Polyester Resins

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Abstract

Polyester resins are one of the largest classes of synthetic resins and are used extensively in the reinforced plastics industry, in water-based paints, powder coatings, lacquers, automotive cements, and glues. Allergic contact dermatitis from polyester resins is rare. When allergic contact dermatitis does occur, it is more often from ancillary components of the resin system, such as accelerators, catalysts, and inhibitors, than the resins themselves. The small amount of allergic contact dermatitis that does occur from polyester resins is mostly due to unsaturated polyester resins and extremely rarely from saturated polyester resins. Occasionally, allergic contact dermatitis may occur from monomers liberated from the hardened resin or its dust. Irritant contact dermatitis from polyester resin systems occurs more frequently than allergic contact dermatitis. Irritant contact dermatitis and chemical burns may occur from additives such as organic peroxides, styrene, and acetone. Contact urticaria is well known to occur from acid anhydrides.

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1 Core Messages

- Allergic contact dermatitis from polyester resins is rare.
- Irritant contact dermatitis from polyester resin systems occurs more frequently than allergic contact dermatitis.
- Allergic reactions are more likely to occur from ancillary components of the resin system, such as cobalt octoate and benzoyl peroxide, than the resins themselves.
- When allergic contact dermatitis occurs from polyester resins, it is mostly due to unsaturated polyester resin monomers and extremely rarely from saturated polyester resins.
- Irritant contact dermatitis and chemical burns may occur from additives such as organic peroxides, styrene, and acetone.
- Contact urticaria may occur from acid anhydrides.

2 Introduction

Polyesters are one of the largest classes of synthetic resins and have widely varying properties depending on their composition. Polyester resins are polycondensates which are prepared in two different forms: saturated and unsaturated resins. They are cost-effective to produce and have many desirable properties such as stiffness, toughness, heat resistance, and stability (Elliot 1993).

Saturated polyester (SP) resins, also termed alkyd or unmodified alkyd resins, are thermoplastic resins manufactured by a condensation reaction between polybasic dicarboxylic acids or their anhydrides (mainly phthalic anhydride, maleic anhydride, or fumaric acid) with polyalcohols (such as glycerol, propylene glycol, diethylene glycol, neopentyl glycol, or trimethylolpropane). They may be modified by oil-containing fatty acids or chemically cross-linked with curing agents such as isocyanates to improve thermal and chemical stability (Kanerva et al. 1996a; Björkner 2006). Saturated polyester resins are commonly used as plasticizers, in paints and powder coatings, adhesives, and surface coatings. They are used in optical equipment for their clarity and color stability (Elliot 1993). Polyethylene terephthalate (PET) is one of the best known members of the saturated polyester resin family and is used in plastic water bottles, containers for liquids and foods, and in synthetic textile fibers, where it is simply called "polyester."

Unsaturated polyester (UP) resins are produced through an esterification reaction of polybasic dicarboxylic acids or their anhydrides with a diol, such as diethylene glycol or 1,2-propylene glycol (Fig. 1). They are versatile materials and are used extensively in the reinforced plastics industry in the manufacture of products for transportation, construction, and marine applications. They are also used for coatings, finishes, lacquers, cements, and glues (Kanerva et al. 1996a; Björkner 2006).

UP resins are thermoset resins, meaning they are converted from liquid to solid through the process of polymerization and once cured cannot be converted back to their liquid form (Updegraff 1982). The cross-linking or polymerization process occurs when the double bond of unsaturated polyesters reacts with a vinyl monomer, resulting in a three-dimensional cross-linked structure. Styrene is the most commonly used monomer for the cross-linking of UP resins. Other cross-linking agents include vinyl toluene and methyl methacrylate. The cross-linking reaction is initiated through a catalyst (or hardener), which is usually an organic peroxide such as benzoyl peroxide or methyl ethyl ketone peroxides, ultraviolet (UV) light, or a combination of the two. An inhibitor such as hydroquinone or para-tertiary butyl catechol is added in small

