polymer collected as a sap from lacquer trees such as *Rhus vernicifera* in China, Japan, and Korea, *Rhus succedanea* in Vietnam and Taiwan, and *Melanorrhoea usitata* in Muanmar and Thailand. Thus, the constituents of a natural lacquer differ, dependent not only on the tree species but also the age, location, and season (time of year) of sap collection (Ma et al. 2012). Today, there are also more complex lacquer formulations include fast drying, hybrid, nano, and synthetic lacquers (Ma et al. 2012). The lacquer may be clear or colored and dries by evaporation or a curing process that produces a hard, durable finish, with the sheen from ultra matte to high gloss.

Allergens and irritants in paints, varnishes, and lacquers are many and may be ingredients from any of a number of components. Thus in order to discuss allergens and irritants in paints, varnishes and lacquers (which from here on in will just be called "paints" unless it is a discussion about a specific varnish or lacquer), we must first briefly talk about paint components.

3 Composition

Besides pigments, paint components include binders, solvents, and a variety of different additives. The constituents of varnishes are very similar to those of paints (e.g., binders, solvents, and additives), but varnishes lack pigments (Conde-Salazar et al. 2007). Binders are the primary ingredients in paints which keep pigments bound and dispersed on the painted surface. Binders provide hardness, flexibility, and influences drying speed. Solvents are used to modify paint viscosity. Solvent-based paints contain about 50% organic solvents which is volatile (Estlander and Jolanki 2014). Additives are usually present in small amounts but provide a significant effect or function for the paint. Additives include catalysts, thickeners, hardeners/curing agents, stabilizers (e.g., UV stabilizers), biocides to inhibit bacterial growth (e.g., preservatives), and others. Even in minute quantities, additives are often the source of the allergic or irritant dermatologic reaction. In particular, preservatives such as the isothiazolinones are major culprits. Since preservation is needed in water-based paints and most paints used today are water-based, this is a significant problem.

Natural lacquer constituents include lipid components (60–70%), water (20–30%), plant gum (4–10%), lacase enzyme (1.5–2%), and glycoprotein (3–5%). The major lipid components from the different trees are urushiol (*Rhus vernicifera*), laccol (*Rhus succedanea*), and thitsiol (*Melanorrhoea usitata*). All of these have a catechol ring structure with lipid side chains. For example, urushiol is a dihydric phenol with a side chain of 15 carbon atoms; however, the side chains can differ somewhat. It is the catechol ring in natural lacquers which can react and bind with proteins, causing the haptens (urushiol, laccol, thitsiol) to become antigenic

and induce an allergic dermatologic reaction (Ma et al. 2012). Synthetic lacquers may contain polyisocyanates, epoxy resins, or polyfunctional acrylates; these can also induce allergic dermatologic reactions.

For an overview of paint, varnish, and lacquer components and additional details about binders, solvents, pigments, and additives, information excerpted from the previous edition of this chapter "Paints, Lacquers, and Varnishes" can be found in Appendix A (Estlander and Jolanki 2014).

4 Significant Issues

What allergic issues do paint, varnish, and lacquer substances cause and of what significance is this as an occupational hazard? A PubMed search of paints using the Mesh headings irritant dermatitis, irritation, photo irritant dermatitis, photo irritation, allergic contact dermatitis, photoallergic contact dermatitis, photosensitivity, and contact urticaria yielded 256 citations from 1957 to 2017, with 60 from 2012 to 2017 of which 24 citations were found to be relevant upon review. A specific search of lacquer using the same Mesh headings yielded five other relevant citations, with one from 2012 to 2017. Additional related articles were also retrieved including earlier literature. Some of the more relevant findings are highlighted here including those from older literature; some other findings are briefly discussed. Tables 1 and 2 provide a detailed listing of contact allergens and irritants.

4.1 Biocides

Biocides inhibit bacterial growth and include isothiazolinones, formaldehyde, and formaldehyde releasers, methyldibromo glutaronitrile, and chloracetamides (less in use today). Among these types, the most significant allergens/irritants are the isothiazolinones. As mentioned, these are preservatives in water-based paints; however, they are also used in other areas such as the cosmetic industry for the same reason.

4.1.1 Isothiazolinones

Isothiazolinones include methylisothiazolinone (MI), methylchloroisothiazolinone (MCI), octylisothiazolinone (OIT), benzisothiazolinone (BIT), and butylbenzisothiazolinone (BBIT). MI was introduced as a stand-alone preservative in 2000 and was initially thought to be safer than MCI, which had been a known contact allergen for years. In 2004, MI was assessed by the Scientific Committee on Consumer Safety (SCCS) as a stand-alone preservative for cosmetics and was considered safe at 100 ppm (0.01%) including the sensitization risk. By 2014, MI was the second most frequently registered isothiazolinone in the Danish Product Register Database (PROBAS), with 884 different products registered, 471 of which were paints and varnishes. MCI/MI was the third most frequently registered with 611 products of which 363 were paints and varnishes. MCI was fourth with 474 products including 275 paints and varnishes. OIT was the fifth most common (111 products with 60 paints and varnishes). The most commonly registered isothiazolinone was BIT (985 products with 544 being paints and varnishes) (Frils et al. 2014).

PROBAS is a Danish database where products with potentially hazardous chemical entities are registered. Products are registered if (a) product/substance is manufactured or imported for occupational use in quantities >100 kg/year; (b) if the product contains at least one registered harmful chemical according to the Danish Ministry of the Environment and the Danish Working Environment Authority (WEA); (c) if the product or material contains >/= 1% of that chemical (but for preservatives the limit is 0.1%); (d) if the product/substance has an occupational exposure limit (set by the WEA); and (e) if materials contain >/= 1% of a substance that has been assigned an occupational exposure limit in the WEA list of limit values for substances and materials. PROBAS is updated at the end of every odd year with data collected from manufacturers in even years (Frils et al. 2014).

The frequency of use as per the PROBAS register is mirrored by the frequency of contact allergy. A retrospective study of consecutively patch tested contact dermatitis patients at

Table 1 Contact allergens. (Adapted/modified from Table 178.1, Estlander and Jolanki 2014)

Synthetic resins	Epoxy chemicals: diglycidyl ether of bisphenol A resin (DGEBA-R): Diglycidyl ether of bisphenol F (DGEBF)
	Formaldehyde resins
	Acrylic paint
	Polyurethane resins: di- and tri-isocyanates
	Polyfunctional acrylates and aziridine hardeners
	Cyclohexanone resins
	p-tert-butylcatechol
	Unsaturated polyester resins
Turpentine and other natural products	Turpentine
	Linseed oil, shellac, dammar, tung oil
	Colophony
	Citrus solvent (limonene)
Preservatives/ Biocides	Biocides
	Isothiazolinones: MCI, MI, BIT, OIT, BBIT
	Formaldehyde and formaldehyde releasers
	Methyldibromo glutaronitrile
Other additives	Chloracetamides
	Iodopropynyl carbamate
	Tetrachloroisophthalonitrile (chlorothalonil)
	N-(Trichloromethylthio)phthalimide
	Chlorocresol
	Butylated hydroxytoluene
Other types of additives	Epoxy hardeners/curing agents: (non-standard) 1,3-benzenedimethanamine (1,3-BDMA) aka m-xylylenediamine (MXDA), *N*-(2phenylethyl) derivatives
	Accelerators and polymerization inhibitors
	Photoinitiators
	Surfactants (dioctyl sodium sulfosuccinate)
Metals and metal salts	Zinc chromate
	Cobalt
	Nickel
	Mercury derivatives
	Organic pigments (azo derivatives)
Paint and varnish removers	Dibutylthiourea
Miscellaneous	Rubber gloves (natural rubber latex)
	Other preservatives (e.g., in barrier creams, hand lotions/creams/ ointments/cleansers)

Table 2 Contact irritants. (Adapted/modified from Table 178.2, Estlander and Jolanki 2014)

