Comparison of product safety data sheet ingredient lists with skin irritants and sensitizers present in a convenience sample of light-curing resins used in additive manufacturing

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**Supplemental File**

Table of Contents

**Introduction3**

**Materials and Methods4**

Resin product inventory4

Table S1. Inventory of de-identified resin samples 4

Analysis of elements in resins6

Table S2. Limits of detection (LOD) and quantification (LOQ) by element (all in mg/kg) for analysis by NIOSH Method 7303 8

Analysis of organic substances in resins9

**Literature review10**

Categorization of elements10

Skin irritants 11

Table S3. Elements detected in resin samples and categorization of their potential to cause skin irritation 12

Skin sensitizers 20

Table S4. Elements detected in resin samples and categorization of their skin sensitization potential22

Categorization of organic substances32

Skin irritants 32

Table S5. Organic substances in resin samples and categorization of their skin irritation potential36

Skin sensitizers 42

Table S6. Organic substances in resin samples and categorization of their skin sensitization potential46

**Results53**

Characteristics of irritants and/or sensitizers per resin sample53

Table S7. Sum of mass concentration of unique elements quantified by ICP-OES that were categorized as irritants and/or sensitizers per resin sample53

Table S8. Sum of mass concentration of unique organic substances (quantified target compounds and semi-quantitative TICs by GC-MS) that were categorized as irritants and/or sensitizers per resin sample56

Table S9. Proportion of total chromium (Cr) in the form of hexavalent chromium (Cr(VI))59

Figure S1. Number of unique elements that were categorized as skin irritants and/or sensitizers per resin product60

Figure S2. Number of unique organic substances that were categorized as skin irritants and/or sensitizers per resin product61

**References62**

# Introduction

Vat photopolymerization (VP) and material jetting (MJ), two types of additive manufacturing (AM) processes, use photopolymer (light-curing) liquid resins to build objects. Chang et al. reported the first case of allergic contact dermatitis among AM workers in a person that handled a VP resin (Chang et al., 2004). Subsequently, more cases of ACD were reported among AM workers who had skin contact with photopolymer resins (Creytens et al., 2017). While it is known that photopolymer resins used in AM process can contain skin irritants and/or sensitizers, product safety data sheets (SDSs) might not declare all ingredients (Creytens et al., 2017). In the current study, 39 commercially-available resin products that were in use by an automotive manufacturer were characterized to determine elemental and organic constituents. Next, a review of available literature was conducted to determine if each detected element or organic substance had propensity to cause skin irritation and/or sensitization. For those elements and organic substances that were categorized as irritants and/or sensitizer, we evaluated the influence of resin manufacturer, system, color, and AM process type on the masses and numbers of these constituents compared product SDSs to the analytical results.

This supplemental file provides additional study details not included in the main text. In the Materials and Methods section, details of the sample digestion procedure and instrument settings for elemental analysis of resin samples are provided, including method limits of detection and quantification (Table S1). Similarly, details of the sample digestion procedure and instrument settings for analysis of organic substances in the resin samples are provided to document the methodology. In the Results, an inventory of the 39 resin samples is provided in Table S2, followed by the detailed literature reviews to ascertain if detected elements or organic substances had propensity to cause skin irritation and/or sensitization (Tables S3 - S6). Masses of elements and organic substances categorized as irritants and/or sensitizers are given in Tables S7 - S9 and the numbers of elements and organic substances categorized as irritants and/or sensitizers are visualized in Figures S1 and S2.

# Materials and Methods

## Resin product inventory

Table S1 summarizes the 39 resin products included in this study. There were 29 resins for VP machines and 10 resins for MJ machines. The resins represented seven different manufacturers (designated A - F). Resins were either a one-part system (not mixed with another component before use) or two-part systems (components are mixed just prior to use so that ingredients do not react and harden during storage). Among VP resins, 17 were a one-part system and 12 were a two-part system. All 10 of the MJ resins were a one-part system. The resin color, which is the color appearance of a printed part, were grouped into seven categories (yellow, green, black, clear, grey, white, and purple).

Table S1. Inventory of de-identified resin samples

| Manufacturer ID | Sample ID | Systema | AM Processb | Color |
| --- | --- | --- | --- | --- |
| A | 1 | 2 | VP | Yellow |
| A | 2 | 2 | VP | Yellow |
| A | 3 | 2 | VP | Yellow |
| A | 4 | 2 | VP | Yellow |
| A | 5 | 2 | VP | Green |
| A | 6 | 2 | VP | Black |
| A | 7 | 2 | VP | Clear |
| A | 8 | 2 | VP | Black |
| A | 9 | 2 | VP | Grey |
| A | 10 | 2 | VP | Clear |
| A | 11 | 1 | VP | Green |
| A | 12 | 1 | VP | Yellow |
| B | 13 | 1 | VP | Clear |
| C | 14 | 1 | VP | Clear |
| D | 15 | 1 | VP | Black |
| D | 16 | 1 | VP | White |
| D | 17 | 1 | VP | Clear |
| D | 18 | 1 | VP | Clear |
| D | 19 | 1 | VP | Clear |
| D | 20 | 1 | VP | Green |
| D | 21 | 1 | VP | White |
| E | 22 | 1 | VP | Black |
| E | 23 | 1 | VP | Clear |
| E | 24 | 1 | VP | Black |
| F | 25 | 1 | VP | White |
| F | 26 | 1 | VP | Clear |
| F | 27 | 1 | VP | Grey |
| F | 28 | 1 | VP | Grey |
| F | 29 | 1 | VP | Black |
| F | 30 | 1 | MJ | Clear |
| F | 31 | 1 | MJ | Grey |
| G | 32 | 1 | MJ | Clear |
| G | 33 | 1 | MJ | Purple |
| G | 34 | 1 | MJ | White |
| G | 35 | 1 | MJ | Black |
| G | 36 | 1 | MJ | Black |
| G | 37 | 1 | MJ | Clear |
| G | 38 | 1 | MJ | White |
| G | 39 | 1 | MJ | White |

a one-part resin = single component that is not mixed with another component before use, two-part resin = two components that are mixed just prior to use

b VP = vat photopolymerization, MJ = material jetting

## Analysis of elements in resins

Thirty-one elements were analyzed for in resins samples using a modified National Institute for Occupational Safety and Health (NIOSH) Method 7303 (NIOSH, 2003). Briefly, approximately 0.1 g of each bulk resin sample was placed in a metals-free 50-mL polypropylene centrifuge tube, 2.5 mL of 12.1 M hydrochloric acid was added to each tube, and the tubes placed in a hot block and heated at 95 °C for 15 minutes. The tubes were removed from the hot block, cooled, and 2.5 mL of 15.6 M nitric acid was added to each. The tubes were placed back in the hot block, heated at 95 °C for 15 minutes, then removed from the hot block, cooled, and diluted to a final volume of 25 mL with deionized water. All resin samples and quality control samples were digested in the same manner. The samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using an Agilent 5800 ICP (Agilent Technologies, Inc., Santa Clara, CA). The ICP instrument conditions were as follows: radio frequency power: 1400 watts, argon plasma flow: 13 L/min, auxiliary argon flow: 1 L/min, and nebulizer argon flow: 0.65 L/min.

All samples with detectable chromium were further analyzed for hexavalent chromium using a modified U.S. Occupational Safety and Health Administration (OSHA) Method ID 215 version 2 (OSHA, 2006). Approximately 1 g of each resin was weighed in tared beakers, to which 1.5 mL of phosphate buffer/Mg(II) solution and a 1:2 magnesium sulfate solution (49.5 g of MgSO4 in 500 mL of deionized water):phosphate buffer solution (68 g of KH2PO4 and 87.1 g K2HPO4 in 1 L of deionized water) was added and the samples swirled to wet the resin. Next, 5.0 mL of spray paint extraction solution (75 g Na2CO3 and 50 g NaOH in 1 L of deionized water) was added to each sample beaker and the beakers were re-swirled. Sample beakers were covered with watch glasses, heated in a water bath at approximately 100 °C for 45 minutes, swirled to facilitate the breakdown of the resin and ensure even desorption, then heated for another 45 minutes. Once heating was complete, the beakers were removed from the water bath and allowed to cool to room temperature. The solution in each beaker was transferred quantitatively with deionized water rinses to a 50-mL graduated centrifuge tube, brought to a 25-mL final volume with deionized water, shaken well, centrifuged for 15 minutes at 5000 rotations per minute, and allowed to settle overnight. Finally, 1.5 mL of each sample was transferred to a vial and analyzed by ion chromatography (Dionex™ ICS-1100, Thermo Scientific, Carlsbad, CA) with an ultraviolet-visible detector (Dionex™ ICS Series Variable Wavelength Detector, Thermo Scientific) at 540 nm (herein IC-UV-Vis). The sample eluent was 250 mM ammonium sulfate/100 mM ammonium hydroxide. Table S2 lists the elements and their respective limits of detection (LOD) and quantification (LOQ).