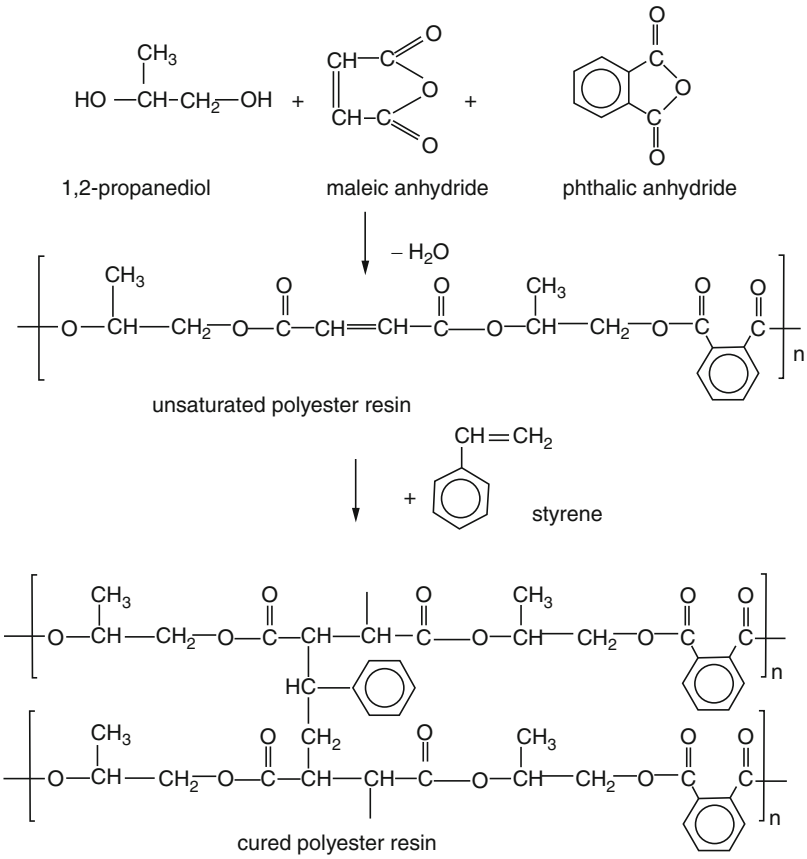

Fig. 1 Unsaturated polyester resin is made by condensing 1,2-propanediol, maleic anhdyride, and phthalic anhydrides. Styrene is used as a cross-linking monomer

quantities to prevent premature polymerization, improve resin stability, prolong shelf life, and modify cure rate to prevent cracking of thick moulded sections (Cassis and Talbot 1998). Accelerators, such as cobalt naphthenate or octoate, or tertiary amines such as dimethyl aniline, diethyl aniline, and dimethyl-p-toluidine, is also necessary for the curing of plastics at room temperature.

The UV-curable polyester system is used in the furniture industry as a top coating and for orthopedic casts and contains vinyl toluene as the cross-linking agent and a benzoin-ether molecule as a photo-initiator (Kanerva et al. 1996a; Björkner 2006). A plasticizer such as dibutyl/dioctyl phthalate or tricresyl phosphate may be added to alter the mechanical properties of the UP resin and make it more flexible. Other ancillary components in UP resin systems include pigments, stabilizers, fillers, flame retardants, and UV-protecting agents.

3 Skin Problems from Polyester Resins

The vast majority of skin problems from polyester resins occurs in the occupational setting and may occur via direct contact or airborne exposure (Tarvainen et al. 1995b). The incidence of ACD from polyester resins is low, with the most common sensitizers being ancillary chemicals such as the organic peroxides and cobalt naphthenate/octoate (Rietschel et al. 2008). Individual components of polyester resin systems reported to have caused ACD are summarized in Table 1. Most cases of occupational dermatoses from polyester resins are of the irritant type (Rietschel et al. 2008). ICD may occur from cyclic acid anhydrides, propylene glycol, styrene, acetone, fiberglass, and the polyester resin dust itself.