Biocides	Tributyltin oxide (TBTO)
	Isothiazolinones: MCI, MI, BIT, OIT, BBIT
	Tetrachloroisophthalonitrile (chlorothalonil)
Organic solvents	Mineral or white spirits
	Xylene and toluene
	Alcohols
	Esters
	Ketones
	Mixtures of solvents (thinners)
	Citrus solvent (limonene)
Other solvents and irritants	Glycols and glycol esters
	Monomers from binders, surface-active agents
	Dusts (e.g., dry powder sprays, dust from sanding paints) and abrasives
	Fiberglass fabrics
	Fillers, putties, plasters
	Cleaning agents: soaps, detergents, caustic soda (sodium hydroxide)
	Amines, ammonia
	Potash
	Paint and varnish removers, paint strippers

Copenhagen University Hospital Gentofte (from Jan 2009–Dec 2013) showed that MI was the second most frequently registered preservative ($n = 830$ with $n = 446$ in paints and varnishes), MCI/MI was the third ($n = 630$ with $n = 354$ in paints and varnishes), and MCI was the fourth ($n = 407$ with $n = 252$ in paints and varnishes). Formaldehyde was the preservative most frequently registered ($n = 894$ with $n = 401$ in paints and varnishes) (Schwensen et al. 2017a). Based on frequency of use, the relative risk of sensitization has been described as MCI > MI > BIT > OIT (Mose et al. 2013). This ranking is consistent with that reported in earlier literature (Aalto-Korte et al. 2007; Geier and Schmuch 1996). The relative risk may change as frequency of use and/or allowed concentrations change.

For allergy testing, MCI is part of the 50 allergens in the baseline panel for patch testing identified by the North American Contact Dermatitis Group (Lachapelle and Maibach 2012). The

European baseline series (used, for example, by the Danish Contact Dermatitis Group) has long included MCI/MI (Mose et al. 2012); and since 2013, MI has also been a recommended part of the European baseline series (Bruze et al. 2013). It has been advocated that the addition of MI to the baseline series is warranted due to the large number of patients testing positive to MI but not MCI/MI (Uter et al. 2013). Currently, many baseline series in North America also include MI.

MI has emerged as one of the most significant contact allergens in water-based paints today. In the current PubMed search, 13 of the 24 relevant citations from 2012 to 2017 discussed MI. Ten citations were specifically about MI with five being new case reports. There were two other more general articles and an additional case report about the isothiazolinones which included MI (Aeerts et al. 2017; Amsler et al. 2017; Bregnbak and Johansen 2013). The case reports were all related to the airborne nature of MI (and MCI/MI) and are summarized below:

1. A 23-year-old non-atopic previously healthy woman developed facial dermatitis with periorbital edema progressing to vesicular dermatitis. She had a burning sensation on her cheeks, malaise, and dizziness after working for 2 months in a new restaurant where the walls were newly painted. Patch testing identified MCI/MI and MI as potential causes and when re-exposed to MI in a new facial cleansing product she experienced marked aggravation of facial dermatitis (Kaae et al. 2012).
2. A 26-year-old man with no history of asthma or atopic dermatitis developed a persistent dry cough and rhinitis (despite use of antihistamines and a steroid/beta2-agonist inhaler) followed within days by an eczematous eruption on the face, eyelids, chest, nape of neck, and folds of elbows with respiratory signs (PFTs showed a 19% reduction in FEV1 upon methacholine challenge) after working for 2 years for a construction company specializing in renovation work where water-based paints and pulverized indoor façade renders were commonly used. Patch testing identified MI and MCI/MI. MI and MCI were both found in the paints and the indoor façade renders, which he had not directly touched as he was the site foreman (Herry et al. 2016).
3. A 24-year-old woman with no history of atopy had two episodes of acute facial dermatitis separated by a 2 month timespan, with each episode relating to similar water-based paints being used (at home and work). An intensely pruritic facial rash with periorbital edema followed by progression to neck and upper chest developed 3 days after the initial episode and 2 days after the second. Each time the rash took several weeks to resolve. Patch testing identified MI, MCI/MI and less strongly OIT. The paint contained MI, MCI and BIT (Wright and Cahill 2016).
4. A 33-year-old woman had three episodes of facial dermatitis with generalized spread over a 10 year span, with the last episode temporally coinciding with a residential move. Thus the patient had a strong suspicion of the interior wall paint she just used with no protective clothing during painting, even though the referring dermatologist suspected photoallergy due to the distribution and her history of tanning bed use. Patch testing at day 5 showed a strong reaction to MI (+++) and a mild reaction to MCI (+) with BIT negative. Paint samples applied to her arm had positive results at 48 h in three of four samples, while nine volunteers (controls) had negative results at 96 h which ruled out irritancy. The four paint samples were then analyzed by HPLC for the presence of MI, MCI, BIT, and BBIT. MI and BIT were found in all four samples but in varying concentrations ranging from 50–100 ppm (MI) and 290–340 ppm (BIT). Neither BBIT nor MCI were detectable. The patient was able to stay in her current home and at 3 months' follow-up her skin was clear (Goodier et al. 2017).
5. A 53-year-old woman with no atopic or allergy story presented with severe respiratory symptoms, facial erythema and periorbital edema 2 days after her apartment was painted. Patch testing identified MI (+) and the paints were preserved with MI (confirmed by paint manufacturer but not noted on the paint container) (Lundov et al. 2013).

6. An otherwise healthy 3-year-old boy presented with a recurrent itchy and erythematous rash (this time in the popliteal fossa and on the dorsal surfaces of his hands) which had been treated as atopic dermatitis by a local dermatologist for about 2 years before being referred for further investigation. During the medical history review, it was noted that at about 3 months of age, his family moved to a freshly painted house and it was about a month later that his first itching rash occurred. A recurrence occurred during a family visit to his aunt's house, which had also been newly painted. Patch testing was done with the European baseline series supplemented by the standard child series; patch and photo patch tests were done with the sunscreen series and with the child's personal products used. Patch tests were positive for MCI/MI (++) and MI (++). MI and MCI/MI were found in the child's shampoo, soap, and sunscreen. The conclusion was that the child has atopic dermatitis which was either triggered or worsened by his severe allergy to MI and MCI/MI. The authors considered this case noteworthy both because of the age of the child when sensitized (3 months) and the level of exposure (Bregnbak and Johansen 2013).

Airborne sensitization and presentation of allergic contact dermatitis due to the continuous evaporation of isothiazolinones (MI, MCI/MI) over days to weeks/months constitute an important health risk. This risk has been confirmed by emission testing of 19 different water-based paints, with MI being found in all 19 paints (concentration range 10–300 ppm), BIT in 16 (concentration range 1.5–360 ppm), and MCI in 4 (concentration range 2–14 ppm) (Lundov et al. 2014). Given the volatile nature of MI, it has been estimated that 75% of MI paint-related allergic reactions are secondary to airborne exposure (Lundov et al. 2012).

An increase in MI sensitization has been occurring worldwide. A study assessing risk factors for MI contact sensitization over a 4-year period (2009–2012) identified freshly painted rooms and paints/lacquers as risk factors for the increase although the greatest risk factor was cosmetics especially leave-on cosmetics with an almost fourfold significant increase ($p < 0.001$, total $n = 14{,}104$). Freshly painted rooms was also a significant risk factor although the numbers were small ($p = 0.043$, total $n = 100$), with paints/lacquers showing a trend ($p = 0.166$, total $n = 403$). Painters headed the list of occupations with a 14% crude (unadjusted) prevalence rate of MI sensitization (14.14%, 95% CI of 9.61–19.79) (Uter et al. 2013).

Regulation is needed for paint manufacturers to identify the presence of MI (or other isothiazolinones) on paint container labels. In March 2016, a recommendation was made by the Committee for Risk Assessment (under the European Chemicals Agency) that MI be classified as a potent skin sensitizer (group 1A) with a concentration limit of <0.0015%, i.e., any products containing MI > = 0.0015% (15 ppm) shall have a warning about the risk of sensitization, either on the product label or on the safety data sheet. EU regulation is still in progress: EU Member States are in the process of formally adopting the recommendation, and the regulation is expected to be in force by Summer 2018 (Editorial 2016). Currently, efforts are being made by some paint manufacturers to produce paints with zero to low amounts of isothiazolinones, and some manufacturers have already begun to voluntarily label their paint products as containing such.