Table S2. Limits of detection (LOD) and quantification (LOQ) by element (all in mg/kg) for analysis by NIOSH Method 7303.a

| Element | LOD | LOQ |
| --- | --- | --- |
| Aluminum | 20 | 53 |
| Antimony | 0.5 | 1.8 |
| Arsenic | 0.5 | 1.5 |
| Barium | 0.008 | 0.027 |
| Beryllium | 0.006 | 0.019 |
| Cadmium | 0.03 | 0.093 |
| Calcium | 3 | 10 |
| Chromium | 0.1 | 0.33 |
| Chromium(VI)b | 0.006 | 0.019 |
| Cobalt | 0.09 | 0.31 |
| Copper | 0.8 | 2.7 |
| Iron | 10 | 38 |
| Lanthanum | 0.2 | 0.53 |
| Lead | 0.3 | 1.1 |
| Lithium | 2 | 5.5 |
| Magnesium | 0.4 | 1.2 |
| Manganese | 0.4 | 1.2 |
| Molybdenum | 0.07 | 0.24 |
| Nickel | 0.2 | 0.76 |
| Phosphorous | 1 | 3.7 |
| Potassium | 10 | 41 |
| Selenium | 0.6 | 2.1 |
| Silver | 0.09 | 0.29 |
| Strontium | 0.05 | 0.18 |
| Tellurium | 0.5 | 1.6 |
| Thallium | 0.9 | 3.0 |
| Tin | 0.2 | 0.57 |
| Titanium | 0.2 | 0.68 |
| Vanadium | 0.4 | 1.2 |
| Yttrium | 0.03 | 0.11 |
| Zinc | 5 | 16 |
| Zirconium | 0.3 | 0.93 |

a LOD and LOQ values were based on a 0.1 g sample size and a 25 mL final volume. The sample-specific LOD and LOQ values were adjusted for the actual mass of sample used in digestion.

b by OSHA Method ID 215 (version 2)

## Analysis of organic substances in resins

Resin samples were quantitatively analyzed for 10 target compounds (acetone, isopropyl alcohol, n-hexane, benzene, methyl methacrylate, toluene, ethylbenzene, styrene, *m,p*-xylene, and *o*-xylene) and qualitatively analyzed to identify other organic compounds present in the samples using gas chromatography-mass spectrometry (GC-MS). Briefly, an aliquot of each sample was weighed out 1.0 g in 10 mL of methanol in a 16-mL amber vial (when necessary, because of small available sample volumes, less than 1.0 g of resin was analyzed but the volume of methanol was adjusted to maintain a 1.0 g:10 mL ratio). Samples were placed in an ultrasonic bath for twenty minutes with ice and allowed to settle for 1 hour while shielded from light. Next, a 100 µL aliquot was removed from each sample and transferred to a micro-vial insert followed by addition of an internal standard mix (pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5, and 1,4-dichlorobenzene-d4) to each micro-vial, then briefly mixed on a vortex, and analyzed using gas chromatography-mass spectrometry (Hewlett Packard Model 7890B GC/Hewlett Packard Model 5975C mass spectrometer). The GC was equipped with a Phenomenex ZB-1, 60 meter, 0.32-mm ID column with a 1.0 μm film thickness (info). The GC instrument settings were column flow = 1.5 mL/min (constant flow), split ratio = 1:10, injection temperature = 300 °C, injection volume: 1 μL. The oven temperature profile was initial temperature = 50 °C, initial hold time = 8.0 min, temperature ramp rate = 5 °C/min to 135 °C with, hold time of 0.0 min followed by ramp rate = 30 °C/min to 300 °C. The analytical run was held at 300 °C for 30.5 min. The mass spectrometer was operated in SCAN mode over the range 35 to 550 amu.

# Literature Review

An extensive review of pertinent government reports, existing peer-reviewed literature, and PubChem database records was performed to identify which identified constituents exhibited propensity to cause dermal irritation and/or sensitization.

## Categorization of elements

Of the 31 total elements analyzed for using ICP (see Table S2), all but two were detectable in at least one resin sample (concentrations of tellurium and vanadium were below their respective LODs in all resins). For the remaining 29 elements, the propensity for skin irritation is summarized in Table S3 and for dermal sensitization data is summarized in Table S4. In both tables, the individual elements determined to be present in the resin samples were listed alphabetically and the major findings of our literature reviews were summarized in the subsequent columns. The irritating/sensitizing potential of each element (and relevant species variants), as determined by the U.S. National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) as well as the American Conference of Governmental Industrial Hygienists (ACGIH®) is given, along with information obtained from peer-reviewed research studies. The property of interest was confirmed or refuted for each elemental formulation, as denoted by “Y” or “N,” respectively (or N/A to reflect the absence of existing data). Based on the collective information presented from these different sources, each element was classified as a sensitizer/irritant or a non-sensitizer/irritant, as indicated by the entry in the second column of the respective row. Elements were assigned “Yes” to indicate a definitive capacity for sensitization/irritation with strong evidence from both sectors and human data supporting the classification, “Yesb” when modest evidence of sensitization/irritation exists but is derived exclusively from animal studies, “Yesc” when notable evidence from one source supports classification as a sensitizer/irritant (though this immunological activity may occur infrequently), “No” when existing evidence indicates a lack of sensitizing/irritating potential, or “--a” when an absence of existing information prevents the accurate identification of the metal’s sensitization/irritation potential.

Overall, there appeared to be a greater degree of congruency between information presented in government reports and primary research studies regarding skin irritation when compared to dermal sensitization. Thirteen (57%) of the 23 total elements identified as skin irritants were consistently implicated by multiple sources as irrefutable inducers of dermal irritation (compared to only 27% of dermal sensitizers), while only 10 (43%) of the 23 confirmed dermal irritants were associated with inconsistent reporting (compared to 73% of skin sensitizers).

### Skin irritants

Twenty-three of the 29 detected elements (79%) quantified by ICP were classified as potential skin irritants based on the findings from our literature review.

Five (17%) of the 29 elements detected in the resin samples were classified as non-irritants, as the government reports and published studies describing these metals both consistently reported a lack of irritating potential by iron, lead, strontium, thallium, and titanium. Only one element (3%) of the 29—lanthanum—was unable to be classified as either a skin irritant or non-irritant due to a lack of information specific to this element.

Table S3. Elements detected in resin samples and categorization of their potential to cause skin irritationa

| Element | Irritant | NIOSH Pocket Guide | OSHA Chemical Database | ACGIH® 2019 TLVs® | Reference(s) |
| --- | --- | --- | --- | --- | --- |
| Aluminum (Al) | Yes | Al = YAl sol salts = YAl oxide = YAl trioxide = Y | Al = N | Al & insol cmpds = N | Al chloride = Y (Lansdown, 1995)Al sulfate = Y (Lansdown, 1995) |
| Antimony (Sb) | Yes | Sb = Y | Sb & cmpds = N | Sb & cmpds = N+b | Sb trioxide = Y (Lansdown, 1995)Sb oxide = Y (Hostýnek et al., 1993)Sb chloride = Y (Lansdown, 1995) |
| Arsenic (As) | Yes | As (inorg) = YcAs (organic) = YAs & inorg cmpds = Y | As (inorg) = NAs (organic) = N | As (inorg) = N | As (inorg) = Y (Lansdown, 1995)As trioxide = Y (Mohamed, 1998) |
| Barium (Ba) | Yes | Ba = N/ABa chlorides = YBa nitrates = YBa sulfates = Y | Ba = N/ABa (sol cmpds) = NBa sulfates = N | Ba = N | Ba = NBa nitrates = Y (WHO, 2001)dBa sulfates = Y (WHO, 2001)d |
| Beryllium (Be) | Yes | Be metal = YcBe & Be cmpds as Be = Yc | Be & Be cmpds as Be = Ne | Be (sol) cmpds = NeBe (sol & insol) cmpds = N | Be (sol) cmpds = Y (Lansdown, 1995)Be alloys = Y (Haberman et al., 1993)Be fluoride = Y (Taylor et al., 2018) |
| Cadmium (Cd) | Yesf | Cd metal = NCdO (fume) as Cd = N | Cd metal = NCdO (fume) as Cd = N | Cd & cmpds = N | Cd chloride = Y (Geier et al., 1996; Lansdown, 1995) |
| Calcium (Ca) | Yes | Ca = N/ACa carbonate = YCa hydrate/oxide = YCa silicates = YCa sulfates = Y | Ca = N/ACa carbonate = NCa hydrate/oxide = NCa silicates = NCa sulfates = N | Ca = N/ACa hydroxide = NCa sulfate = N | Ca = NCa chloride = Y (Lansdown, 1995)Ca thioglycolate = Y (Lansdown, 1995)Ca Mg acetate = Y (Cushman et al., 1991) |
| Chromium (Cr) | Yes | Cr metal = YCr(II) cmpds as Cr = NCr(III) cmpds as Cr = NCr(VI) oxide = N | Cr metal = NCr(II) cmpds as Cr = NCr(III) cmpds as Cr = NCr(VI) oxide = N | Cr metal = NCr(III) cmpds = NCr(VI) cmpds = N | Cr (soluble) cmpds = Y (Katz and Salem, 1993)Potassium dichromate = Y (Turčić et al., 2013) |
| Cobalt (Co) | Yes | Co metal dust = YcCo metal dust & fume = YcCo carbonyl = Y | Co metal dust & fume = NCo carbonyl = NA | Co & inorg cmpds = N | Co metal = Y (Lansdown, 1995)Co chloride = Y (Turčić et al., 2013) |
| Copper (Cu) | Yes | Cu metal/fume = YcCu dusts & mists = Yc CuO fume as Co = NCu monoxide fume = NCu(II)oxide fume = N | Cu metal/fume = NCu dusts & mists = N | Cu metal/fume = NCu dusts & mists = N | Cu metal = YCu sulfate = Y (Hostynek and Maibach, 2004; Lansdown, 1995) |
| Iron (Fe) | No | Fe carbonyl = NeFe oxide dust & fume = NFe salts (sol) = Y[Fe(II) chloride, Fe(III) chloride, Fe sulfate, Fe nitrate] | Fe carbonyl = N Fe oxide dust & fume = NFe salts (sol) = N | Fe oxide = NFe salts (soluble) = N+b | Fe = N (European Chemicals Agency, 2018) |
| Lanthanum (La) | --g | La = N/A | La = N/A | La = N/A | La = N/A |
| Lead (Pb) | No | Pb = N | Pb (inorg) = N | Pb (inorg) = N | Pb = N/A |
| Lithium (Li) | Yesf | Li = N/ALi hydride = Y | Li = N/ALi hydride = N | Li = N/ALi hydride = N | Li = N (0)Li succinate = Y (Cuelenaere et al., 1992) |
| Magnesium (Mg) | Yesf | Mg = N/AMgO fume = NMg carbonate = Y | Mg = N/AMgO fume = N | Mg = N/AMgO fume = N | Mg sulfate = N (Johnson et al., 2018a)Ca Mg acetate = Y (Cushman et al., 1991) |
| Manganese (Mn) | Yesf | Mn metal = NMn cmpds/fume = NMn oxide/trioxide = N | Mn cmpds/fume = N | Mn & inorg cmpds = N | Mn chloride = Y (Shallcross et al., 2014)Mn oxide = Y (Shallcross et al., 2014)Potassium permanganate = Y (Shallcross et al., 2014) |
| Molybdenum (Mo) | Yesd | Mo metal = NMo (sol) = N | Mo dust & insol cmpds = NMo (sol) = N | Mo (sol) cmpds = NMo (insol cmpds) = N | Mo metal = Y (Lansdown, 1995)Sodium molybdenate = Y (Stokinger, 1981)d |
| Nickel (Ni) | Yesf | Ni metal & cmpds = NNi carbonyl = N | Ni metal/insol cmpds = NNi (sol) cmpds = NNi carbonyl = N | Ni metal/inorg cmpds = NNi (sol) inorg cmpds = NNi (insol) inorg cmpds = N | Ni sulfate = Y (Turčić et al., 2013)Ni chloride = Y (Zhang et al., 2021) |
| Phosphorous (P) | Yes | Phosphoric acid = YP = N (skin burns)P oxy/trichloride = YP trichloride = YP pentachloride = YP sulfides = Y | P = N/A | Phosphoric acid = NP = NP oxy/trichloride = NP pentachloride = NP pentasulfate = N | P (inorg) cmpds = Y (Weiner et al., 2001)P trichloride = Y (Francois and Stephen, 2015)P pentasulfide = Y (Francois and Stephen, 2015) |
| Potassium (K) | Yesf | K = N/AK hydrate/hydroxide = Y | K = N/AK hydroxide = N/AK persulfate = N/A | K hydroxide = N+b | Potassium = N (Lansdown, 1995) |
| Selenium (Se) | Yesf | Se = N | Se = N | Se = N | Se = NSe dioxide = YSe disulfide = Y (Lansdown, 1995)Selenious acid = Y (Lansdown, 1995)Se oxychloride = Y (Lansdown, 1995) |
| Silver (Ag) | Yesf | Ag = NAg nitrate = N | Ag & sol cmpds = N/A | Ag & fumes = NAg (sol) cmpds = N | Ag = Y (Group and Lea, 2010) |
| Strontium (Sr) | No | Sr = N/A | Sr = N/A | Sr = N/A | Sr = N/ASr chloride = NSr nitrate = N (Fatemi et al., 2016)Sr chloride = N (Lee et al., 2009) |
| Thallium (Th) | No | Th (sol cmpds) = Ne | Th (sol cmpds) = Ne  | Th & cmpds = Ne | Thallium = N/A |
| Tin (Sn) | Yes | Sn metal = YSn (organic cmpds) = YSn(II)oxide = NSn(IV)oxide = N | Sn metal = NSn (organic cmpds) = Ne,hSn oxide = N | Sn (inorg) cmpds = NSn (organic cmpds) = Ne | Sn (organic cmpds) = Y (Winship, 1988)Sn chloride = Y (de Fine Olivarius et al., 1993)Tributyl tin oxide = Y (Lewis and Emmett, 1987; Lyle, 1958) |
| Titanium (Ti) | No | Ti = N/ATiO2 = N | Ti = N/ATiO2 = N | Ti = N/ATiO2 = N | Ti = N/A |
| Yttrium (Y) | Yesd | Y = N | Y = N | Y = N | Y nitrate = Y (Lambert et al., 1993)d |
| Zinc (Zn) | Yes | Zn = N/AZn chloride fume = YZn oxides = NZn stearate = Y | Zn = N/AZn chloride fume = NZn oxides = NZn stearate = N | Zn = N/AZn oxides = N | Zn = NZn chloride = Y (Lansdown, 1995)Zn sulfate = YZn acetate = Y (Lansdown, 1995) |
| Zirconium (Zr) | Yes | Zr = Y (granuloma) | Zr = N | Zr = N | Zr = Y (Epstein and Allen, 1964) (granuloma) |