Table 1 Reported causative allergens in polyester resins

Actual allergen in resin	
Maleic acid	Malten and Zielhuis (1964)
Fumaric acid	Malten and Zielhuis (1964)
Adipic acid	Malten and Zielhuis (1964) and Guin (2001)
Adipic polyester	Sowa et al. (2005)
Phthalic anhydride	Malten and Zielhuis (1964), Lidén et al. (1984), and Tarvainen et al. (1995b)
Maleic anhydride	Minamoto et al. (2002b)
Methyl tetrahydrophthalic anhydride[a]	Kanerva et al. (1997)
Polyethylene terephthalate[a]	Lung et al. (2009)
Maleic esters	Minamoto et al. (2002b) and Malten (1984)
Polyester methacrylate	Bjlyeste (1982)
Methyl methacrylate	Wehle (1966)
Diethylene glycol maleate	Tarvainen et al. (1993a), Kanerva et al. (1999b), and Pfäffli et al. (2002)
Cross-linking monomers	
Styrene	Key et al. (1961), Bourne and Milner (1963), Sjöborg et al. (1982), and Conde-Salazar et al. (1989)
Vinyltoluene	Sjöborg et al. (1982)
Triglycidyl isocyanurate[a]	Nishioka et al. (1988), Mathias (1988), Dooms-Goossens et al. (1989), Munro and Lawrence (1992); Foulds and Koh (1992), McFadden and Rycroft (1993), and Aalto-Korte and Suuronen (2016)
Hardening catalysts	
Benzoyl peroxide	Bourne and Milner (1963), Malten and Zielhuis (1964), Vincenzi et al. (1991), Minamoto et al. (2002a), and Tsovilis et al. (2005)
Cyclohexanone hydroperoxide	Malten (1964)
Methyl ethyl ketone peroxide	Bourne and Milner (1963), Malten and Zielhuis (1964), Stewart and Beck (1992), Bhushan et al. (1998), and Minamoto et al. (2002a)
Cobalt salts	Bhushan et al. (1998), Minamoto et al. (2002a), and Aalto-Korte and Suuronen (2016)
Cobalt naphthenate	Key et al. (1961), Bourne and Milner (1963), Malten and Zielhuis (1964), Kadlec et al. (1974), Schena et al. (1995), Tarvainen et al. (1995b), and Tarvainen (1996)
Cobalt octoate (cobalt-2-ethylhexanoate)	Kanerva et al. (1996b), Anavekar and Nixon (2006), and Cahill and Andersen (2010)
Dimethyl aniline	Wehle (1966)
Dimethyl-p-toluidine	Haddad et al. (1996)
Terephthalic acid diglycidylester[a]	Geier et al. (2001)
Inhibitors	
Hydroquinone	Wehle (1966) and Torres et al. (1993)
Para-tertiary butyl catechol	Freeman (1986), MacFarlane et al. (1990), Estlander et al. (1998), and Minamoto et al. (2002a)
Plasticizers	
Pthalates (dibutyl/ dimethyl/dioctyl phthalate)	Malten and Zielhuis (1964) and Malten (1984)
Tricresyl phosphate	Key et al. (1961)
Other	
Phthalic anhydride/ trimellitic anhydride/ ethylene glycol/ neopentyl glycol monomers (PTGC)	Moffit and Sansom (2002), Gach et al. (2005), and Nassif et al. (2007)