Octylisothiazolinone (OIT) or more specifically 2-*N*-octyl-4-isothiazolin-3-one was a fungicide initially developed specially for latex and oil paints but has been more widely used in adhesives, wood preservatives, metalworking fluids, stains, cleaning agents, and others including textiles such as mattress textiles (Aalto-Korte et al. 2007). Occupational allergic contact dermatitis has been reported in painters and in workers in paint factories. A 56-year-old man developed acute eczema on the face, hands, and arms from using latex paint containing OIT (Oleaga et al. 1992). A 29-year-old female technician in a factory mixing paint ingredients for roof sheets developed eczema on the right wrist that spread to the face and extremities with generalized lymphadenitis in 10 days; patch testing using OIT 1% in olive oil was positive to OIT. A 48-

year-old male worker took over the previous 29-year-old technician's work while she was on sick leave, and after 3 days of mixing the paints, a severe contact dermatitis developed with rapid spread from hands to arms, thighs, and face; again patch testing using OIT in olive oil was positive (Thormann 1982). A 31-year-old man developed recurrent episodes of hand dermatitis beginning 6 weeks after working in a paint factory even though he was wearing gloves – as the occasional splash on exposed skin resulted in dermatitis. His work required him to add a mildewcide (Skane M-8) into the paint mixer. Patch testing using diluted concentrations of Skane M-8 were positive. Skane M-8 contains OIT (Mathias et al. 1983). A review of 202 painters working in eight paint companies identified 3.6% of painters who developed erythema while hand painting with water-based paints and additional investigations identified OIT was one of the culprits (Fischer et al. 1995).

Photo-aggravation

A 2017 retrospective study of airborne allergic contact dermatitis caused by water-based paints containing MCI/MI or MI was conducted by the Dermatology and Allergy Group of the French Society of Dermatology, and 44 cases were identified between 2012 and 2016. In three of the 44 patients who reacted positively to MCI/MI, photo-aggravation of dermatitis occurred after exposure to sunlight. Only one of the three patients was tested with MI alone, with a positive result (Amsler et al. 2017).

Co-Exposure and Cross-Sensitization

Cross-sensitization between isothiazolinones can occur but a distinction would need to be made between cross-sensitization and co-exposure with simultaneous reactions. A 2013 study found that all patients with concomitant positive patch test results to MCI/MI, OIT, and BIT were painters, suggesting co-exposure with concomitant sensitization and not cross-sensitization (Mose et al. 2013). A 2015 study also found that simultaneous reactions between MI and BIT as well as between MI and OIT resulted from co-exposure and not from cross-sensitization (Geier et al. 2015). However, a more recent study assessing concomitant allergic reactions concluded that, in almost half of their cases, OIT reactions were better explained by cross-sensitization to MI and/or MCI than by specific exposure to OIT (Aalto-Korte and Suuronen 2017). This differs from the author's own earlier observations of separate sensitizations to these chemicals (Aalto-Korte et al. 2007) and a 1996 study which concluded that no cross-sensitization existed between MCI/MI, BIT, and OIT (Geier and Schmuch 1996). Additionally, a recent study in mice has shown cross-sensitization between MI, BIT, and OIT (Schwensen et al. 2017b).

4.1.2 Formaldehyde and Formaldehyde Releasers

Formaldehyde and formaldehyde-releasing preservatives were once widely used in water-containing products such as metal-working fluids and occupational sensitization was common in machinists who handled them, as well as other occupations including cosmetologists and painters. Contact allergy to formaldehyde releasers without formaldehyde allergy is rare (Aalto-Korte et al. 2008). As of March 2009, paints, lacquers, and varnishes were the most frequently registered products containing formaldehyde in PROBAS (Estlander and Jolanki 2014). Examples of formaldehyde and some formaldehyde-releasing biocides and other products in paints, lacquers, and varnishes include: Formaldehyde, 2-Bromo-2-nitropropane-1-3-diol, Dimethylol urea, Melamine/formaldehyde resin, Methanamine, *N*-methylolchloracetamide, Polyoxymethylene urea, Tetramethylol acetylenediurea, Tris(hydroxymethyl)-nitromethane, and Tris(*N*-hydroxyethyl) hexahydrotriazine.

4.1.3 Other Biocides

3-iodo-2-propynyl-butylcarbamate (IPBC) is a fungicide added to paints and wood treatments to prevent fungal decay of wood (and used in other industries such as cosmetics). It can cause airborne allergic contact dermatitis. A case report described a 34-year-old woman with a history of atopic dermatitis who had been working in a paint factory for 6 years before developing

dermatitis on the hands, neck, scalp, and face upon transfer to the section of the factory where the ingredients of wood-preservation products were mixed. Patch test results to 0.1%, 0.03%, and 0.01% IPBC were all positive (Jensen et al. 2003).

Methyldibromo Glutaronitrile (MDGN) is a potent contact allergen which was once widely used then became mostly found in cosmetics and hand soaps (Zacharia et al. 2003). But MDGN has since been banned from both leave-on and rinse-off cosmetic products in the European Union, since 2005 and 2008, respectively; however, it may still be used in occupational products.

4.2 Synthetic Resins

Synthetic resins include the following: Epoxy chemicals: diglycidyl ether of bisphenol A resin (acronyms are DGEBA-R or less commonly BADGE – bisphenol A diglycidyl ether), formaldehyde resins, acrylic paint, polyurethane resins: di- and tri-isocyanates, polyfunctional acrylates, and aziridine hardeners, cyclohexanone resins, *p*-tert-butyl catechol, and unsaturated polyester resins. A recent PubMed search provided many relevant new citations between 2012 and 2017 plus case reports, confirming that this is a current issue. Earlier relevant citations were also retrieved and discussed here.

4.2.1 Epoxy Resins

Epoxy resins, in particular diglycidyl ether of bisphenol A resin (DGEBA-R), and secondly diglycidyl ether of bisphenol F (DGEBF), are most often the contact allergens in epoxy paints. Resins derived from diglycidyl ether of bisphenol A (DGEBA-R) is considered the most important sensitizer in epoxy systems and a significant occupational hazard for painters. In 209 cases of occupational contact allergy to epoxy chemicals, the largest occupational group was painters ($n = 41$) (Aalto-Korte et al. 2015). In a study where patch testing was performed in 20,808 consecutive patients from 2005 to 2009, a positive patch test reaction to epoxy resin monomer was seen in 1% ($n = 275$) and the frequency was higher in males (1.9%) versus females (1%). A follow-up job inquiry questionnaire was returned by 188 patients who identified painting as the third highest job category (6.9%, $n = 13$), again with a male predominance (11.4% M, $n = 10$ vs. 3% F, $n = 3$). Paint was identified as the second most frequent source of epoxy resin exposure in the workplace (30.1%, $n = 28$) (Bangsgaard et al. 2012).

Non-occupational exposure and sensitization is also not uncommon, especially since the epoxy resins are volatile. A 10-year study of 6042 general dermatology patients patch tested with DGEBA-R identified non-occupational sensitization in 35% (21/59) of patients with 65% (38/59) being occupational cases (Majasuo et al. 2012). Eyelid dermatitis is associated with allergic sensitization due to the resins' volatile nature, and cases have been reported: (1) In a housewife who had occasional contact to hobby varnishes for 3 years and prior contact to epoxy glues and varnishes in her father's carpenter workshop, where similar eczema had occurred for the first time (Ozkaya 2012); and (2) In a middle-aged woman who paints (canvases not walls) as a hobby and was subsequently found to be allergic to DGEBA-R (Lolatgis and Nixon 2015). Airborne contact dermatitis (AirbCD) assessed via a retrospective analysis of 201,344 consecutively patch tested patients from 1994 to 2013 identified 1,203 AirbCD cases of which 8% (95%CI 6.8–10.3) were positive to epoxy resin based on BADGE, i.e., DGEBA-R 1.0% (Breuer et al. 2015).