a cmpds = compounds, inorg = inorganic, insol = insoluble, sol = soluble, Y = Yes, N = No, N/A = not applicable.

b The current TLV for this metal has been derived from exposure-response relationships wherein skin irritation is the primary endpoint of interest.

c Listed by the NIOSH pocket guide as having the potential to cause dermatitis (irritant or allergic type is not specified).

d Classification of the metal’s irritation potential reflects data obtained specifically from *in vivo* animal studies (only provided when no human data exists for the respective metal).

e Listed in NIOSH Pocket Guide to Chemical Hazards, OSHA Technical Manual, Ch. 2 (Appx A), or ACGIH® TLV® book as having Skin Notation. According to Dotson et al. Reg Tox Pharm. (2011) a NIOSH Skin Notation indicates “potential for dermal absorption; prevent skin contact”, an OSHA Skin Notation indicates “potential for dermal absorption”, and an ACGIH Skin Notation indicates “Potential significant contribution to overall exposure by the cutaneous route.”

f Occasionally reported as a skin irritant.

g --= No classification due to lack of existing information.

h OSHA Chemical Database says NIOSH has skin notation for organic compounds but there is nothing in NIOSH Pocket Guide.

### Skin sensitizers

Twenty-two of the 29 total elements (76%) quantified by ICP were ultimately classified as potential dermal sensitizers; however, based on collective findings from the literature review, only 6 (27%) of the 22 positively identified sensitizers appeared to likely pose a significant hazard with respect to allergic contact allergy. Specifically, arsenic, beryllium, chromium, cobalt, copper, and nickel were the only elements that were consistently recognized as viable contact allergens in multiple government documents, as well as in primary research findings (ATSDR, 2005; OSHA, 2011). This observation was consistent with findings from epidemiological studies of metal allergy, as these agents represent some of the most frequently implicated contact allergens responsible for causing allergic contact dermatitis (ACD) in the general population (Bocca and Forte, 2009; Bregnbak et al., 2015; Thyssen and Menne, 2010). It is also worth noting that these elements exhibit the distinctive propensity to induce dermal sensitization when encountered in various chemical formulations—a feature evident in many of the government documents referenced here.

Concurrently, the other 16 (73% of the 22 total identified sensitizers) elements classified as potential skin sensitizers likely represent uncommon, though not completely insignificant, sources of contact allergy. These elements were not routinely recognized in government guidance documents as prominent hazards with respect to dermal hypersensitivity responses, but evidence generated from human case reports and *in vivo* studies suggests that certain individuals may be at risk for developing contact sensitivity to these agents (Forte et al., 2008). Some of the elements comprising this collection of potential sensitizers included aluminum, iron, silver, tin, and zinc—metals, which have been implicated in many epidemiological studies of metal-induced ACD, though most frequently associated with very low rates of allergic responsivity (Davis et al., 2011; Forte et al., 2008). Unlike the other elements classified as prominent dermal sensitizers, majority of these elements seem to exhibit immunogenic activity that is selectively associated with a limited number of chemical formulations. For example, chromium is able to trigger allergic sensitization when present in numerous different valence states and compounds with varying degrees of solubility; comparatively, while zinc is capable of causing skin sensitization, this process is selectively associated with only a few soluble formulations of the metal, including zinc sulfate (Bregnbak et al., 2015; Hansen et al., 2003; Hansen et al., 2006).

Six of the 29 total elements (21%) were identified as non-sensitizers based on available information. Two of these elements—barium and magnesium—have been repeatedly demonstrated (in various formulations) to lack any notable degree of allergenic activity with respect to the skin, even when administered at doses exceeding concentrations of 25% (Cushman et al., 1991; Elmore, 2005; Frykstrand et al., 2015; Hartwig et al., 2017; Hiatt et al., 1988; Johnson et al., 2018a; Johnson et al., 2018b). The other four elements—lanthanum, lithium, thallium, and yttrium— have been occasionally shown to produce negative results in assessments of skin sensitization; however, the limited amount of information that currently exists regarding these elements is also a likely contributor to their classification as non-sensitizers.

For one of the 29 total elements (3%) present in the resin samples, no information could be obtained from existing literature peer-reviewed literature, government reports, or PubChem database records regarding the potential for strontium to cause skin sensitization. Strontium’s allergenic potential has yet to be studied in human subjects*, in vivo* models, or *in vitro* assays; accordingly, future studies will be required to clarify whether this element has the capacity to cause dermal sensitization and the development of contact allergy.

Table S4. Elements detected in resin samples and categorization of their skin sensitization potentiala