[a]Saturated polyester (SP) resin allergens

Although saturated polyester resins are not generally considered to be sensitizing, cyclic acid anhydrides, particularly phthalic anhydrides, have been reported to cause irritant contact dermatitis (ICD) (Malten and Zielhuis 1964) and are a well-known cause of immediate IgE-mediated hypersensitivity manifesting as asthma, allergic rhinitis, and contact urticaria (Jolanki et al. 1987, 1997; Tarvainen et al. 1995a; Kanerva et al. 1999a, 2000). A recent case series from the Finnish Institute of Occupational Health (FIOH) described 21 patients with contact urticaria from cyclic acid anhydrides, including one case caused

by maleic acid anhydride in the production of polyester resins (Helaskoski et al. 2009). In one case of contact urticaria caused by methyl hexahydrophthalic anhydride, the reaction was enhanced by wiping off the substance with an alcohol disinfectant, which was presumed to enhance penetration of the allergen (Kanerva et al. 1999a). There are only rare reports of cyclic acid anhydrides causing ACD (Kanerva et al. 1997).

Various inhibitors of UP-resin systems are known to induce contact leukoderma/vitiligo. Horio et al. (1977) described occupational leukoderma from para-tertiary butyl catechol (PTBC) in a polyester resin plant worker. Moroni and Tomasini (1992) reported a case of contact leukoderma likely resulting from hydroquinone, parabenzoquinone, and PTBC used as inhibitors in fiberglass-reinforced polyester resin for boat building.

Most reports of skin problems from polyester resins involve workers in the reinforced plastics and plastic composites industries, for example, workers involved in lamination and moulding of boat and airplane components (Tarvainen et al. 1995b; Minamoto et al. 2002a). Other at-risk occupations include automotive repair workers using UP-resin based car putties and cements and those working with powder paints (Kanerva et al. 1999b; Aalto-Korte and Suuronen 2016). In the fiberglass-reinforced plastics (FRP) industry, occupational dermatoses may be due to a number of causative agents, including UP resin, ancillary resin chemicals, glass fiber, and dust comprising glass fiber and UP-resin particles (Minamoto et al. 2002a).

4 Allergic Contact Dermatitis

4.1 Unsaturated Polyester (UP) Resins

Despite UP resins being used extensively in the reinforced plastics industry and in applications such as surface coatings, paints, cements, automotive putties, and glue, there are only infrequent cases of ACD from UP resin described in the literature. Unsaturated polyester resins are far less sensitizing than epoxy resins (Malten and Zielhuis 1964).

ACD was first reported from UP resins in 1955 (Lieber 1955). Five patients with ACD and positive patch tests to UP resins were reported from a group of 30 workers in an airplane factory (Malten 1956). Most cases of ACD from UP resins have been reported in lamination workers (Malten 1956; Bourne and Milner 1963; Lidén et al. 1984), painters (Kadlec et al. 1974), and in those working with UV light-cured inks (Björkner 1982). Other common occupational causes of ACD from UP resins include in automotive repair putties (Aalto-Korte and Suuronen 2016), in the manufacture of UP cement and resin moulds (Tarvainen et al. 1993a; Kanerva et al. 1999b) and in workers in the fiberglass-reinforced plastics industry (Tarvainen et al. 1993b, Minamoto et al. 2002a, b).

Guin (2001) reported a machine repairman who had developed ACD from adipic acid while working in the synthesis of polyester resins. Adipic polyester, produced from adipic acid and propylene glycol, is a thermoplastic polyester used as a plasticizer in vinyl gloves and has also caused ACD (Sowa et al. 2005).

The FIOH previously described eight cases of occupational contact allergy caused by UP-resin car putties/cements (Tarvainen et al. 1993a; Kanerva et al. 1999b), in several of whom, the causative allergen was identified as diethylene glycol maleate (DEGM). The FIOH has recently published a case series of 11 new patients with occupational contact allergy to components of polyester resin systems (Aalto-Korte and Suuronen 2016). Of these, five reacted to UP-resin car putties (although chemical analysis was not performed to identify the causative allergen), three to cobalt salts used as catalysts, and three to triglycidyl isocyanurate (TGIC) used a curing agent in polyester powder spray paints. Although rates of ACD from polyester resins remain low, automotive body repair workers appear to be one of the at-risk populations.