4.2.2 Isocyanates

Isocyanates are low molecular weight compounds with reactive —N=C=O groups, making them excellent cross-linking agents to produce resins such as polyurethane. They can be classified based on the number of reactive groups, i.e., monoisocyanates, diisocyanates, and polyfunctional or multifunctional isocyanates (Frick et al. 2003). Most commonly, di- or tri-isocyanates react with various multifunctional alcohols to make polyurethane resins.

Isocyanates are widely used in the manufacturing of rigid and flexible foams, fibers, and coatings such as paints, lacquers, and varnishes. Isocyanates are either aromatic or aliphatic. Aromatic isocyanates include toluene diisocyanate (TDI), diphenylmethane-4,4-diisocyanate (MDI), and isophorone diisocyanate (IPDI). Aromatics are widely used since they are cheaper; however, they may discolor when exposed to light and moisture. Thus aliphatic isocyanates are often used to produce polyurethanes for coatings (Donovan et al. 2009). For example, aliphatic polyisocyanates based on hexamethylene-1,6-diisocynate (HDI) are commonly used in lacquers, coatings and spray paints (Aalto-Korte et al. 2010). (Refer to Appendix A for further description.)

Isocyanates are known contact irritants and allergens. They can induce respiratory symptoms including asthma, airway irritation, and hypersensitivity pneumonitis. In particular, the monomeric HDI, IPDI, and TDI are highly volatile at ambient temperatures. Polyisocyanates based on HDI have higher molecular weights thus less volatile and were initially introduced to reduce respiratory symptoms (Aalto-Korte et al. 2010). Contact dermatitis is less common but can result in a rash, itching, hives, swelling of extremities, and irritation or serious burns to the eyes (Schaal et al. 2017). Below are illustrative cases, reports, and studies of allergic contact dermatitis to various isocyanates:

1. A 27-year-old woman developed a severe eczematous eruption within 4 days of beginning employment as a nameplate laminator where she was required to apply a polyurethane resin coating to nameplates placed upon a board at waist level. Her work included mixing Chem-Dec 808 isocyanate (a urethane prepolymer) with Chem-Dec polyol and using a foot pedal to deliver the mixture via a penlike device onto the nameplates. Her sole protection was a pair of gloves which only reached her wrists. She was seen by her family physician, but despite initial treatment with antihistamines and a 4-day course of prednisone, 6 days after the initial eruption, she presented to the emergency room with erythema and pruritus affecting her face, ears, arms, abdomen, and legs. Vesicles were also present on her arms. She required IV corticosteroids and was discharged on a tapering course of prednisone. She was patch tested with the North American Standard Screening Series, an isocyanate series, and CHEM-Dec 808 isocyanate 1% in petrolatum. At day 7, she had a +++ reaction to Chem-Dec 808 isocyanate 1%, and a ++ reaction to the aromatic isocyanate MDI 0.1% in petrolatum was also seen. The manufacturer would not release the complete ingredients in Chem-Dec 808; however it is known that the primary ingredient was dicyclohexylmethane-4,4′-diisocyanate (DMDI), an aliphatic isocyanate. She was considered to have had an uncommon cross-reaction to the aromatic isocyanate MDI as she had no previous MDI exposure (Donovan et al. 2009).
2. A 2017 study highlighted issues and identified preventative measures with methylene bisphenyl isocyanate (MDI), used during spray-on-truck bed-lining (STBL) processes. Acute exposure to MDI during STBL tasks have resulted in fatalities due to acute asthmatic reactions. Ventilation system and process characteristics were assessed during 18 site visits to 9 STBL companies. Results indicated that increases in ventilation characteristics (airflow, face velocity, capture velocity, etc.) had the greatest effect on reducing MDI exposures and would be useful preventative measures to put in place (Schaal et al. 2017).
3. MDI is also found in lacquers. An outbreak of allergic contact dermatitis occurred among workers after a water-repellent lacquer, based on MDI, was introduced at a laminate flooring manufacturing plant. Five out of twenty workers had a contact allergy. Of the five workers patch tested, four reacted to the lacquer or a diisocyanate including MDI. This lacquer was a one-component polyurethane lacquer composed of 80% polymeric diphenylmethane diisocyanate (MDI) according to the product safety sheet; however, the manufacturer indicated that it actually

contained about 20% each of the monomeric isomers diphenylmethane-2-4-diisocynate (2,4-MDI) and diphenylmethane-4,4′-diisocyanate (4,4′-MDI) (Frick et al. 2003; Aalto-Korte et al. 2010).

4. Aliphatic polyisocyanates based on hexamethylene-1,6-diisocyanate (HDI) are used in lacquers and paints. The aliphatic polyisocyanates hexamethylene 1,6-diisocyanate biuret, hexamethylene 1,6-diisocyanate isocyanurate, and hexamethylene 1,6-diisocyanate trimer, asymmetrical are used in hardeners of two-component polyurethane paints and are among the new contact allergens identified between 2008 and 2015 (respectively in a packer working in a paint factory; a painter and an office worker working in a paint factory; and a laboratory worker working in a paint factory) (de Groot 2015). These were the four cases of occupational contact allergy to HDI-based aliphatic polyisocyanates in hardeners of two-component polyurethane paints seen at the FIOH from 2000 to 2009. The authors of the paper believed that theirs was the first report of contact allergy to aliphatic polyisocyanates in humans (Aalto-Korte et al. 2010).
   (a) A 37-year-old female packer in a paint factory developed facial dermatitis twice while packing a hardener with a constituent (Desmodur N75 MPA/X) that contained 75% HDI-based aliphatic polyisocyanate.
   (b) A 53-year-old female office worker in a paint factory spilled some samples of three hardeners for industrial paints on her left forearm and thigh and subsequently developed allergic dermatitis on the same areas 1½ weeks later. Patch test results were positive to Desmodur N3390 BA (which contained 90% of an isocyanurate-type HDI trimer), Desmodur N3300, and Desmodur N3200.
   (c) A 38-year-old male with a history of mild atopic dermatitis worked as a painter in an aircraft repair workshop. His primary job was grinding of surfaces painted with two-component paints. He developed new skin symptoms on his thighs and feet and facial swelling. Patch test results were positive to Desmodur N3300 with additional reactions to three other hardeners, all of which contained polymeric HDI.
   (d) A 33-year-old female laboratory worker in a paint factory developed dermatitis on her face, backs of hands, and forearms after working for 2 months. When she left her job, the dermatitis healed. Patch test results were positive to Desmodur N3300 initially and on subsequent testing also positive to Desmodur N3900 and N3200.

4.2.3 Polyfunctional Acrylates

Some lacquers may contain 85–90% of polyfunctional acrylates, which can cause allergic contact dermatitis.

1. Occupational contact dermatitis from ultraviolet-cured lacquer for painting wood, containing dipropylene glycol diacrylate (DPGDA), has been reported (Estlander et al. 1998).
2. A case of disseminated allergic contact dermatitis occurring in a screen process printer, caused by ultraviolet-cured transparent lacquer containing multifunctional acrylates (methylpropane triacrylate and pentaerythritol triacrylate), has also been reported. This was a 54-year-old man with no history of atopy who developed disseminated skin changes (upper and lower extremities, face, neck and upper chest) which included erythema with vesicles and papules accompanied by severe pruritus. As per the material safety data sheet, the lacquer contained 85–90% multifunctional acrylates and 10–15% photoinitiators and surfactants. Patch tests using the acrylates and the lacquer were all highly positive (++/+++) (Kiec-Swierczynski et al. 2006).

Varnishes may contain acrylates. Four cases of sensitization to acrylates in people who work with varnishes were reported in 2007 (Conde-Salazer et al. 2007).