| Element | Sensitizer | NIOSH Pocket Guide | OSHA Chemical Database | ACGIH® 2019 TLVs® | Literature |
| --- | --- | --- | --- | --- | --- |
| Aluminum (Al) | Yesb | Al = NAl sol salts = NAl oxide = NAl trioxide = N | Al = N | Al & insol cmpds = N | Al chloride = Y (Forte et al., 2008; Lansdown, 1995)Al sulfate = Y (Lansdown, 1995)Al acetate = Y (Lansdown, 1995; O'driscoll et al., 1991)Al hydroxide = Y (Böhler‐Sommeregger and Lindemayr, 1986)  |
| Antimony (Sb) | Yesb | Sb = N | Sb & cmpds = N | Sb & cmpds = N | Sb trioxide = Y (Lansdown, 1995; Wu and Chen, 2017) |
| Arsenic (As) | Yes | As (inorg) = YcAs (organic) = YdAs & inorg cmpds = N | As (inorg) = NAs (organic) = N | As (inorg) = N | Arsenical cmpds = Y (Lansdown, 1995; Wahlberg and Boman, 1986)As trioxide = Y (Holmqvist, 1951) |
| Barium (Ba) | No | Ba = N/ABa chlorides = NBa nitrates = NBa sulfates = N | Ba = N/ABa (sol cmpds) = NBa sulfates = N | Ba = N | Ba = N (Johnson et al., 2018b) |
| Beryllium (Be) | Yes | Be metal = YcBe & Be cmpds as Be = Yc | Be & Be cmpds as Be = Ne | Be (sol) cmpds = YeBe (sol & insol) cmpds = N | Be = Y (Davis et al., 2011; Lansdown, 1995)Be (sol) cmpds = Y (Forte et al., 2008; Haberman et al., 1993)Be alloys = Y (Forte et al., 2008) |
| Cadmium (Cd) | Yesb | Cd metal = NCdO (fume) as Cd = N | Cd metal = NCdO (fume) as Cd = N | Cd & cmpds = N | Cd metal = Y (Lansdown, 1995; Motolese et al., 1993; Wahlberg and Wennersten, 1977)Cd chloride = Y (Motolese et al., 1993) |
| Calcium (Ca) | Yesb | Ca = N/ACa carbonate = NCa hydrate/oxide = NCa silicates = NCa sulfates = N | Ca = N/ACa carbonate = NCa hydrate/oxide = NCa silicates = NCa sulfates = N | Ca = N/ACa hydroxide = NCa sulfate = N | Ca = N (Lansdown, 1995)Ca hypochlorite = Y (Salphale and Shenoi, 2003)Ca ammonium nitrate = Y (Pasricha and Gupta, 1983) |
| Chromium (Cr) | Yes | Cr metal = NCr(II) cmpds as Cr = YCr(III) cmpds as Cr = YCr(VI) oxide = Y | Cr metal = NCr(II) cmpds as Cr = NCr(III) cmpds as Cr = NCr(VI) oxide = N | Cr metal = NCr(III) cmpds = YCr(VI) cmpds = Ye | Cr metal = Y (Iyer et al., 2002)Cr(VI) cmpds = Y (Forte et al., 2008; Lansdown, 1995) Cr(III) cmpds as Cr = Y (Bregnbak et al., 2015)Cr(VI) oxide = Y (Forte et al., 2008) |
| Cobalt (Co) | Yes | Co metal dust = YcCo metal dust & fume = YcCo carbonyl = N | Co metal dust & fume = NCo carbonyl = NA | Co & inorg cmpds = Y | Co metal = Y (Forte et al., 2008; Militello et al., 2020)Co alloys = Y (Arslan et al., 2015)Co chloride = Y (De La Cuadra and Grau‐Massanés, 1991) |
| Copper (Cu) | Yes | Cu metal/fume = YcCu dusts & mists = Yc CuO fume as Co = NCu monoxide fume = NCu(II)oxide fume = N | Cu metal/fume = NCu dusts & mists = N | Cu metal/fume = NCu dusts & mists = N | Cu metal = Y (Davis et al., 2011; Forte et al., 2008; Nonaka et al., 2011)Cu alloys = Y (Suárez et al., 2002)Cu oxide = Y (Motolese et al., 1993)Cu sulfate = Y (Saltzer and Wilson, 1968) |
| Iron (Fe) | Yesb | Fe carbonyl = NeFe oxide dust & fume = NFe salts (sol) = Nd | Fe carbonyl = N Fe oxide dust & fume = NFe salts (sol) = N | Fe oxide = NFe salts (sol) = N | Fe = Y (Davis et al., 2011; Lansdown, 1995; Nonaka et al., 2011)Ferric chloride = Y (Baer, 1973)Ferric sulfate = Y (Hemmer et al., 1996) |
| Lanthanum (La) | No | La = N/A | La = N/A | La = N/A | La = N (Diezel et al., 1989) |
| Lead (Pb) | Yesb | Pb = N | Pb (inorg) = N | Pb (inorg) = N | Pb oxide = Y (Czarnecki and Fritsch, 1978)Pb acetate = Y (Czarnecki and Fritsch, 1978) |
| Lithium (Li) | No | Li = N/ALi hydride = N | Li = N/ALi hydride = N | Li = N/ALi hydride = N | Li = N (0)f |
| Magnesium (Mg) | No | Mg = N/AMgO fume = NMg carbonate = N | Mg = N/AMgO fume = N | Mg = N/AMgO fume = N | Mg sulfate = N (Johnson et al., 2018a)Mg carbonate = N (Frykstrand et al., 2015)Mg ascorbate = N (Elmore, 2005) |
| Manganese (Mn) | Yesb | Mn metal = NMn cmpds/fume = NMn oxide/trioxide = N | Mn cmpds/fume = N | Mn & inorg cmpds = N | Mn metal = N (Davis et al., 2011; Lansdown, 1995; Nonaka et al., 2011)Mn dioxide = Y (Motolese et al., 1993)Mn alloys = Y (Ortiz-Ruiz et al., 2006) |
| Molybdenum (Mo) | Yesb | Mo metal = NMn (sol) = N | Mo dust & insol cmpd = NMn (sol) = N | Mo & insol cmpd = NMn (sol) = N | Mo metal = Y (Lansdown, 1995; Navarro-Triviño et al., 2021)Mo chloride = Y (Krecisz et al., 2006) |
| Nickel (Ni) | Yes | Ni metal & cmpds = YNi carbonyl = N | Ni metal/insol cmpds = NNi (sol) cmpds = NNi carbonyl = N | Ni metal/inorg cmpds = NNi (sol) inorg cmpds = NNi (insol) inorg cmpds = N | Ni metal = Y (Militello et al., 2020)Ni chloride = Y (Jerschow et al., 2001)Ni sulfate = Y (Forte et al., 2008; Lansdown, 1995)  |
| Phosphorous (P) | Yesb | Phosphoric acid = NP = NP oxy/trichloride = NP trichloride = NP pentachloride = NP sulfides = N | P = N/A | Phosphoric acid = NP = NP oxy/trichloride = NP pentachloride = NP pentasulfate = N | P = N (0)P inorg cmpds = Y (Abdullah et al., 1997) |
| Potassium (K) | Yesb | K = N/AK hydrate/hydroxide = N | K = N/AK hydroxide = N/AK persulfate = N/A | K = N/AK hydroxide = N | K = N (Lansdown, 1995)K chloride = Y (Zabala et al., 1993) |
| Selenium (Se) | Yesb | Se = N | Se = N | Se = N | Se = NSe disulfide = Y (Lansdown, 1995)Sodium selenite = Y (Richter et al., 1987) |
| Silver (Ag) | Yesb | Ag = NAg nitrate = N | Ag & sol cmpds = blank | Ag & fumes = NAg (sol) cmpds = N | Ag = Y (Lea, 2010; Lopez Rodriguez and Goday Bujan, 2020)Ag nitrate = Y (García et al., 2016) |
| Strontium (Sr) | --g | Sr = N/A | Sr = N/A | Sr = N/A | Sr = N/A |
| Thallium (Th) | No | Th (sol cmpds) = Ne | Th (sol cmpds) = Ne | Th & cmpds = Ne | Th = Ne (Osorio-Rico et al., 2017) |
| Tin (Sn) | Yesb | Sn metal = NSn (organic cmpds) = NSn(II)oxide = NSn(IV)oxide = N | Sn metal = NSn (organic cmpds) = Ne,hSn oxide = N | Sn (inorg) cmpds = NSn (organic cmpds)= Ne | Sn = Y (Davis et al., 2011; Nonaka et al., 2011)Sn(II) chloride = Y (de Fine Olivarius et al., 1993; van Amerongen et al., 2020)Stannous fluoride = Y (van Amerongen et al., 2020) |
| Titanium (Ti) | Yesb | Ti = N/ATiO2 = N | Ti = N/ATiO2 = N | Ti = N/ATiO2 = N | Ti = Y (Davis et al., 2011)Ti nitrate = Y (Zigante et al., 2020)Ti oxalate = Y (Zigante et al., 2020) |
| Yttrium (Y) | No | Y = N | Y = N | Y = N | Y = N/A |
| Zinc (Zn) | Yesb | Zn = N/AZn chloride fume = NZn oxides = NZn stearate = N | Zn = N/AZn chloride fume = NZn oxides = NZn stearate = N | Zn = N/AZn oxides = N | Zn = Y (Davis et al., 2011; Nonaka et al., 2011)Zn sulfate = Y (Yanagi et al., 2005)Zn oxide = Y (Bircher, 2018) |
| Zirconium (Zr) | Yesb | Zr = N (granuloma) | Zr = N | Zr = N | Zr = Y (Lansdown, 1995)Zr chloride = N (Ikarashi et al., 1996)Zr dioxide = Y (Epstein and Allen, 1964) |

a cmpds = compounds, inorg = inorganic, insol = insoluble, sol = soluble, Y = Yes, N = No, N/A = not applicable.

b Occasionally reported as a skin sensitizer.

c Listed by the NIOSH pocket guide as having the potential to cause dermatitis (irritant or allergic type is not specified).

d Listed by the NIOSH pocket guide as having the potential to cause “irritation, possible dermatitis.”

e Listed in NIOSH Pocket Guide to Chemical Hazards, OSHA Technical Manual, Ch. 2 (Appx A), or ACGIH® TLV® book as having Skin Notation. According to Dotson et al. Reg Tox Pharm. (2011) a NIOSH Skin Notation indicates “potential for dermal absorption; prevent skin contact”, an OSHA Skin Notation indicates “potential for dermal absorption”, and an ACGIH Skin Notation indicates “Potential significant contribution to overall exposure by the cutaneous route.”

f (0) Metal has been determined to exhibit a lack of skin sensitizing potential based on findings from PubMed search (metal AND skin AND allergy/sensitization).

g --=No classification due to lack of existing information.

h OSHA Chemical Database says NIOSH has skin notation for organic compounds but there is nothing in NIOSH Pocket Guide.

## Categorization of organic substances

Eight of 10 target substances were quantified (all but n-hexane and benzene) and 79 substances were tentatively identified by GC analysis in at least one resin sample. Supplemental Tables S5 and S6 list these substances and whether they were categorized as an irritant and/or a sensitizer, respectively.

### Skin irritants

Among the 54 organic substances categorized as skin irritants, for 93% (50/54) there was human evidence in multiple studies to support our conclusions (i.e., substances indicated by “Yes” without a footnote in Table S5). One substance, dimethoxydimethylsilane, was categorized as a rare irritant (designated by “Yesb” in Table S5). Three substances were categorized as irritants based only on *in vivo* animal data (designated by “Yesc” in Table S5). For example, methyl isobutyl ketone (MIBK) was designated a skin irritant in the NIOSH Pocket Guide to Chemical Hazards and a review of available *in vivo* animal testing data by the Cosmetic Ingredient Review Expert (CIRE) Panel concluded that it was an irritant (Johnson, 2004; NIOSH, 2022). A record for MIBK in the PubChem database indicated that this substance was not a skin irritant. (<https://pubchem.ncbi.nlm.nih.gov/compound/7909>); however, based on the NIOSH designation and *in vivo* animal data, for purposes of the current study, MIBK was categorized as a skin irritant.