4.1.1 Hardened Resin

Although for some years it was believed that hardened resin contained no reactive monomers,

several authors have demonstrated otherwise. In a chemical analysis of polyester resin dust, dibutyl phthalate was shown to comprise 3.5% of the cured resin (Bourne and Milner 1963). Small amounts of unreacted DEGM were identified in UP-resin car putties (Tarvainen et al. 1993a; Pfaffli et al. 2002). Free phthalic anhydride causing ACD has been identified in the dust from a hardened UP-resin glue (Tarvainen et al. 1995b).

ACD has been reported from the dust of UP resin in reinforced plastic products (Bourne and Milner 1963; Tarvainen et al. 1993b, 1995b) and car repair putty (Tarvainen et al. 1993a; Kanerva et al. 1999b; Dooms-Goossens and De Jonge 1985). Grinding the resin can give airborne allergic reactions many years after it has been hardened (Kanerva et al. 1999b; Pfäffli et al. 2002).

4.1.2 Ancillary Chemicals

Vinyl Monomers

ACD has been reported from styrene, which is the most commonly used cross-linking monomer in the production of UP resins (Key et al. 1961; Bourne and Milner 1963; Sjoborg et al. 1982; Conde-Salazar et al. 1989).

Cobalt

Cobalt salts including cobalt naphthenate and cobalt octoate (cobalt-2-ethylhexanoate) are used as hardening catalysts for polyester resins. Cobalt octoate is a metal salt of carboxylic acid. When combined with a catalyst such as benzoyl peroxide, cobalt octoate enables the curing of unsaturated polyester resins at room temperature (Foussereau et al. 1982; Anavekar and Nixon 2006). Occupational ACD has been reported from cobalt octoate used as a paint drying component in a paint/ink used by an offset printer (Kanerva et al. 1996b) and as an accelerator in polyester resin used by a spa bath laminator (Anavekar and Nixon 2006) and a boat builder (Cahill and Andersen 2010). Occupational ACD from cobalt naphthenate used as an accelerator in unsaturated polyester resins has also been reported by multiple authors (Key et al. 1961; Bourne and Milner 1963; Malten and Zielhuis 1964; Kadlec et al. 1974; Tarvainen et al. 1995b; Tarvainen 1996). Lymphomatoid-like allergic contact dermatitis in a marble worker was reported from cobalt naphthenate (Schena et al. 1995).

Organic Peroxides

ACD from organic peroxides used as polyester resin catalysts was first described in the 1960s. Early case reports include ACD caused by benzoyl peroxide (Bourne and Milner 1963; Malten and Zielhuis 1964), cyclohexanone hydroperoxide (Malten 1964), and methyl ethyl ketone hydroperoxide (Bourne and Milner 1963; Malten and Zielhuis 1964). More recently, ACD has been reported from benzoyl peroxide in a prosthetic limb (Vincenzi et al. 1991) and in a marble glue (Tsovilis et al. 2005) and from methyl ethyl ketone peroxide in a polyester spray paint (Stewart and Beck 1992). In one report, a worker producing moulded children's rides from fiberglass-reinforced plastic was found to have occupational ACD caused by both methyl ethyl ketone peroxide and cobalt but not by the UP resin itself (Bhushan et al. 1998).

Inhibitors

Para-tertiary butyl catechol (PTBC), which is used as an inhibitor for polyester resin systems, is a rare occupational allergen. There are a few case reports of ACD caused by PTBC in the literature (Estlander et al. 1998; Minamoto et al. 2002a), notably several from prosthetic limbs (Freeman 1986; MacFarlane et al. 1990). However, the FIOH was found PTBC to be one of the most common causes of *active* sensitization, alongside acrylates and para-phenylenediamine (Estlander 1998). As a result, in the late 1990s, they lowered their patch test concentration from 1% to 0.25%.