1. A 33-year-old woman with no prior skin disease presented with a history of erythematous

itching, exudative lesions followed by scaling affecting the flexor surfaces of her forearms, abdomen, right thigh, and both cheeks 10 days after working with new varnishes at her work place. The varnishes contained tripropylene glycol diacrylate, 203 acrylate, and glycerol propoxy triacrylate. She stopped handling the varnish and was treated with topical corticosteroids and the lesions disappeared 2 weeks later. Patch testing results were positive for several acrylates including tripropylene glycol diacrylate.

2. A second case involved a 41-year-old man with no prior skin disease who presented with eczema 15 days after starting work at a varnish plant and patch testing was positive for dipropylene glycol diacrylate.
3. A third case was a 40-year-old man with no prior skin disease who presented with eczema a few days after casual contact with new varnishes – patch test results were positive for various acrylates.
4. A fourth case was a 28-year-old man with no prior skin disease who presented with a 15-day history of erythema. He used a new varnish which contained diipropylene glycol diacrylate and tripropylene glycol diacrylate.

Paints may contain acrylates. A UV-cured paint containing acrylates induced an occupational conjunctivitis with it being the sole manifestation of the contact allergy. With no history of atopy, a 28-year-old man who worked as a screen-printer presented with a 2-month history of itching of both eyes with conjunctival erythema. Symptoms started a month after he began using a screen-printing process with a UV-cured paint, to print onto plastic bottles. He wore cotton gloves with no other protective measures but except for the eyes there were no other skin manifestations. His eyelids would swell after a working day, and a mild hyperemia of the bulbar and tarsal conjunctivae without papillary or follicular hypertrophy would be noted. Symptoms would improve on the weekends and would disappear when away from work for a week. A conjunctival scraping showed moderate lymphocytic reaction with increased eosinophils, and a bacterial culture was negative. An ophthalmologist had considered his conjunctivitis as probably allergic in nature. Patch testing with the European baseline series, the paint (0.2%, 0.1%, and 0.05% in petrolatum), and a (meth)acrylate series showed positive reactions to trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate however only TMPTA was present in the paint. It was interesting to note that he had a focal flare of his conjunctivitis concurrent with the positive patch tests to TMPTA (Mancuso and Berdondini 2008).

4.2.4 Polyester Resins

Polyester resins are condensation products of difunctional or polyfunctional monomers. Unsaturated polyester resins are made by condensing a di- or polyhydric alcohol with a di- or polybasic organic acid or anhydride. The curing reaction occurs when an unsaturated cross-linking monomer (e.g., styrene or methyl methacrylate) and an oxidizing catalyst (e.g., benzoyl peroxide) are mixed together (Tarvainen et al. 1993). Contact allergy to raw materials or components of polyester resin systems is considered quite rare but has been reported. Six cases of allergic dermatitis from car-repair painting due to unsaturated polyester resin cements were reported in 1993. All six cases had eczema on their hands with one whose eczema was limited to fingertips injured by cyanoacrylate glue (after wrenching his fingers too vigorously out of the dried glue). Four of the six also had eczema on airborne areas (wrists, face, neck), and it was concluded that they developed skin symptoms from the sanding dust of the finished product. All cases healed on sick leaves and relapsed in a day or two after returning to work (Tarvainen et al. 1993). An analysis of patients from the Finnish Institute of Occupational Health (FIOH) between December 1993 and February 2015 identified 11 cases of occupational contact allergy caused by components of polyester resins. Six of the 11 were painters (three car painters, a painter of cabins of mining machines, a painter of tractor cabins, and a spray painter of bicycles) (Aalto-Korte and Suuronen 2016).

4.2.5 Others

Epoxy hardeners/curing agents in particular the nonstandard 1,3-benzenedimethanamine (1,3-BDMA), also known as *m*-Xylylenediamine (MXDA), is a newer epoxy hardener; and *N*-(2phenylethyl) derivatives resemble MXDA and are used as curing agents to harden epoxy paints and coatings. A report in 2016, which appeared to be the first case series of contact allergy to derivatives of 1,3-BDMA, described six patients examined at the Finnish Institute of Occupational Health between 2013 and 2015. Patch tests with one of two hardener ingredient mixtures, each of which contained derivatives of 1,3-BDMA, were positive for all six patients, five of whom were painters and one was a floor layer. All presented with symptoms of eczema with varying locations but most consistently on the forearms, wrists, face, and eyelids. Two of the patients also tested positive to DGEBA-R (Pesonen et al. 2016).

4.3 Irritant Contact Dermatitis

Although the focus of this chapter has been on allergic contact dermatitis from paints/varnishes/lacquers, prolonged skin irritation resulting solely in an irritant dermatitis may also occur. A case-controlled study in dockyard painters in the United Kingdom versus in China showed that irritant symptoms from skin, eyes, or nose were higher in all painters versus controls, and that the relative risks for skin, eye, and nasal irritations were all higher in Chinese painters when compared to British painters. It appeared that there was a direct correlation between duration of exposure and irritant symptoms (Chen et al. 2001).

Important causative agents for irritant dermatitis include organic solvents, paint dusts, and remnants of biocides. Organic solvents used as paint thinners or for cleaning brushes and spray guns are common causes of irritant dermatitis. Similarly, skin irritation can occur if clothing becomes soaked by accidental splashes of solvents and the soaked clothing is allowed to remain in contact with the skin for a prolonged period. This speaks to the painter's hygiene and painting style.

Production of powder paints (nanoparticles) can cause skin irritation either topically or via inhalation, for example, during the powder handling or packaging stages (Aitken et al. 2006).

Biocides may be skin irritants. In particular, the antifouling agent tri-butyltin oxide (TBTO) is a biocide used in marine paints and others. TBTO is a strong skin irritant with corrosive properties. A 39-year old shipwright developed pruritus, erythema, and vesiculation on both wrists and forearms with a few lesions on the abdomen after using an antifouling paint for wooden blocks, where his skin was oversprayed by the paint. The skin irritation was noted within about an hour, with erythema and ulceration noted on the second day. The paint contained 10–11.7% TBTO and was labelled as irritant or corrosive. Other constituents included xylene, cuprous oxide, and copper thiocyanate. A prior exposure to a TBTO containing paint 2 months previously also resulted in a similar dermatitis on both wrists, and at least four other workers performing similar tasks also developed dermatitis on that prior occasion. The authors noted that TBTO has a strong irritant potential, which can be manifested by merely brushing a contaminated arm across the mouth or by wearing shoes contaminated with TBTO sometime earlier (Lewis and Emmett 1987).

5 Summary

There are many potential contact allergens and irritants in paints, varnishes, and lacquers. People with anticipated frequent exposures such as painters should take protective measures (e.g., gloving and masking as needed) to reduce the possibility of a dermatologic reaction.

Appendix A

Composition of Paints, Varnishes, and Lacquers

Excerpted from Estlander T, Jolanki R. **Chapter 61 Paints, Lacquers, and Varnishes** Kanerva's Occupational Dermatology 2nd ed. 2014

A.1. Binders

Binder is the main ingredient in paints, lacquers, and varnishes. It is the actual film-forming agent in paints. It keeps the pigments bound and permanently dispersed on the painted surface, and it provides the most important properties of the coating: hardness, flexibility, and speed of drying. Binders include synthetic or natural resins and oils, alkyds, epoxy resin compounds, formaldehyde resins, acrylic resins, polyurethane resins, water-dispersible polymers and other synthetic resins, polystyrene resins, and cyclohexanone resins (Rose and Vance 1997; Fischer and Adams 1999; Estlander et al. 2000).

Natural resins and oils originate from trees, plants, fish, and insects. Dammar, Japanese lacquer, and shellac are suitable for lacquers and varnishes because they dry quickly, although the film formed is brittle. Copal is a fossilized resin which is used in varnishes. Natural oils, such as flaxseed or linseed oil, perilla, tung and pine (tall) oils, soybean and ricin oils are all used in oil-based paints. Since the 1980s, synthetic alkyd resins have widely replaced natural binders (Fischer and Adams 1999; Estlander et al. 2000).