For three substances (1,4-dioxane, benzyl alcohol, glycerin), categorization as a skin irritant was made based on human data, though available literature was sometimes conflicting. The NIOSH Pocket Guide for Chemical Hazards designated 1,4-dioxane as a skin irritant (NIOSH, 2022). The Agency for Toxic Substances and Disease Registry (ATSDR), in a Health Evaluation of 1,4-dioxane, concluded based on a literature review of two animal studies, that 1,4-dioxane was a skin irritant (DeRosa et al., 1996). Later, ATSDR published a Toxicological Profile for 1,4-dioxane citing the same animal studies, but concluded it was not a skin irritant (ATSDR, 2012). The PubChem database record for this chemical (<https://pubchem.ncbi.nlm.nih.gov/compound/31275>) cites numerous reports that indicated 1,4-dioxane was a skin irritant in humans and experimental animals, so it was categorized as an irritant for this study. Lashmar et al. applied 10% benzyl alcohol to skin of nude mice and reported it was a severe skin irritant (Lashmar et al., 1989). Benzyl alcohol is used as a fragrance, preservative, and pH adjuster in some cosmetics products at concentrations less than 5% (Johnson et al., 2017). The Research Institute for Fragrance Materials (RIFM) Expert Panel for Fragrance Safety reviewed available literature on the irritant properties of benzyl alcohol. Benzyl alcohol was reported to cause skin irritation among humans in nine of 14 reviewed studies; most responses were to 5 to 20% benzyl alcohol. Responses in laboratory animals following dermal application of benzyl alcohol ranged from mild to severe irritation. RIFM concluded that benzyl alcohol was not a skin irritant at concentrations likely to be encountered in consumer products that contain this fragrance (Belsito et al., 2012). Canavez et al. performed a hazard assessment and risk characterization for benzyl alcohol and concluded that it presents a low risk of skin irritation based on expected concentrations in cosmetics products (Canavez et al., 2021). However, concentrations of benzyl alcohol used in cosmetic products (generally <5%) are expected to be lower than could be encountered in occupational scenarios. Based on the nine human studies that reported skin irritation, for the purposes of the current study, benzyl alcohol was categorized as a skin irritant. Glycerin (glycerol) was designated a skin irritant in the NIOSH Pocket Guide to Chemical Hazards (NIOSH, 2022). Some reports in the literature indicate that glycerin has anti-irritant properties (Atrux-Tallau et al., 2010; Korponyai et al., 2011; Szél et al., 2015), whereas other studies have reported that glycerin is slightly irritating to skin for humans and some animal species (Becker et al., 2019; Calabria et al., 2008). Though the literature is conflicting on the irritant properties of glycerin, given that there are reports of skin irritation in humans, for purposes of this study, glycerin was categorized as a skin irritant.

Information was available in the literature to determine that 11 substances were not irritants (hexamethyldisiloxane, dimethyl sulfoxide, tetrahydrofurfuryl alcohol, bisphenol-A, camphene, *N,N*-dimethylacrylamide, dodecamethylcyclohexasiloxane, triethylene glycol, tetrahydrofuran, 2-butanone, and 1,2-propylene glycol). use of diabetes medical devices such as glucose sensors and insulin pumps are associated with development of contact dermatitis among some users. Patch testing results implicate isobornyl acrylate and *N,N*-dimethylacrylamide as the main allergens in these devices and sensors that are responsible for development of ACD among some users; however, it is possible that for some of these observed cases, dermatitis is irritative contact dermatitis (ICD) rather than ACD (Herman et al., 2020). Development of dermatitis from use of diabetes medical devices may stem from skin contact with plastics, glues, and adhesives. Given the numerous potential offending agents, clinical examination alone does not allow a distinction between ICD and ACD (Herman et al., 2020). Current knowledge limits understanding of whether *N,N*-dimethylacrylamide is a skin irritant, so for purpose of this study it was not categorized as an irritant. The Cosmetic Ingredient Review Expert Panel reported that 2-ethoxyethyl acetate was a mild skin irritant in laboratory animals (Johnson, 2002). NIOSH, in development of a Skin Notation Profile for 2-ethoxyethyl acetate, noted that much of the available laboratory animal testing data used a 24-hour exposure, which was much longer than a typical 8-hour work shift and concluded that this substance was not a significant skin irritant under typical workplace scenarios (NIOSH, 2014). The NIOSH Pocket Guide to Chemical Hazards designated 2-butanone as a skin irritant (NIOSH, 2022). Wahlberg exposed the volar forearm of one male volunteer to 2-butanone (methyl ethyl ketone) for up to 5 minutes and reported that it was not a skin irritant (Wahlberg, 1984). The ATSDR reviewed available literature on dermal effects of 2-butanone (ATSDR, 2020a) and cited one study that indicated exposure to 2-butanone caused skin irritation among 41 workers; however, the study design was deemed inadequate to be used to derive health guidance values. Additionally, the ATSDR noted that prior published toxicology studies using rabbits and guinea pigs exposed to undiluted 2-butanone developed only minimal irritation. Based on these reports, 2-butanone was not categorized as a skin irritant for the current study.

For 22 of 87 (25%) organic substances, no information could be found on their skin irritation potential in the peer-reviewed literature, Government reports, or records in the PubChem database: methoxytrimethylsilane, 1-methoxyacetate ethanol, 5-methyl-2(5H)-furanone, *(Z)-*2-butenoic acid, *(Z)-*methylester-2-butenoic acid, *N*-(2-Methylpropyl)formamide, 2-hydroxyethyl acetate, nitrosobenzene, 2-methyl-1,3-dioxolane, 2-hydroxypropyl methacrylate, 3,3,5-trimethylcyclohexene, 1-nitrosopiperidine, 2,7-dimethyl-1,6-octadiene, 4,4’-sulfonylbisbenzamine, decamethylcyclopentasiloxane, tetradecamethylcycloheptasiloxane, ethylene glycol dimethacrylate, *(E)-*2-butenoic acid, 3,5,5-trimethyl cyclohexene, 1,1,3-trimethyl cyclohexane, *(E)-*2-penten-1-ol, and allyl crotonate.

Table S5. Organic substances in resin samples and categorization of their skin irritation potential

| Substance | CAS No. | Irritant | Reference(s) |
| --- | --- | --- | --- |
| Acetone | 67-64-1 | Yes | (ATSDR, 1994; Branco et al., 2005; NIOSH, 2022) |
| Isopropyl alcohol | 67-63-0 | Yes | (Tasar et al., 2021) |
| Methyl methacrylate | 80-62-6 | Yes | (Borak et al., 2011; NIOSH, 2022; Tokumura et al., 2010; WHO, 1998a) |
| Toluene | 108-88-3 | Yes | (Angelova-Fischer et al., 2012; NIOSH, 2022; Wahlberg, 1984; Wigger-Alberti et al., 2000) |
| Ethylbenzene | 100-41-4 | Yes | (ATSDR, 2010; Fishbein, 1985; NIOSH, 2022) |
| *m,p*-Xylene | 1330-20-7 | Yes | (Ahaghotu et al., 2005; NIOSH, 2022) |
| Styrene | 100-42-5 | Yes | (NIOSH, 2022) |
| *o*-Xylene | 95-47-6 | Yes | (Ahaghotu et al., 2005; NIOSH, 2022) |
| Methoxytrimethylsilane | 1825-61-2 | --a | N/A |
| Dimethoxydimethylsilane | 1112-39-6 | Yesb | <https://pubchem.ncbi.nlm.nih.gov/compound/66187>  |
| Hexamethyldisiloxane | 107-46-0 | No | <https://pubchem.ncbi.nlm.nih.gov/compound/24764>  |
| Acetic acid | 64-19-7 | Yes | (Banerjee et al., 2003; Soltanipoor et al., 2018) |
| Acrylic acid | 79-10-7 | Yes | (Commission, 2002; NIOSH, 2017, 2022; Tokumura et al., 2010) |
| Methacrylic acid | 79-41-4 | Yes | (NIOSH, 2022; CIRE Panel, 2005b; Tokumura et al., 2010) |
| 1-Methoxyacetate ethanol | 4382-77-8 | -- | N/A |
| 2-Butoxyethanol | 111-76-2 | Yes | (ATSDR, 1998; NIOSH, 2011b, 2022; WHO, 1998b; Zissu, 1995) |
| Isopropyl methacrylate | 4655-34-9 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/20769>  |
| Dimethylester carbonic acid | 616-38-6 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/12021> |
| Methyl isobutyl ketone | 108-10-1 | Yesc | (Johnson, 2004; NIOSH, 2022) |
| Tetramethoxymethane | 1850-14-2 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/74613> |
| 5-Methyl-2(5H)-furanone | 591-11-7 | -- | N/A |
| *(Z)*-2-Butenoic acid | 503-64-0 | -- | N/A |
| Butylester acetic acid | 123-86-4 | Yes | (NIOSH, 2022; WHO, 2005) |
| Ethanol | 64-17-5 | Yes | (NIOSH, 2022) |
| Methyl acrylate | 96-33-3 | Yes | (NIOSH, 2022; Tokumura et al., 2010; WHO, 1998a) |
| Allyl alcohol | 107-18-6 | Yes | (NIOSH, 2022; Politano et al., 2006) |
| 1,1,2-Trimethoxyethane | 24332-20-5 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/47520> |
| *(Z)*-Methylester-2-butenoic acid | 4358-59-2 | -- | N/A |
| Triethanolamine | 102-71-6 | Yes | NTP (Knaak et al., 1997; Lessmann et al., 2009; NTP, 2004) |
| *N*-(2-Methylpropyl)formamide | 6281-96-5 | -- | N/A |
| 1-Butanol | 71-36-3 | Yes | (McLain, 2008; NIOSH, 2022) |
| 1-Methoxy-2-propanol | 107-98-2 | Yes | (NIOSH, 2022; CIRE Panel, 2008) |
| Dimethyl sulfoxide | 67-68-5 | No | (Banerjee et al., 2003; Primavera and Berardesca, 2005) |
| Cyclohexanone | 108-94-1 | Yes | (NIOSH, 2020, 2022) |
| 1-Chlorobutane | 109-69-3 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/8005>  |
| Butyl isocyanate | 111-36-4 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/8110> |
| 2-Chloroethyl acrylate | 2206-89-5 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/16627> |
| 2-Hydroxyethyl acetate | 542-59-6 | -- | N/A |
| 2,2-Dimethoxypropane | 77-76-9 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/6495> |
| Nitrosobenzene | 586-96-9 | -- | N/A |
| Tetrahydrofurfuryl alcohol | 97-99-4 | No | (Lashmar et al., 1989) |
| Ethyl butyrate | 105-54-4 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/7762> |
| Triethylamine | 121-44-8 | Yes | (NIOSH, 2022) |
| 2-Methyl-1,3-dioxolane | 497-26-7 | -- | N/A |
| 1,4-Dioxane | 123-91-1 | Yes | (DeRosa et al., 1996; ILO, 2008; NIOSH, 2022); <https://pubchem.ncbi.nlm.nih.gov/compound/31275>  |
| 2-Methoxyethyl acrylate | 3121-61-7 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/18392>  |
| Propylene carbonate | 108-32-7 | Yes | (CIRE Panel, 1987) |
| 1,1'-Thiobis-benzene | 139-66-2 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/8766>  |
| Bisphenol A | 80-05-7 | No | (Hulzebos and Gerner, 2010; NIOSH, 2011a) |
| 2-Hydroxyethyl methacrylate | 868-77-9 | Yes | (Tokumura et al., 2010) |
| 2-Hydroxyethyl acrylate | 818-61-1 | Yes | (Tokumura et al., 2010) |
| 2-Hydroxypropyl methacrylate | 923-26-2 | -- | N/A |
| 3,3,5-Trimethylcyclohexanol | 116-02-9 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/8298>  |
| 3,3,5-Trimethylcyclohexene | 503-45-7 | -- | N/A |
| Camphene | 79-92-5 | No | <https://pubchem.ncbi.nlm.nih.gov/compound/6616>  |
| Bisphenol A diglycidyl ether resin | 1675-54-3 | Yes | (Peristianis et al., 1988) |
| 1-Nitrosopiperidine | 100-75-4 | -- | N/A |
| 2,4,6-Trimethoxy-1,3,5-triazine | 877-89-4 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/13419>  |
| 2,4,6-Trimethylbenzoic acid | 480-63-7 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/10194>  |
| 2,4-bis(1,1-Dimethylethyl)phenol | 96-76-4 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/7311>  |
| Butylated hydroxytoluene | 128-37-0 | Yesc | (Lanigan and Yamarik, 2002; NIOSH, 2022) |
| 2,7-Dimethyl-1,6-octadiene | 40195-09-3 | -- | N/A |
| 2,2-Dimethyl-1,3-propanediol | 126-30-7 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/31344>  |
| Hexamethylene diacrylate  | 13048-33-4 | Yes | (Malten et al., 1979) |
| *N,N*-Dimethylacrylamide | 2680-03-7 | No | (Herman et al., 2020) |
| 3,3'-Sulfonyldianiline | 599-61-1 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/11741>  |
| 4,4'-Sufonylbisbenzamine | 80-08-0 | -- | N/A |
| Decamethylcyclopentasiloxane | 541-02-6 | -- | N/A |
| Dodecamethylcyclohexasiloxane | 540-97-6 | No | <https://pubchem.ncbi.nlm.nih.gov/compound/10911>  |
| Tetradecamethylcycloheptasiloxane | 107-50-6 | -- | N/A |
| Triethylene glycol | 112-27-6 | No | (Ballantyne and Snellings, 2007; CIRE Panel, 2006) |
| Triethylene glycol dimethacrylate | 109-16-0 | Yes | (Heratizadeh et al., 2018; Van Miller et al., 2003) |
| Tetraethylene glycol diacrylate | 17831-71-9 | Yes | (Nethercott et al., 1984) |
| Ethylene glycol dimethacrylate | 97-90-5 | -- | N/A |
| Benzyl alcohol | 100-51-6 | Yes | (Belsito et al., 2012; Lashmar et al., 1989) |
| Glycerin | 56-81-5 | Yes | (Becker et al., 2019; Calabria et al., 2008; NIOSH, 2022) |
| Tetrahydrofuran | 109-99-9 | No | (Fowles et al., 2013; NIOSH, 2022) |
| Propylene glycol methyl ether acetate | 108-65-6 | Yesc | (CIRE Panel, 2008) |
| 2-Butanone | 78-93-3 | No | (ATSDR, 2020a) |
| Cyclohexane | 110-82-7 | Yes | (NIOSH, 2022) |
| *(E)*-2-butenoic acid | 107-93-7 | -- | N/A |
| 3,5,5-Trimethyl cyclohexene | 933-12-0 | -- | N/A |
| 1,1,3-Trimethyl cyclohexane | 3073-66-3 | -- | N/A |
| 2-Hexanone | 591-78-6 | Yes | (ATSDR, 2020b; NIOSH, 2022) |
| *(E)*-2-penten-1-ol | 1576-96-1 | -- | N/A |
| 1,2-Propylene glycol | 57-55-6 | No | (Lessmann et al., 2005) |
| Allyl crotonate | 20474-93-5 | -- | [N/A](https://pubchem.ncbi.nlm.nih.gov/compound/5354763)  |

