

ER-91**Historical Evidence Density and Hazard Classification of UV-Curable (Meth)acrylate Monomers****Occupational Exposure, Surveillance, SDS Asymmetry and the Limits of Cross-Monomer Hazard Ranking**

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Statement of Significance

A safety data sheet is a regulatory communication document, not a calibrated league table of intrinsic toxicity. UV-curable monomers that were used widely in printing, coatings and other high-contact industrial processes generated decades of occupational case reports, patch-test programmes and targeted toxicology. Less common monomers may have a thinner evidence base. ER-91 examines how this unequal evidence density can create apparent asymmetry between hazard records without implying that a strongly classified substance is over-classified or that a lightly classified substance is intrinsically safer. The central engineering rule is conservative: absence of classification or a short SDS hazard section is not evidence of low hazard, and an evidence-rich hazard history cannot be transferred quantitatively to an untested analogue.

Abstract

Historical UV printing provides an unusually clear natural experiment in chemical evidence generation. Beginning in the 1970s, dermatitis investigations repeatedly identified multifunctional acrylates including TMPTA, PETA, HDDA and later TPGDA in workers exposed to UV-curing inks and coatings [1-7]. A large UK study subsequently used Graphical, Paper and Media Union membership to quantify skin complaints across printing activities, while current UK HSE guidance continues to identify UV-cured ink use as a printing activity with elevated skin-risk concern [8,15]. These records do not establish a simple intrinsic-hazard ranking between monomers. They show that commercial prevalence, contact opportunity, diagnostic attention, analytical availability and regulatory follow-up determine how much evidence accumulates around a substance. ECHA's C&L Inventory notification scheme requires a notifier to record whether "no classification" reflects a lack of data, inconclusive data, or data conclusive for non-classification; absence of classification therefore cannot by itself be read as absence of hazard [14]. Independent occupational studies also show that SDS can omit clinically relevant sensitizers [11,12]. ER-91 therefore proposes a four-layer interpretation model separating intrinsic hazard, exposure opportunity, evidence density and regulatory/SDS expression. The framework is intended for UV-curable formulations and VPP, where engineers often compare candidate monomers by SDS severity alone. Such comparison is not scientifically valid unless evidence density, purity, exposure route and test history are also considered.

1. Scope and evidence boundary

ER-91 addresses a narrow question: why can two chemically plausible UV-curable monomers appear very different in SDS severity or literature notoriety even when the available records do not justify treating that difference as a quantitative ranking of intrinsic hazard? The paper does not downgrade any harmonised or self-classified hazard, does not recommend substituting one sensitising monomer for another, and does not claim that historical use alone caused a regulatory classification.

Four layers are kept separate throughout: intrinsic hazard, real-world exposure, evidence density, and regulatory/SDS expression. ER-92 owns the distinct problem of residual reactants, impurities and manufacturing conversion. ER-93 owns occupational contact dermatitis as a disease and prevention problem. ER-94 owns molecular structure-hazard relationships among reactive diluents. ER-95 owns photoinitiator migration and substitution. ER-86 owns finished-device extractables-and-leachables qualification. ER-80 owns in-can stability and premature polymerisation. This scope separation is essential because a data-density argument cannot be used to infer molecular toxicology.

2. Historical UV printing created concentrated human evidence

The earliest UV-curing ink literature is unusually rich in direct occupational observations. Emmett and Kominsky reported eight men employed in UV-ink manufacture with allergic contact dermatitis; seven reacted to TMPTA, six to HDDA, four to PETA and three to epoxy-acrylate oligomers [1]. Smith investigated dermatitis in press minders handling UV inks and identified PETA as the causal sensitizer in that incident [3]. Björkner, Dahlquist and Fregert later reported six patients from four printing plants with contact allergy to PETA, TMPTA and acrylated prepolymers [2]. These are not abstract hazard screens: they arose from workers, actual formulations and repeated industrial exposure.

The literature then differentiated mechanisms and compounds. Björkner characterised TMPTA as a strong allergen in a guinea-pig maximisation test while linking the study to dermatitis among printing workers [4]. Malten and co-workers followed workers using HDDA and butanediol diacrylate and described delayed irritant dermatitis without observing contact sensitisation during their four-year cohort [5]. Whitfield and Freeman identified TPGDA in UV-curing screen-printing ink as the allergen in two workers [6]. Morgan and Fewings later reported rapid sensitisation to HDDA in two printing-industry cases, including one after a single accidental exposure [7]. The historical record therefore contains different endpoints, exposure intensities and diagnostic designs. It should not be collapsed into a single “bad monomer” ranking.