Alkyds or alkyd resins are condensation products of poly-alcohols; e.g., glycerol, pentaerythritol and sorbitol, and polycarboxylic acids or corresponding anhydrides such as phthalic anhydride, adipic acid, and maleic acid. Common alkyd binders are formed after modification with oils containing unsaturated fatty acids. These include linseed, soybean, sunflower, cottonseed, and pine oil. Linseed oil and similar drying oils can be combined with colophony (rosin) to produce a paint resistant to climatic conditions while also having good color retention.

Polyester resin binders are alkyds containing no modifying oils. Styrene and vinyl toluene are used as cross-linking agents for these alkyds. Epoxidized alkyd resins are alkyds modified with epoxidized oils which are formed by reacting double bonds in unsaturated fatty drying oils with oxygen to form an epoxide ring.

Paints based on alkyd resins need no hardeners. They are hardened by the evaporation of organic solvents or water, followed by the reaction of the binder with the oxygen in the air (Fischer and Adams 1999; Estlander et al. 2000).

Epoxy resin compounds. Paints, varnishes, and lacquers based on epoxy resins are used in various industrial applications because of their strength and durability. A hardener must be added to two-component epoxy paints that cure at ambient temperature before their application. The paint hardeners include polyamines, e.g., diethylenetriamine, triethylenetetramine, trimethylhexamethylenediamine, isophoronediamine, and 1,3-xylylene diamine and often also a catalyst, such as 2-,4-,6-tris(dimethylaminomethyl)phenol (tris-DMP).

One-component epoxy powder paints that are heat-cured contain a hardener which can only be activated by heating. Polyfunctional aromatic amines, solid polyamides, and organic anhydrides can be used as curing agents (Jolanki 1991; Estlander et al. 2000; Ponten 2006). See ▶ Chap. 52, "Epoxy Resins" for additional information.

Formaldehyde resins. Urea, melamine, phenol, or substituted phenols can be modified with formaldehyde to produce corresponding resins. An excess of free formaldehyde must be removed in order to prevent interference with the film-forming properties of paint. These resins can also be used to cross-link alkyd resins. The curing takes place by heating. Phenol formaldehyde resins (PFRs) remain stable in temperature variations and are resistant to moisture, acids, and solvents (Fischer and Adams 1999; Estlander et al. 2000). For more information, refer to ▶ Chap. 53, "Contact Allergy to Phenol-Formaldehyde Resins" in the textbook.

Acrylic resins. Multifunctional acrylates are used in the formulations of UV-curable coatings. The most commonly used multifunctional acrylates in industrial UV-curable acrylate paints and coatings are trimethylolpropane triacrylate (TMPTA), pentaerythritol triacrylate (PETA), or hexanediol diacrylate (HDDA). A photoinitiator system is also needed.

Multifunctional acrylates can be combined with polyfunctional aziridine (PFA) cross-linking agents. Commercially available PFA cross-linking agents are usually synthesized from

ethyleneimine or propyleneimine and TMPTA or PETA. A PFA cross-linker is added to the aqueous acrylic component before its use. The cross-linking reaction is self-curing, but heat or UV radiation may be used to enhance the reaction, resulting in faster drying of the products.

PFA is also used to cross-link water-based polyurethane emulsions, such as lacquers and top-coats. (Kanerva et al. 1995; Fischer and Adams 1999; Estlander et al. 2000; Bjorkner 2006). For more information, refer to ▶ Chap. 51, "Acrylic Resins" chapter.

Polyurethane resins. Polyurethane coatings are formed by the reaction of isocyanate groups with hydroxyl groups of polyalcohol components. The polymerization reaction is usually catalyzed by tertiary amines. Mainly di- or triisocyanates, e.g., toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), hexamethylene diisoxyanate (HDI), or their trimers are used in the reaction. Unmodified polyurethane resins can be formulated in one- or two-component systems. They can be modified with natural drying oils, resulting in coatings which dry in the air and are polymerizable, like alkyl resins. Polyurethane resins are durable, heat resistant, and flexible (Fischer and Adams 1999; Estlander et al. 2000; Frick 2006). For more information, refer to ▶ Chap. 54, "Polyurethane Resins" in the textbook.

Water-dispersible polymers and other synthetic binders mostly include polyvinyl acetate, polyacrylate, copolymers of vinyl acetate and acrylate, and copolymers of styrene and acrylate. These are used in water-based latex paints. The latexes may contain small amounts of ammonia (0.3% w/w), formaldehyde (0.06% w/w) or other biocides (e.g., mixture of isothiazolinones), surfactants and polymerization inhibitors (e.g., hydroquinone or benzyl peroxide), and even traces of monomers, e.g., mono(meth)acrylates (Hansen et al. 1987; Fischer and Adams 1999; Estlander et al. 2000).

Polystyrene resins are made from polymerized styrene and have good insulating power. Synthetic rubber, known as styrene-butadiene or chlorinated rubber latex, can be used in paints for floor coverings or tank linings (Fischer and Adams 1999).

Cyclohexanone resin can be added to increase the hardness and water resistance of any paint but is most often used in floor paints. Paint may contain 5% cyclohexanone resin. Various manufacturers make cyclohexanone resins (Bruze et al. 1988).

A.2. Solvents

Paint solvents include water and organic solvents. They are used to modify the paint viscosity required for the application methods of brushing, rolling dipping, and spraying. Solvents are chosen for their solvency, evaporation, and suitability for product use (Leira 1997; Estlander et al. 2000).

Solvent-based paints contain about 50% organic solvents, which is the volatile component of paints, Until the 1970s, turpentine was the most often used solvent in many countries in construction paints, but it was later replaced by aliphatic and alicyclic hydrocarbon solvents, such as white spirits. Paints used for other purposes may also contain xylene, toluene, alcohols (e.g., n-butanol and isopropanol), and ketones. The use of D-limonene, the principal component of the oil extracted from citrus fruit rinds, has expanded dramatically. It may also be used in paints and other coatings (van Faassen and Borm 1991; Wieslander et al. 1994; Rose and Vance 1997; Estlander et al. 2000).

Solvent-based paints dominated the construction paint market until the 1970s (Hansen et al. 1987). New environmental regulations and consumer demand have led to the development of low VOC and zero VOC paints and finishes. The first latex-type water-based paint was introduced in 1957 (Rose and Vance 1997; Wieslander et al. 1994).

Water-based paints contain water-dispersible polymer binders. They can also contain alkyl resin and a mixture of polyacrylate and polyurethane binders. Although water is the main solvent in these types of paints, comprising about 30–85% of the raw materials, up to 10% organic solvents may be used to improve the film-forming properties of the paint. Totally solvent-free paints and varnishes (VOC less than 0.1%) for decorate

finishes are available. Powder paints are also free from solvents (Wieslander and Norback 1997; Fischer and Adams 1999; Estlander et al. 2000; Kaukiainen 2005).

A.3. Pigments

Pigments are fine ground powders dispersed throughout the paint to give it a color. They also have other properties: they can alter paint flow and provide corrosion resistance. Pigments also have limited solubility to water and solvents, and good color fastness. They must be opaque but may be either inorganic or organic (Rose and Vance 1997).

The most commonly used inorganic pigment is white titanium dioxide, which can be used in combination with zinc oxide. Titanium dioxide is also one of the most broadly applied nanomaterialsand is used in numerous other commercial products (Aitken et al. 2006). Other white pigments include lithopone white (mainly consisting of zinc sulfate and barium sulfate), zinc oxide, and antimony trioxide. The use of white lead (basic lead carbonate) has been banned in most countries because it can cause lead poisoning, although paint with significant lead content may still be used in industry and by the military. Red pigments include iron oxides and Cadmium Red (containing cadmium sulfide and cadmium selenide). Yellow pigments include lead chromate, strontium chromate, zinc chromate, and lead chromate. Chrome Green (containing lead chromate and ferric ferrocyanide) and chromium oxide are examples of green pigments. Blue color is obtained using, e.g., a certain iron oxide, and violet color with, e.g., manganese ammonium pyrophosphate. Carbon black is the most commonly used black pigment (Rose and Vance 1997; Fischer and Adams 1999).