Plasticizers

ACD has been reported from dibutyl phthalate, dimethyl phthalate, and dioctyl phthalate (Malten and Zielhuis 1964), in addition to tricresyl phosphate, which are used as plasticizing agents (Key et al. 1961).

4.2 Saturated Polyester (SP) Resins

4.2.1 Resin Allergens

The phthalic anhydrides have been reported to cause IgE-mediated respiratory diseases and contact urticaria but rarely ACD. Kanerva et al. (1997) reported the case of a boring machine worker who developed ACD, in addition to allergic rhinitis and an immediate contact skin reaction, from methyl tetrahydrophthalic anhydride. Lung et al. (2009) described a 4-year old boy with ACD caused by a polyethylene terephthalate (PET) mesh in a cochlear implant.

4.2.2 Cross-Linking Agents

Triglycidyl isocyanurate (TGIC) is a trifunctional epoxy compound used as a cross-linking agent in saturated polyester resin-based powder spray paints and automotive coatings. There are reports of occupational ACD to TGIC in factory workers producing the raw chemical (Nishioka et al. 1988), in workers manufacturing polyester powder paints (Munro and Lawrence 1992; Foulds and Koh 1992), and in spray painters using polyester powder paints (Mathias 1988; Dooms-Goossens et al. 1989; McFadden and Rycroft 1993; Aalto-Korte and Suuronen 2016).

Geier and colleagues (2001) described the case of a factory worker with airborne ACD to terephthalic acid diglycidylester used as a hardener in a polyester resin-based powder spray coating.

4.3 Nonoccupational Sources

Nonoccupational ACD from UP resin is infrequent but has been reported from "hypoallergenic" nail varnish (Shaw 1989), UP glue used domestically (Sjoborg et al. 1982), and limb prostheses. Several authors have described ACD from components of polyester resin-based limb prostheses, including to the UP resin itself (MacFarlane et al. 1986), to the inhibitor PTBC (Freeman 1986; MacFarlane et al. 1990), to benzoyl peroxide (Vincenzi et al. 1991), and to dimethyl-p-toluidine (Haddad et al. 1996).

More recently, several authors have described a case series of ACD from an original polyester resin compound comprising phthalic anhydride, trimellitic anhydride, ethylene glycol, and neopentyl glycol monomers (termed PTGC), which is used as an alternative to toluene sulfonamide formaldehyde resin in some nail polishes (Moffit and Sansom 2002; Gach et al. 2005; Nassif et al. 2007).

5 Irritant Contact Dermatitis

Multiple chemicals used in the production of polyester resins, and the resins themselves, have been reported to cause ICD. In one workplace study, ICD was reported from both chemicals and mechanical irritants such as glass fiber and dust created in the production of fiberglass-reinforced polyester resin (Minamoto et al. 2002a). In a study of 43 workers with occupational dermatoses employed in the plastics composite industry, 21 were diagnosed with ICD; in 2 cases this was due to dust from ground UP resin, in 1 case due to solvent, and in 18 cases due to glass fiber used in fiberglass-reinforced polyester resin (Tarvainen et al. 1995b).

ICD has been reported from the cross-linking styrene monomer (Rietschel and Fowler 2008) or, in earlier times, diallylphthalate (Fregert 1971). Styrene is classified as a mild irritant, although it has been reported to cause blisters (Bourne and Milner 1963) and even chemical burns (Bruze et al. 2000). Prolonged exposure to styrene has caused a case of skin atrophy, neurogenic muscular atrophy, and anxiety reaction (Araki et al. 1971). Levels of styrene vapor exceeding 300 ppm (1260 mg/m^3) have been reported to induce erythema of the skin (Stewart et al. 1968). Even at levels of 50 ppm (215 mg/m^3), styrene vapor may irritate conjunctival and nasal mucous membranes (Gotell et al. 1972). It is thought that the vinyl group in styrene is responsible for causing the mucous membrane irritation (Alarie 1973). However, workers may develop a tolerance to the irritation after prolonged exposure (Gotell et al. 1972).