3. The UK union record: evidence generation, not proof of causality

The proposition that organised labour contributed to UK printing-skin surveillance is partly supported, but the strongest retrievable evidence is more specific than a claim that unions “caused” monomers to be classified. Livesley et al. sent questionnaires to approximately 2,600 members of the Graphical, Paper and Media Union in Nottinghamshire [8]. Among 1,189 respondents directly involved in printing, 490 (41%) reported a skin complaint at some time; prevalence was highest among workers in printing processes. The published process table recorded 67 reports among 148 respondents involved daily with UV-cured inks, varnishes or lacquers. Because a printing worker can be involved in multiple processes and material contacts, this process-level figure should not be read as a monomer-specific incidence rate. A clinical validation study from the same programme confirmed substantial occupationally related irritant dermatitis [9].

The methodological importance is that union membership supplied an identifiable worker population across multiple sites and processes. This increased surveillance visibility. Current HSE guidance still identifies UV-cured ink use, cleaning, solvents and other press-room activities as contexts with substantial dermatitis concern [15]. The defensible conclusion is therefore not “trade-union pressure made certain monomers hazardous”; it is that mature industrial sectors with organised workforces, repeated exposures and health-surveillance infrastructure can generate much denser human evidence than newer or niche applications.

4. Evidence density is not intrinsic hazard

A chemical can accumulate a large adverse-effect record for at least two independent reasons: it may genuinely be hazardous, and it may have been used often enough, long enough and visibly enough for the hazard to be detected repeatedly. Conversely, a low-use or recently introduced substance can remain data-poor. The two situations are not symmetric. Extensive adverse evidence raises concern; sparse evidence does not establish safety.

Table 1. Four-layer interpretation model for monomer hazard records

Layer	Question	Typical evidence	What must not be inferred
Intrinsic hazard	What can the substance do under defined exposure?	Validated irritation/sensitisation, toxicology, mechanistic data	A low number of reports does not prove low intrinsic hazard.
Exposure opportunity	Who contacted it, at what	Industrial use history, tasks, spills,	A common compound can generate

Layer	Question	Typical evidence	What must not be inferred
	concentration and frequency?	aerosol/mist, skin contact	more cases simply because exposure is broader.
Evidence density	How intensely has the substance been studied and surveilled?	Case series, patch-test inclusion, cohort studies, regulatory dossiers	More papers do not by themselves prove greater potency.
Regulatory/SDS expression	How is available evidence communicated?	CLP classification, SDS sections, workplace guidance	A shorter or softer SDS is not a quantitative safety ranking.

5. Why SDS severity cannot be used as a cross-monomer ranking

Under CLP, a substance without harmonised classification must still be self-classified from the relevant available data. ECHA's C&L Inventory notification requirements distinguish three reasons for “no classification”: lack of data, inconclusive data, or data conclusive for non-classification [14]. It follows that non-classification is not a single state and cannot be interpreted as evidence of low hazard without knowing which of the three applies. That distinction is directly relevant to formulation screening: hazard communication reflects the evidence available and the legal classification process, not a continuous experimental scale on which every monomer has been tested identically.

SDS completeness adds a second asymmetry. Keegel et al. compared 100 MSDS presented by workers at an occupational dermatology clinic with manufacturer ingredient information and found sensitizers were much less consistently listed than irritants; the authors concluded that MSDS were inadequate for protection and diagnosis in suspected occupational contact dermatitis [11]. In a later Finnish occupational clinic series, chemical analysis was often required when SDS did not reveal the acrylic compounds to which patients reacted; the authors concluded that SDS of anaerobic sealants often lacked skin-sensitisation warnings despite the presence of sensitising methacrylates [12]. Thus both “severe SDS” and “mild SDS” require interpretation.

6. Case studies: data-rich and newly visible monomers

Table 2. Illustrative evidence histories; not a potency ranking

Monomer / family	Evidence-generating context	What the record demonstrates	What it does not demonstrate
TMPTA	UV inks, printing plants, hardeners; human patch tests plus animal sensitisation [1-4]	Longstanding, repeated evidence for contact sensitisation in exposed settings	That every other multifunctional acrylate is safer.
HDDA	UV inks, coating work, accidental exposure [1,5,7]	Both irritant and allergic-contact outcomes have been documented	A universal sensitisation rate independent of concentration and exposure.
TPGDA	UV screen printing [6]	A clinically relevant allergen in specific exposed workers	That TPGDA is intrinsically more hazardous than a less-studied analogue.
DPGDA	Medical-device investigation: targeted chemical analysis of insulin pumps followed by aimed patch testing [13]	A comparatively newer exposure context can rapidly create new evidence	That earlier sparse literature meant the compound was safe.
Technical acrylate mixtures	Printing, adhesives, coatings [2,11,12]	Composition and undeclared constituents can affect diagnosis and hazard communication	That the nominal ingredient alone explains every reaction.