Organic pigments are used for special purposes. They are generally purer but more expensive. Examples include Para Red, Lithol Reds, Pigment Red 170, Toluidine Red, Phthalocyanine Green and Blues, and Dioxazine Violet.

Extenders are fillers used in paint pigment. They do not provide as much cover as primary pigments and have a significant impact on the overall characteristics and performance of the paint, including durability, scrubbability, and the retention of color. Extender pigments are mainly made from clay, silica, talc, and chalk (Fischer and Adams 1999; Estlander et al. 2000).

A.4. Additives

Additives are used in paints in small percentages to ensure, e.g., their stability, quality, and desired application properties. Additives include biocides, driers, emulsifiers or surfactants, thixotropic agents (thickeners), plasticizers, stabilizers, antioxidant antiskinning agents, photoinitiators, and corrosion inhibitors.

Biocides are used to prevent growth of microbes (bacteria, fungi) mainly in water-based paints. They are used for conserving the binder and the paint during production and storage. Biocides are effective even after the paint has dried, and thus prolong its life. Oil-based paints do not usually contain antimicrobials, but some exterior paints can contain an antimildew agent. A great number of biocides are available for use in paints. Antifouling agents are used in marine paints and are usually toxic to underwater organisms. These include copper, organic tin, tetramethylthiuram disulfide (TMTD), and zinc carbamates (Estlander et al. 2000).

Driers can feature one or more metal salts, e.g., cobalt, manganese, iron, lead, zinc, and tin naphthenates, oleates, octoactes, and resonates.

Emulsifiers or surfactants include sodium pyrophosphates, dioctyl sodium sulfosuccinate, sodium lauryl sulfate, and non-ionic detergents. They help to maintain pigment-particle dispersion in water-based latex emulsions. Antifoaming agents prevent the formation of foam during the manufacturer and application of water-based latex paints.

Thixotropic agents (thickeners) such as polyamides are added to oil-based paints, whereas cellulose derivatives are used for the same purpose in water-based latex paints.

Plasticizers are added to paints to increase the flexibility of the resinous film. They include dibutyl and dioctyl phthalates, adipic and sebacic acids, and their esters, polyester resins, and castor

oil. Coalescing agents include pine oil, butyl cellosolve, and tributyl phosphate; these are volatile substances that temporarily plasticize a liquid coating.

Stabilizers have an effect on the heat and light resistance of paint. Examples are benzophenones in nonpigmented coatings and epoxy resin in paints based on vinyl chloride polymers or copolymers. Ammonia and volatile amines are used to stabilize paint at a pH of 8–9.

Antioxidants or antiskinning agents prevent coatings from drying too early. They include oximes, e.g., butyraldoxime, methyl ethyl ketone oxime, and cyclohexanone oxime. Hydroquinone and substituted phenols are used in some specialized industrial paints.

Photoinitiators are needed in UV-curable products to initiate the polymerization process, e. g., benzophenononones.

Corrosion inhibitors in paints protect metallic surfaces from oxidation.

References

Aalto-Korte K, Suuronen K (2016) Occupational contact allergy to components of polyester resin systems. Contact Dermatitis 75:14–18

Aalto-Korte K, Suuronen K (2017) Patterns of concomitant allergic reactions in patients suggest cross-sensitization between octylisothiazolinone and methylisothiazolinone. Contact Dermatitis 77 (6):385–389

Aalto-Korte K, Alanko K, Henriks-Eckerman M-L et al (2007) Occupational allergic contact dermatitis from 2-N-octyl-4-isothiazolin-3-one. Contact Dermatitis 56:160–163

Aalto-Korte K, Kuuliala O, Suuronen K (2008) Occupational contact allergy to formaldehyde and formaldehyde releasers. Contact Dermatitis 59:280–289

Aalto-Korte K, Pesonen M, Kuuliala O et al (2010) Contact allergy to aliphatic polyisocyanates based on hexamethylene-1,6-diisocyanate (HDI). Contact Dermatitis 63(6):357–363

Aalto-Korte K, Pesonen M, Suuronen K (2015) Occupational allergic contact dermatitis caused by epoxy chemicals: occupations, sensitizing products, and diagnosis. Contact Dermatitis 73(6):336–342

Aerts O, Goossens A, Lambert J et al (2017) Contact allergy caused by isothiazolinone derivatives: an overview of non-cosmetic and unusual cosmetic sources. Eur J Dermatol 27(2):115–122

Aitken RJ, Chaudry MQ, Boxall ABA et al (2006) Manufacture and use of nanomaterials: current status in the UK and global trends. In-depth review. Occup Med 56:300–3006

Amsler E, Alerts O, Raison-Pevron N et al (2017) Airborne allergic contact dermatitis caused by isothiazolinones in water-based paints: a retrospective study of 44 cases. Contact Dermatitis 77(3):163–170

Bangsgaard N, Thyssen JP, Menne T et al (2012) Contact allergy to epoxy resin: risk occupations and consequences. Contact Dermatitis 67:73–77

Bjorkner B (2006) Acrylic resins. In: Frosch PI, Menne T, Lepoittevin J-P (eds) Contact dermatitis, 4th edn. Springer, Berlin, pp 584–594

Bregnbak D, Johansen JD (2013) Airborne sensitization to isothiazolinones observed in a 3-month-old boy. Contact Dermatitis 69(1):55–56

Breuer K, Uter W, Geier J (2015) Epidemiological data on airborne contact dermatitis – results of the IVDK. Contact Dermatitis 73:239–247

Bruze M, Boman A, Bergqvist-Karlsson A et al (1988) Contact allergy to a cyclohexanone resin in humans and Guinea pigs. Contact Dermatitis 59:344–352

Bruze M, Engfeldt M, Gonçalo M et al (2013) Recommendation to include methylisothiazolinone in the European baseline patch test series – on behalf of the European Society of Contact Dermatitis and the European Environmental and Contact Dermatitis Research Group. Contact Dermatitis 69(5):263–270

Chen R, Semple S, Dick F et al (2001) Nasal, eye, and skin irritation in dockyard painters. Occup Environ Med 58:542–543

Conde-Salazar L, Vargas I, Tevar E et al (2007) Sensitization to acrylates in varnishes. Dermatitis 18(1):45–48

de Groot AC (2015) New contact allergens: 2008–2015. Dermatitis 26(5):199–215

Donovan JCH, Kudla I, DeKoven JG (2009) Rapid development of allergic contact dermatitis from dicyclohexylmethane-4,4′-diisocyanate. Dermatitis 20(4):214–217

Editorial (2016) Methylisothiazolinone, quo vadis? Contact Dermatitis 75:263–264

Estlander T, Jolanki R (2014) Chapter 61 Paints, lacquers, and varnishes. In: Rustemeyer T, Elsner P, John SM, Maibach HI (eds) Kanerva's occupational dermatology, 2nd edn. Srpinger, Berlin, pp 675–689

Estlander T, Jolanki R, Kanerva L (1998) Occupational contact dermatitis from UV-cured lacquer containing dipropylene glycol diacrylate. Contact Dermatitis 39:36

Estlander T, Jolanki R, Kanerva L (2000) Paints, lacquers and varnishes. In: Kanerva L, Elsner P, Wahlberg JE, Maibach HI (eds) Handbook of occupational dermatology. Springer, Berlin, pp 426–678

Fischer T, Adams RM (1999) Paints, lacquers and varnishes. In: Adams RM (ed) Occupational skin disease, 2nd edn. WP Saunders, Philadelphia, pp 470–483

Fischer T, Bohlin S, Edling C et al (1995) Skin disease and contact sensitivity in house painters using water-based paints, glues and putties. Contact Dermatitis 32:39–45

Frick M (ed) (2006) Polyurethane resins. In: Frosch PJ, Menne T, Lepoittevin J-P (eds) Contact dermatitis, 4th edn. Springer, Berlin, pp 603–606

Frick M, Isaksson M, Bjorkner B et al (2003) Occupational allergic contact dermatitis in a company manufacturing boards coated with isocyanate lacquer. Contact Dermatitis 48:255–260