a -- = No information identified in the literature.

b Occasionally reported as a skin irritant.

c Classification of the organic substance’s irritation potential reflects data obtained specifically from *in vivo* animal studies (only provided when no human data exists for the respective substance).

N/A = not applicable.

### Skin sensitizers

Twenty-three organic substances were categorized as skin sensitizers. Among these 23, for 74% (17/23) there was human evidence in multiple studies to support our conclusions (i.e., substances indicated by “Yes” without a footnote in Table S5). Four substances (styrene, butyl isocyanate, butylated hydroxytoluene, and glycerin) were categorized as a rare sensitizer (designated by “Yesb” in Table S6) and the o-, m-, and p-xylene isomers were categorized as sensitizers based only on *in vivo* animal data (designated by “Yesc” in Table S6).

Among the rare sensitizers, styrene was categorized as a skin sensitizer based on results from patch testing of boat builders (Minamoto et al., 2002). In this study, of 29 boat builders, one had a positive patch test reaction to styrene. A review of available literature indicated that undiluted butylated hydroxytoluene (BHT) caused an allergic reaction in three of 15 humans that were patch tested. In another study, some humans, most with eczematous dermatitis, had a positive patch test reaction to BHT at concentrations of < 5%, though responses were rare. Based on this literature, the CIRE Panel concluded that BHT was not a significant skin sensitizer when used in cosmetic products (Lanigan and Yamarik, 2002); however, occupational exposures to BHT are likely to be higher than in cosmetic products so for purposes of the current study, BHT was categorized as a rare skin sensitizer based on reports of positive reactions in humans to patch tests.

Literature was conflicting for some organic substances categorized as a skin sensitizer. Lessmann et al. reported that, based on human patch testing data, triethanolamine was a weak sensitizer; the prevalence of positive reactions was 1.5% among 676 male metalworkers (Lessmann et al., 2009). In a review, the National Toxicology Program reported that several studies documented prevalence of sensitization to triethanolamine among persons with occupational exposure to cutting oils and the general public that apply some cosmetics to the skin (NTP, 2004). One *in vitro* study used the *in vitro* DRPA to screen 82 chemicals for skin sensitizing potential and reported that triethanolamine was not a sensitizer (Kawakami et al., 2020). For the purposes of this study, more weight was given the available human occupational exposure data and triethanolamine was categorized as a skin sensitizer. Results of a study with the *in vitro* DRPA indicated that benzyl alcohol was not a skin sensitizer (Kawakami et al., 2020). In contrast, numerous studies on the sensitizing potential of benzyl alcohol in consumer products demonstrate that it was a skin sensitizer in humans (Api et al., 2015; Belsito et al., 2012; Canavez et al., 2021). For the current study, benzyl alcohol was categorized as a sensitizer. García-Gavín et al. reported that among 1450 patients that were patch tested with isopropyl alcohol, 44 of 1450 (3%) had an allergic response (García-Gavín et al., 2011). Zhang et al. developed a two-stage modified local lymph node assay (LLNA) to assess the skin sensitizing potential of chemicals. Using female BALB/c mice, results from the first screening stage of the modified LLNA indicated that isopropyl alcohol was not a sensitizer; however, this result was based on responses in two animals (Zhang et al., 2017). For the current study, more weight was given to the human data and isopropyl alcohol was categorized as a skin sensitizer.

For some organic substances, literature was conflicting and the compounds were not categorized as skin sensitizers. Acetic acid was designated a skin sensitizer in the NIOSH Pocket Guide to Chemical Hazards (NIOSH, 2022). This designation was consistent with a case report of alcohol-induced anaphylaxis with positive skin prick test to acetic acid (Añíbarro and Seoane, 2018). The direct peptide reactivity assay (DPRA) is a cell-free *in vitro* tool used to determine the skin sensitization potential of chemicals based on the intrinsic characteristic of chemical sensitizers to bind to proteins. Dik et al. adapted the DRPA to test the inhalation sensitizing potential of several chemicals and reported that acetic acid was more likely a respiratory irritant rather than a respiratory sensitizer (Dik et al., 2016). Banerjee et al. used human peripheral blood mononuclear lymphocyte cells in a predictive *in vitro* assay that measured cytokine secretion in response to chemical challenge. Cells exposed to acetic acid secreted interleukin (IL)-1α, which is upregulated by irritant molecules, but not IL-1β, which is stimulated by allergens (Banerjee et al., 2003). The RIFM Expert Panel for Fragrance Safety reviewed available literature and indicated that acetic acid was not a skin sensitizer based on an expected threshold for sensitization and the concentrations of this chemical observed in consumer products (Api et al., 2019b). Though occupational exposures to acetic acid are ostensibly higher compared with consumer products, given the scarcity of data to support acetic acid as a respiratory or skin sensitizer, for purposes of this study it was not categorized as a skin sensitizer. Parker and Turk reported that acrylic acid was a dermal sensitizer using guinea pigs though responses were only observed at the highest tested dose (5%) (Parker and Turk, 1983). The NIOSH Pocket Guide for Chemical Hazard also designated acrylic acid as a skin sensitizer (NIOSH, 2022). Since the time of those publications, comprehensive reviews of available animal and human data determined that acrylic acid was not a skin sensitizer and that historical reports of sensitization in animals was likely from the impurity α,β-diacryloxypropionic acid in acrylic acid test reagents (acrylic acid made by modern distillation methods no longer contains this impurity) (Commission, 2002; NIOSH, 2017). Based on available human occupational exposure data and uncertainties surrounding some prior animal studies, for the purposes of the current study, acrylic acid was not categorized as a skin sensitizer.