Phthalic anhydride used in the manufacture of polyester resins can cause ICD, and even caustic blisters especially on moist skin, where the anhydride is transformed into the corresponding acid (Malten and Zielhuis 1964).

Organic peroxides such as hydrogen peroxide and benzoyl peroxide are used as 3–10% solutions to catalyze the hardening reactions of UP resins. They are weak sensitizers but strong irritants (Haustein et al. 1985; Mora Morillas et al. 1987; Aguirre et al. 1994; Kanerva et al. 1998). In the plastic composite industry, organic peroxides have caused severe ICD (Bourne and Milner 1963). Reactive organic peroxide molecules in unhardened resin dust may cause stinging on uncovered areas of the skin during spray lamination (Schumes 1990). Patients with atopic dermatitis are particularly prone to irritant reactions from benzoyl peroxide (Ockenfels et al. 2009). Hydrogen peroxide is also an irritant but very rarely an allergen (Aguirre et al. 1994; Kanerva et al. 1998).

In addition to chemicals included in the resin system, mould-release agents (chemicals which produce a slip effect between the resin and the mould) have also caused ICD (Bourne and Milner 1963). Acetone dissolves liquid UP resin and is used to clean equipment and spills in UP-resin industries. With repeated contact, acetone may defat the skin and disrupt the epidermal barrier (Fartasch 1997), and it has been reported to be a contributing factor for ICD in the moulded polyester resin industry (Bourne and Milner 1963; Tarvainen et al. 1993b, 1994). Chlorinated hydrocarbon solvents such as methylene chloride and trichloroethane are often used for cleaning purposes and are also skin irritants (Midtgard and Knudsen 1994).

5.1 Skin Testing and Chemical Investigations

UP resins have been patch tested at concentrations of 0.5–10% (Tarvainen et al. 1993a; Kanerva et al. 1999b) but also at 20% in acetone (Foussereau et al. 1982). It has been suggested that the test concentration may need to be at least 5% (Kanerva et al. 1999b); however it is not clear at what concentration active sensitization occurs. Aalto-Korte and Suuronen (2016) recommended that the UP-resin component of polyester car putties and lamination resins be tested at 5% in petrolatum, that polyester powder paint be tested at 10% and cured polyester putty/dust at 20%.

Benzoyl peroxide is traditionally tested at 1% in petrolatum. Patch testing with benzoyl peroxide can be problematic as it can be challenging to discriminate irritant reactions from weak positive allergic reactions (Ockenfels et al. 2009). The IVDK trialed parallel patch testing benzoyl peroxide at 1% and 0.5% for a 6-month period from 1993 to 1994. The results showed that decreasing the concentration halved the proportion of positive reactions but did not improve the reaction index or positivity ratio; thus interpretation was not made easier. As such, the German Contact Dermatitis Research Group (DKG) has maintained the higher patch test concentration in their test series (Ockenfels et al. 2009). A similar phenomenon was observed by Geier et al. (2003) when testing with the rubber chemical *N*-(cyclohexylthio)phthalimide.

Erikstam and colleagues (2001) conducted chemical analyses showing that degradation of TGIC used in their patch test preparation was the cause of a false-negative patch test reaction. Retesting with a new preparation of fresh TGIC powder yielded a positive result. They recommended that if a false-negative reaction occurs in the setting of high suspicion of an allergen, the patient should be retested with a new patch test preparation of fresh material, in addition to their own materials.

When allergy to polyester resins is suspected, it is important to test with specialized patch test series, in addition to the patient's own products. A retrospective review by Shmidt et al. (2010) found that of 193 patients with positive patch tests to plastics and glues, 162 of these were only identified using specialized test series and would have been missed using the baseline series alone (Shmidt et al. 2010).

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