Friis UF, Menne T, Flyvhome A-A et al (2014) Isothiazolinones in commercial products at Danish workplaces. Contact Dermatitis 71(2):65–74

Geier J, Schmuch A (1996) No cross-sensitization between MCI/MI, benzisothiazolinone and octylisothiazolinone. Contact Dermatitis 34:148–149

Geier J, Lessmann H, Schmuch A et al (2015) Concomitant reactivity to methylisothiazolinone, benzisothiazolinone, and octylisothiazolinone. International Network of Departments of Dermatology data. 2009–2013. Contact Dermatitis 72:337–339

Goodier MC, Ljungberg L, Persson C et al (2017) Allergic contact dermatitis from methylisothiazolinone in residential wall paint. Dermatitis 28(4):284–287

Hansen MK, Larsen M, Cohr K-H (1987) Waterborne paints, a review of their chemistry and toxicology and the results of determination made during their use. Scand J Work Environ Health 13:473–485

Herry J, Esquirol Y, Giordano-Labadie F (2016) An intriguing occupational atypical dermatitis with respiratory symptoms. Contact Dermatitis 75(5):322–323

Jensen CD, Thormann J, Andersen KE (2003) Airborne allergic contact dermatitis from 3-iodo-2-propynl-butylcarbamate at a paint factory. Contact Dermatitis 48:155–157

Jolanki R (1991) Occupational skin diseases from epoxy compounds, epoxy resin compounds, epoxy acrylates and 2,3-epoxypropyl trimethyl ammonium chloride (thesis). Acta Derm Venereol Suppl (Stock) 159:1–80

Kaae I, Menne T, Thyssen JP (2012) Presumed primary contact sensitization to methylisothiazolinone from paint: a chemical that became airborne. Contact Dermatitis 66:340–355

Kanerva L, Estlander T, Jolanki R et al (1995) Occupational allergic contact dermatitis and contact urticarial caused by polyfunctional aziridine hardener. Contact Dermatitis 33:304–309

Kaukiainen A (2005) Health effects of occupational exposure to organic solvents and paint components (thesis). Finnish Institute of Occupational Health, University of Tampere, People and Work Research Reports 70:1–101

Kiec-Swierczynska M, Krecisz B, Swierczynska-Machura D (2006) Occupational allergic contact dermatitis disseminated from multifunctional acrylates in ultraviolet cured lacquers. Int J Occup Med Environ Health 19(1):77–78

Lachapelle JM, Maibach HI (2012) Patch testing and prick testing. a practical guide, official publication of the ICDRG. 3rd ed, Springer-Verlag, Berlin Heidelberg

Leira H (1997) Organic solvents. In: Brune D, Gerhardsson G, Crockford GW, Norback D (eds) Major industries and occupations (the workplace, vol 1). International Occupational Safety and Health Information Centre (CIS) International Labour Office/Scandinavian Science Publishers, Geneva/Oslo, pp 650–660

Lewis PG, Emmett EA (1987) Irritant dermatitis from tributyl tin oxide and contact allergy from chlorocresol. Contact Dermatitis 17:129–132

Lolatgis HA, Nixon R (2015) Allergic contact dermatitis following epoxy resin exposure to a paint in a recreational setting. Australas J Dermatol 56(4):312–313

Lundov MD, Zachariae C, Menne T et al (2012) Airborne exposure to preservative methylisothiazolinone causes severe allergic reactions. BMJ 345:e8221

Lundov MD, Friis UF, Menne TK et al (2013) Methylisothiazolinone in paint forces a patient out of her apartment. Contact Dermatitis 69(4):252–253

Lundov MD, Kolarik B, Bossi R et al (2014) Emission of isothiazolinones from water-based paints. Environ Sci Technol 48(12):6989–6994

Ma X-m, Lu R, Miyakoshi T (2012) Recent advances in research on lacquer allergy. Allergol Int 61:45–50

Majasuo S, Liippo J, Lammintausta K (2012) Non-occupational contact sensitization to epoxy resin of bisphenol A among general dermatology patients. Contact Dermatitis 66:148–153

Mancuso G, Berdondini RM (2008) Occupational conjunctivitis as the sole manifestation of airborne contact allergy to trimethylopropane triacrylate contained in a UV-cured paint. Contact Dermatitis 59:372–373

Mathias CGT, Andersen KE, Hamann K (1983) Allergic contact dermatitis from 2-n-octyl-4-isothiazolin-3-one, a paint mildewcide. Contact Dermatitis 9:507–509

Mose AP, Lundov MD, Zachariae C et al (2012) Occupational contact dermatitis in painters – an analysis of patch test data from the Danish Contact Dermatitis Group. Contact Dermatitis 67(5):293–297

Mose AP, Frost S, Ohlund U et al (2013) Allergic contact dermatitis from octylisothiazolinone. Contact Dermatitis 69:49–52

Oleaga JM, Aguirre A, Landa N et al (1992) Allergic contact dermatitis from Kathon 893. Contact Dermatitis 27:345–346

Ozkaya E (2012) Neighborial allergy: a hidden cause of nonoccupational airborne contact dermatitis in a housewife from epoxy resin. Dermatitis 25:124–125

Pesonen M, Kuuliala O, Suomela S, Aalto-Korte K (2016) Occupational contact dermatitis caused by 1,3-benzenedimethanamine, N-(2-phenylethyl) derivatives in hardeners for epoxy paint and coatings. Contact Dematitis 75(6):358–362

Ponten A (2006) Epoxy resin systems. In: Frosch PJ, Menne T, Lepoittevin J-P (eds) Contact dermatitis, 4th edn. Springer, Berlin, pp 595–599

Rose FG, Vance CJ (1997) The paint industry. In: Brune D, Gerhardsson G, Crockford GW, Norback D (eds) Major industries and occupations (the workplace vol 2). International Occupational Safety and Health Information Centre (CIS) International Labour Office/Scandinavian Science Publishers, Geneva/Oslo, pp 350–360

Schaal NC, Brazile WJ, Finnie KL et al (2017) Effects of known determinants on methylene bisphenyl isocyanate (MDI) concentration during spray-on-truck bed-lining processes. Ann Work Expo Health 61(7):872–882

Schwensen JF, Friis UF, Menne T et al (2017a) Contact allergy to preservatives in patients with occupational contact dermatitis and exposure analysis of preservatives in registered chemical products for occupational use. Int Arch Occup Environ Health 90(4):319–333

Schwensen JF, Menne Bonefield C, Zachariae C et al (2017b) Cross-reactivity between methylisothiazolinone, octylisothiazolinone and benzisothiazolinone using a modified local lymph node assay. Br J Dermatol 176(1):176–183

Tarvainen K, Jolanki R, Estlander T (1993) Occupational contact allergy to unsaturated polyester resin cements. Contact Dermatitis 28:220–224

Thormann J (1982) Contact dermatitis to a new fungicide, 2-n-octyl-4-isothiaolin-3-one. Contact Dermatitis 8:204

Uter W, Geier J, Bauer A et al (2013) Risk factors associated with methylisothiazolinone contact sensitization. Contact Dermatitis 69(4):231–238

Van Fassen A, Borm PJA (1991) Composition and health hazards of Netherlands. Environ Health Perspect 92:147–154

Wieslander G, Norback D, Edling C (1994) Occupational exposure to water-based paints and symptoms from skin and eyes. Occup Environ Med 51:181–186

Wieslander G, Norback D (1997) Water-based paints in the construction industry. In: Brune D, Gerhardsson G, Crockford GW, Norback D (eds) Major industries and occupations (the workplace, Vol 2). International Occupational Safety and Health Information Centre (CIS) International Labour Office/Scandinavian Science Publishers. Geneva/Oslo, pp 690–696

Wright AM, Cahill JI (2016) Airborne exposure to methylisothiazolinone in paint causing allergic contact dermatitis: an Australian perspective. Australas J Dermatol 57:294–295

Zachariae C, Rastogi S, Devantier C et al (2003) Methyldibromo glutaronitrile: clinical experience and exposure-based risk assessment. Contact Dermatitis 48:150–154