7. The exposure denominator matters

Counting dermatitis reports without an exposure denominator is not a valid comparison of sensitising potency. A monomer used in thousands of presses for decades can generate more clinical cases than a chemically similar monomer used by a small specialised sector, even if their intrinsic potencies were equal. The reverse problem also occurs: a very potent sensitizer may generate few published cases if exposure is tightly controlled or if the substance is not included in routine patch-test panels. Warshaw et al. analysed print-machine operators referred for patch testing over 1998-2014 [10]; because the denominator is a referred clinic population rather than a workforce, such datasets are conditioned by referral and testing practice.

Patch-test availability itself is part of the evidence system. Once a compound becomes recognised, it is more likely to be included in specialist series, which increases the probability of detecting subsequent cases. DPGDA provides a modern example: targeted chemical analysis of medical devices identified the monomer and prompted specific patch testing, creating evidence that could not have existed when the analyte was not being sought [13].

8. Implications for VPP formulation decisions

VPP changes the exposure pattern but not the epistemic problem. Operators handle uncured resin during filling, draining, failed-print recovery, vat cleaning, filter changes and spill management. A formulation engineer comparing candidate reactive diluents should therefore treat SDS classification as one input, not as a standalone optimisation metric. The decision record should separately capture harmonised/self-classification, human evidence, validated experimental evidence, exposure route, concentration, purity/impurities, and the amount of genuinely missing information.

A “milder” SDS for a less-studied monomer is not a licence to market the resin as low hazard. Uncertainty must remain visible rather than being converted into a safety claim, and absence of a classification or warning must be distinguished from evidence that the relevant classification criteria are not met.

9. Evidence-density qualification framework

- Record the legal classification separately from any internal comparative score. Never translate pictograms or H-statements directly into a continuous toxicity ranking.
- Build a human-evidence ledger: exposed population, industrial sector, exposure route, concentration if known, diagnostic method, and whether the report is a case, cohort, surveillance dataset or controlled study.
- Record experimental sensitisation and irritation evidence independently; do not combine the two endpoints.
- Record data gaps explicitly. “No study found” and “negative study” are different states.
- Check whether the analytical identity was verified. Technical-grade monomers, mixtures and undeclared constituents can distort attribution; ER-92 owns this layer.
- For VPP, qualify the finished resin and cured part in addition to raw-monomer data. Exposure and conversion state are part of the risk picture.

10. Limitations and falsifiable propositions

ER-91 does not prove that historical commercial volume quantitatively determines SDS severity, because a cross-monomer dataset linking production tonnage, number of exposed workers, number of toxicology studies and final classification was not identified. The historical printing literature demonstrates unequal evidence generation, not a causal regression between market size and regulatory severity. Likewise, the UK union study demonstrates union-enabled access to a worker population; it does not show that union complaints caused individual classifications.

A falsifiable future analysis would assemble matched monomers with production/use history, regulatory dossier completeness, number and type of human reports, standardised sensitisation/irritation results and current CLP classifications. Only then could the “evidence-density bias” be quantified rather than used as a qualitative caution.

11. Conclusions

The historical UV-printing record explains why certain multifunctional acrylates are exceptionally visible in occupational toxicology. TMPTA, HDDA, PETA and TPGDA were used in processes that produced repeated skin contact, recognised outbreaks, patch testing and subsequent surveillance. The UK printing-industry programme further shows how an organised workforce can make occupational disease measurable across sites. This evidence should be respected, not discounted.

The equally important conclusion is that evidence density and intrinsic hazard are not the same variable. Regulatory classification is evidence-driven; SDS can omit relevant sensitizers; and a short hazard history may simply be a sparse history. For VPP, the scientifically defensible practice is therefore to preserve uncertainty, compare evidence quality rather than SDS severity alone, and require formulation-specific qualification before claiming that a less familiar monomer is safer.

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Version note

v0.3 applies the independent addendum correction to the exact v0.2 candidate: the unsupported Aalto-Korte 2021 citation was removed from the TPGDA Table 2 cell, which now relies only on Whitfeld & Freeman [6]. Aalto-Korte & Suuronen 2021 remains correctly cited in §5 for its reviewer-verified SDS/chemical-analysis and anaerobic-sealant propositions. No other scientific claim, boundary or bibliography entry was changed.