For 35 of 87 (40%) organic substances, no information could be found on their skin sensitization potential in the peer-reviewed literature, Government reports, or records in the PubChem database: methoxytrimethylsilane, dimethoxydimethylsilane, 1-methoxyacetate ethanol, dimethylester carbonic acid, methyl isobutyl ketone, tetramethoxymethane, 5-methyl-2(5H)-furanone, *(Z)-*2-butenoic acid, 1,1,2-trimethoxyethane, *(Z)-*methylester-2-butenoic acid, *N*-(2-Methylpropyl)formamide, 1-chlorobutane, 2-chloroethyl acrylate, 2-hydroxyethyl acetate, 2,2-dimethoxypropane, nitrosobenzene, 2-methyl-1,3-dioxolane, 1,4-dioxane, 1,1’-thiobis-benzene, 3,3,5-trimethylcyclohexanol, 3,3,5-trimethylcyclohexene, 1-nitrosopiperidine, 2,4,6-trimethoxy-1,3,5-triazine, 2,4,6-trimethylbenzoic acid, 2,7-dimethyl-1,6-octadiene, 3,3’-sulfonyldianiline, 4,4’-sulfonylbisbenzamine, tetradecamethylcycloheptasiloxane, toluene, cyclohexane, *(E)-*2-butenoic acid, 3,5,5-trimethyl cyclohexene, 1,1,3-trimethyl cyclohexane, *(E)-*2-penten-1-ol, and allyl crotonate. As detailed in Table S6, information was available to determine that 31 organic substances were not sensitizers.

Table S6. Organic substances in resin samples and categorization of their skin sensitization potential

| Substance | CAS No. | Sensitizer | Reference(s) |
| --- | --- | --- | --- |
| Acetone | 67-64-1 | No | (ATSDR, 1994; Pendlington et al., 2008) |
| Isopropyl alcohol | 67-63-0 | Yes | (García-Gavín et al., 2011) |
| Methyl methacrylate | 80-62-6 | Yes | (Aalto-Korte et al., 2007; Borak et al., 2011; Estlander et al., 1984; Heratizadeh et al., 2018; WHO, 1998a) |
| Toluene | 108-88-3 | --a | N/A |
| Ethylbenzene | 100-41-4 | No | (ATSDR, 2010) |
| *m,p*-Xylene | 1330-20-7 | Yesc | (Sándor et al., 2009; Zhang et al., 2017) |
| Styrene | 100-42-5 | Yesb | (Minamoto et al., 2002) |
| *o*-Xylene | 95-47-6 | Yesc | (Sándor et al., 2009; Zhang et al., 2017) |
| Methoxytrimethylsilane | 1825-61-2 | -- | N/A |
| Dimethoxydimethylsilane | 1112-39-6 | -- | N/A |
| Hexamethyldisiloxane | 107-46-0 | No | <https://pubchem.ncbi.nlm.nih.gov/compound/24764>  |
| Acetic acid | 64-19-7 | No | (Api et al., 2019b; Banerjee et al., 2003; Dik et al., 2016) |
| Acrylic acid | 79-10-7 | No | (Commission, 2002; NIOSH, 2017) |
| Methacrylic acid | 79-41-4 | No | (CIRE, 2005b) |
| 1-Methoxyacetate ethanol | 4382-77-8 | -- | N/A |
| 2-Butoxyethanol | 111-76-2 | No | (NIOSH, 2011b) |
| Isopropyl methacrylate | 4655-34-9 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/20769>  |
| Dimethylester carbonic acid | 616-38-6 | -- | N/A |
| Methyl isobutyl ketone | 108-10-1 | -- | N/A |
| Tetramethoxymethane | 1850-14-2 | -- | N/A |
| 5-Methyl-2(5H)-furanone | 591-11-7 | -- | N/A |
| *(Z)*-2-Butenoic acid | 503-64-0 | -- | N/A |
| Butylester acetic acid | 123-86-4 | No | (Kawakami et al., 2020; WHO, 2005) |
| Ethanol | 64-17-5 | No | (Kreipe et al., 2021) |
| Methyl acrylate | 96-33-3 | Yes | (ACGIH, 2019; Dearman et al., 2007) |
| Allyl alcohol | 107-18-6 | Noc | <https://pubchem.ncbi.nlm.nih.gov/compound/7858> |
| 1,1,2-Trimethoxyethane | 24332-20-5 | -- | N/A |
| *(Z)*-Methylester-2-butenoic acid | 4358-59-2 | -- | N/A |
| Triethanolamine | 102-71-6 | Yes | (Lessmann et al., 2009; NTP, 2004) |
| *N*-(2-Methylpropyl)formamide | 6281-96-5 | -- | N/A |
| 1-Butanol | 71-36-3 | No | (McLain, 2008) |
| 1-Methoxy-2-propanol | 107-98-2 | No | (Kawakami et al., 2020; CIRE Panel, 2008) |
| Dimethyl sulfoxide | 67-68-5 | No | (Banerjee et al., 2003; Cruz et al., 2009) |
| Cyclohexanone | 108-94-1 | No | (Api et al., 2020; NIOSH, 2020) |
| 1-Chlorobutane | 109-69-3 | -- | N/A |
| Butyl isocyanate | 111-36-4 | Yesb | <https://pubchem.ncbi.nlm.nih.gov/compound/8110> |
| 2-Chloroethyl acrylate | 2206-89-5 | -- | N/A |
| 2-Hydroxyethyl acetate | 542-59-6 | -- | N/A |
| 2,2-Dimethoxypropane | 77-76-9 | -- | N/A |
| Nitrosobenzene | 586-96-9 | -- | N/A |
| Tetrahydrofurfuryl alcohol | 97-99-4 | Noc | <https://pubchem.ncbi.nlm.nih.gov/compound/7360> |
| Ethyl butyrate | 105-54-4 | No | <https://pubchem.ncbi.nlm.nih.gov/compound/7762> |
| Triethylamine | 121-44-8 | No | (Yamaga et al., 2021) |
| 2-Methyl-1,3-dioxolane | 497-26-7 | -- | N/A |
| 1,4-Dioxane | 123-91-1 | -- | N/A |
| 2-Methoxyethyl acrylate | 3121-61-7 | Yes | <https://pubchem.ncbi.nlm.nih.gov/compound/18392>  |
| Propylene carbonate | 108-32-7 | No | (Panel, 1987) |
| 1,1'-Thiobis-benzene | 139-66-2 | -- | N/A |
| Bisphenol A | 80-05-7 | Yes | (NIOSH, 2011a) |
| 2-Hydroxyethyl methacrylate | 868-77-9 | Yes | (Aalto-Korte et al., 2007; Christoffers et al., 2013; Heratizadeh et al., 2018; CIRE Panel, 2005a) |
| 2-Hydroxyethyl acrylate | 818-61-1 | Yes | (Christoffers et al., 2013; Spencer et al., 2016) |
| 2-Hydroxypropyl methacrylate | 923-26-2 | Yes | (Aalto-Korte et al., 2007; Christoffers et al., 2013; Gonçalo et al., 2018; Heratizadeh et al., 2018; CIRE Panel, 2005a; Spencer et al., 2016) |
| 3,3,5-Trimethylcyclohexanol | 116-02-9 | -- | N/A |
| 3,3,5-Trimethylcyclohexene | 503-45-7 | -- | N/A |
| Camphene | 79-92-5 | No | <https://pubchem.ncbi.nlm.nih.gov/compound/6616>  |
| Bisphenol A diglycidyl ether resin | 1675-54-3 | Yes | (Bangsgaard et al., 2012; Ponting et al., 2019) |
| 1-Nitrosopiperidine | 100-75-4 | -- | N/A |
| 2,4,6-Trimethoxy-1,3,5-triazine | 877-89-4 | -- | N/A |
| 2,4,6-Trimethylbenzoic acid | 480-63-7 | -- | N/A |
| 2,4-bis(1,1-Dimethylethyl)phenol | 96-76-4 | Noc | <https://pubchem.ncbi.nlm.nih.gov/compound/7311>  |
| Butylated hydroxytoluene | 128-37-0 | Yesb | (Lanigan and Yamarik, 2002) |
| 2,7-Dimethyl-1,6-octadiene | 40195-09-3 | -- | N/A |
| 2,2-Dimethyl-1,3-propanediol | 126-30-7 | Noc | <https://pubchem.ncbi.nlm.nih.gov/compound/31344>  |
| Hexamethylene diacrylate  | 13048-33-4 | Yes | (Botella-Estrada et al., 1992; Christoffers et al., 2013; Ido et al., 2012; Kiec-Swierczynska et al., 2005; Parker and Turk, 1983) |
| *N,N*-Dimethylacrylamide | 2680-03-7 | Yes | (Mowitz et al., 2019; Ulriksdotter et al., 2020) |
| 3,3'-Sulfonyldianiline | 599-61-1 | -- | N/A |
| 4,4'-Sufonylbisbenzamine | 80-08-0 | -- | N/A |
| Decamethylcyclopentasiloxane | 541-02-6 | Nod | (Kawakami et al., 2020) |
| Dodecamethylcyclohexasiloxane | 540-97-6 | Nod | (Kawakami et al., 2020) |
| Tetradecamethylcycloheptasiloxane | 107-50-6 | -- | N/A |
| Triethylene glycol | 112-27-6 | No | (Ballantyne and Snellings, 2007; CIRE Panel, 2006) |
| Triethylene glycol dimethacrylate | 109-16-0 | Yes | (Aalto-Korte et al., 2007; Christoffers et al., 2013; Heratizadeh et al., 2018; Santosh et al., 1999) |
| Tetraethylene glycol diacrylate | 17831-71-9 | Yes | (Nethercott et al., 1984) |
| Ethylene glycol dimethacrylate | 97-90-5 | Yes | (Aalto-Korte et al., 2007; Heratizadeh et al., 2018; Kanerva et al., 1995; CIRE Panel, 2005a; Wallenhammar et al., 2000) |
| Benzyl alcohol | 100-51-6 | Yes | (Api et al., 2015; Belsito et al., 2012; Canavez et al., 2021) |
| Glycerin | 56-81-5 | Yesb | (Hannuksela and Förström, 1976; Preston and Finch, 2003; Tamagawa-Mineoka et al., 2007) |
| Tetrahydrofuran | 109-99-9 | No | (Fowles et al., 2013; NIOSH, 2022) |
| Propylene glycol methyl ether acetate | 108-65-6 | Noc | (Kawakami et al., 2020; CIRE Panel, 2008) |
| 2-Butanone | 78-93-3 | No | (Api et al., 2019a; ATSDR, 2020a) |
| Cyclohexane | 110-82-7 | -- | N/A |
| *(E)*-2-butenoic acid | 107-93-7 | -- | N/A |
| 3,5,5-Trimethyl cyclohexene | 933-12-0 | -- | N/A |
| 1,1,3-Trimethyl cyclohexane | 3073-66-3 | -- | N/A |
| 2-Hexanone | 591-78-6 | No | (ATSDR, 2020b; Johnson, 2004) |
| *(E)*-2-penten-1-ol | 1576-96-1 | -- | N/A |
| 1,2-Propylene glycol | 57-55-6 | No | (Kawakami et al., 2020; Lessmann et al., 2005; Zhang et al., 2017) |
| Allyl crotonate | 20474-93-5 | -- | N/A |

a -- = No information identified in the literature.

b Occasionally reported as a skin sensitizer.

c Classification of the organic substance’s sensitization potential reflects data obtained specifically from *in vivo* animal studies (only provided when no human data exists for the respective substance).

d Categorization based on *in vitro* data.

N/A = not applicable.

# Results

## Characteristics of irritants and/or sensitizers per resin sample

Masses of elements and organic substances categorized as irritants and/or sensitizers are summarized in Tables S7 - S9. The numbers of elements and organic substances categorized as irritants and/or sensitizers are shown as bar charts in Figures S1 and S2.

Table S7. Sum of mass concentration of unique elements quantified by ICP-OES that were categorized as irritants and/or sensitizers per resin sample.

| Manufactuer ID | Sample ID | Systema | AM Processb | Irritant and sensitizer (mg/kg) | Irritant (mg/kg) | Sensitizer (mg/kg) |
| --- | --- | --- | --- | --- | --- | --- |
| A | 1 | 2 | VP |  10.02 |  0.35 |  0.43 |
| A | 2 | 2 | VP |  976.99 |  2.94 |  --c |
| A | 3 | 2 | VP |  251.42 |  1.33 |  0.23 |
| A | 4 | 2 | VP |  13.24 |  0.08 |  -- |
| A | 5 | 2 | VP |  357.60 |  0.58 |  0.35 |
| A | 6 | 2 | VP |  307.49 |  1.49 |  -- |
| A | 7 | 2 | VP |  17.94 |  0.50 |  -- |
| A | 8 | 2 | VP |  241.00 |  1.30 |  0.45 |
| A | 9 | 2 | VP |  91.10 |  0.79 |  0.33 |
| A | 10 | 2 | VP |  8.27 |  0.05 |  -- |
| A | 11 | 1 | VP |  796.82 |  0.48 |  2.10 |
| A | 12 | 1 | VP |  571.77 |  0.09 |  1.78 |
| B | 13 | 1 | VP |  852.82 |  0.83 |  0.34 |
| C | 14 | 1 | VP | 3582.82 |  1.60 |  0.34 |
| D | 15 | 1 | VP |  257.00 |  0.15 | 27.03 |
| D | 16 | 1 | VP |  534.78 |  3.43 |  -- |
| D | 17 | 1 | VP |  534.51 |  0.10 |  -- |
| D | 18 | 1 | VP |  375.30 |  0.06 |  0.00007 |
| D | 19 | 1 | VP |  376.73 |  0.70 |  0.61 |
| D | 20 | 1 | VP |  537.86 |  0.06 |  0.44 |
| D | 21 | 1 | VP |  359.10 |  0.06 |  3.00 |
| E | 22 | 1 | VP |  177.25 |  0.13 |  0.70 |
| E | 23 | 1 | VP |  175.01 |  0.52 |  -- |
| E | 24 | 1 | VP |  212.21 |  0.07 |  -- |
| F | 25 | 1 | VP | 2120.44 |  3.30 |  1.70 |
| F | 26 | 1 | VP | 4755.25 |  1.40 |  0.38 |
| F | 27 | 1 | VP | 4425.21 | 17.90 | 19.00 |
| F | 28 | 1 | VP |  506.80 |  1.43 | 23.14 |
| F | 29 | 1 | VP |  477.23 |  0.14 |  0.39 |
| F | 30 | 1 | MJ | 1147.74 |  0.69 |  0.47 |
| F | 31 | 1 | MJ |  255.15 |  0.69 |  2.60 |
| G | 32 | 1 | MJ |  698.67 |  0.41 | 140.33 |
| G | 33 | 1 | MJ |  495.40 |  0.08 |  0.27 |
| G | 34 | 1 | MJ |  494.36 |  0.20 | 41.48 |
| G | 35 | 1 | MJ |  803.14 |  0.98 |  -- |
| G | 36 | 1 | MJ |  417.38 |  2.57 |  0.67 |
| G | 37 | 1 | MJ |  575.94 |  0.12 | 47.89 |
| G | 38 | 1 | MJ |  587.93 |  0.32 | 81.00 |
| G | 39 | 1 | MJ |  211.51 |  0.09 |  -- |

a one-part resin = single component that is not mixed with another component before use, two-part resin = two components that are mixed just prior to use.

b VP = vat photopolymerization, MJ = material jetting.

c None present.

Table S8. Sum of mass concentration of unique organic substances (quantified target compounds and semi-quantitative TICs by GC-MS) that were categorized as irritants and/or sensitizers per resin sample.

| Manufacturer | Sample ID | Systema | AM Processb | Irritant and sensitizer (mg/kg) | Irritant (mg/kg) | Sensitizer (mg/kg) |
| --- | --- | --- | --- | --- | --- | --- |
| A | 1 | 2 | VP |  15 | 20144 | -- |
| A | 2 | 2 | VP |  --c |  3490 | -- |
| A | 3 | 2 | VP |  -- |  3273 | -- |
| A | 4 | 2 | VP |  210 | 23660 |  97000 |
| A | 5 | 2 | VP |  37000 |  175 |  520 |
| A | 6 | 2 | VP |  110314 |  -- |  37000 |
| A | 7 | 2 | VP |  22170 | 39913 | 360000 |
| A | 8 | 2 | VP |  63000 |  1000 | -- |
| A | 9 | 2 | VP |  190000 |  1320 | -- |
| A | 10 | 2 | VP |  4300 |  -- | -- |
| A | 11 | 1 | VP |  104191 |  1435 | -- |
| A | 12 | 1 | VP |  151000 |  27 | -- |
| B | 13 | 1 | VP |  43701 |  398 | -- |
| C | 14 | 1 | VP |  -- |  8087 | -- |
| D | 15 | 1 | VP | 100064 |  691 | 170000 |
| D | 16 | 1 | VP |  3800 |  2305 | -- |
| D | 17 | 1 | VP |  71190 |  552 | 111800 |
| D | 18 | 1 | VP |  17350 |  234 | -- |
| D | 19 | 1 | VP |  23673 |  239 | -- |
| D | 20 | 1 | VP |  55901 |  175 |  84000 |
| D | 21 | 1 | VP |  84088 |  749 | 140790 |
| E | 22 | 1 | VP | 356000 |  -- | -- |
| E | 23 | 1 | VP |  31310 |  200 | -- |
| E | 24 | 1 | VP |  62638 |  335 | -- |
| F | 25 | 1 | VP |  -- | 11952 |  1500 |
| F | 26 | 1 | VP |  -- | 10800 | -- |
| F | 27 | 1 | VP |  -- | 11600 | -- |
| F | 28 | 1 | VP |  46000 |  3763 | -- |
| F | 29 | 1 | VP |  53000 |  14 | -- |
| F | 30 | 1 | MJ |  24000 |  9550 | -- |
| F | 31 | 1 | MJ |  76064 |  607 | 130000 |
| G | 32 | 1 | MJ |  4720 |  1462 | -- |
| G | 33 | 1 | MJ |  13123 |  199 | -- |
| G | 34 | 1 | MJ |  8826 |  162 | -- |
| G | 35 | 1 | MJ |  5150 |  1666 | -- |
| G | 36 | 1 | MJ |  5186 |  1548 | -- |
| G | 37 | 1 | MJ |  4616 |  361 | -- |
| G | 38 | 1 | MJ |  3529 |  556 | -- |
| G | 39 | 1 | MJ  |  80628 |  1300 | -- |

a one-part resin = single component that is not mixed with another component before use, two-part resin = two components that are mixed just prior to use.

b VP = vat photopolymerization, MJ = material jetting.

c None present.

Table S9. Proportion of total chromium (Cr) in the form of hexavalent chromium (Cr(VI))

|  |  |  |  |
| --- | --- | --- | --- |
| Sample ID | Total Cr | Cr (VI) | Cr(VI)/Total Cr (%) |
| 5\* | 0.6 | <0.006 | N/A |
| 6\* | 2.7 |  0.1 | 4.1 |
| 12\* | 0.25 |  0.009 | 3.4 |
| 13\* | 0.2 | <0.006 | N/A |
| 14 | 3.9 |  0.3 | 6.4 |
| 18\* | 0.1 | <0.006 | N/A |
| 20\* | 0.3 | <0.006 | N/A |
| 24\* | 0.2 |  0.009 | 4.4 |
| 25 | 8.9 |  2.1 | 23.6 |
| 27 | 20.0 |  1.4 | 7.0 |
| 28\* | 0.4 | <0.006 | N/Aa |
| 29\* | 25.0 |  0.2 | 0.8 |
| 32\* | 36 |  0.02 | 0.05 |
| 34\* | 0.12 |  0.007 | 5.7 |
| 35\* | 0.16 |  0.01 | 7.5 |
| 36\* | 0.08 |  0.007 | 8.4 |
| 37 | 0.24 |  --b | N/A |
| 38\* | 0.61 | <0.006 | N/A |
| 39 | 0.21 |  0.03 | 13.8 |

\* Resins were not entirely broken-down during sample preparation and results are expected to be biased low.

a Cr(VI) level below analytical limit of detection (0.006 mg/kg) which precluded calculation of proportion.

b Resin hardened during storage and could not be analyzed for Cr(VI) content.



Figure S1. Number of unique elements that were categorized as skin irritants and/or sensitizers per resin product. White infill = element is both irritant and sensitizer, black infill = element is irritant only, patterned infill = element is sensitizer only.



Figure S2. Number of unique organic substances that were categorized as skin irritants and/or sensitizers per resin product. White infill = element is both irritant and sensitizer, black infill = element is irritant only, patterned infill = element is sensitizer only.

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