

# Surface Metallization and Electroforming on Vat-Printed Photopolymers: Activation, Seed Layers, Adhesion, Coverage and Qualification

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## Statement of Significance

A metal-coated vat-printed polymer is not qualified by visual coverage or by a single resistance value. Metallization performance emerges from a chain of coupled states: the printed polymer surface, its cure and cleaning history, activation or catalytic chemistry, seed-layer continuity, metal nucleation and growth, adhesion at the polymer/metal interface, three-dimensional coverage, conductor thickness and the environmental or mechanical duty of the finished article. Electroforming adds a further requirement: the printed mandrel must support a continuous conductive surface during deposition and then be separated or removed without damaging the electroformed shell. This review separates these states and defines a minimum evidence architecture for electroless metallization and electroforming routes based on SLA, DLP and related vat-photopolymerised structures.

Keywords: vat photopolymerisation; metallization; electroless plating; electroforming; surface activation; seed layer; conductive coating; adhesion; copper; SLA; DLP; sacrificial mandrel

## Abstract

Vat photopolymerisation provides geometrically complex polymer substrates and sacrificial mandrels that can subsequently receive metallic layers. Published routes include catalyst-containing stereolithography resins, ZnO-containing DLP resins activated by laser irradiation, grafted interfacial layers for electroless copper on ultra-smooth SLA substrates, selective palladium catalysis in vat-printed plastronic parts, thiol-rich photocurable networks that bind metal ions directly, and self-activating DLP resins containing inexpensive metal precursors. These studies demonstrate that printable geometry and metallizability are coupled: additives or catalytic precursors can alter optical cure behaviour, while roughening, grafting, laser activation and surface chemistry can change nucleation and adhesion. Electroforming on additively manufactured mandrels further shows that seed-layer uniformity and current distribution can control shell continuity and thickness. This Engineering Review therefore treats metallization as a multi-state qualification problem rather than a coating add-on. 3Dresyns conductive soluble resins and Ag/Cu conductive coating routes are included only as manufacturer implementation examples; their catalogue positioning is not treated as independent evidence of plating adhesion, shell integrity or electroforming performance.

## 1. Scope and boundaries

ER-79 covers metal deposition on vat-printed photopolymer parts and on printed polymer mandrels used as temporary tooling for electroforming. The main focus is electroless Cu/Ni-type metallization, selective surface activation and the transition from a polymer geometry to a continuous metallic surface or free-

standing electroform. Electrolyte formulation details are considered only where they control compatibility with the polymer or deposition outcome.

The scope is distinct from ER-07 and RP-01, which address electrically functional photopolymer materials and electrical-property regimes; ER-79 asks how a metal layer is created and qualified on a printed polymer surface. ER-09 and ER-85 address sacrificial-removal and indirect-manufacturing routes; ER-79 uses sacrificial removal only as the final electroforming step. ER-43 addresses multimaterial VPP interfaces broadly, and ER-53 addresses adhesion of photopolymers to substrates/build platforms. ER-88 owns surface-topography metrology and finishing operations, which ER-79 uses only as an activation-state variable; ER-79 is restricted to the metal-on-photopolymer interface and deposited-metal continuity.

## 2. Metallization routes are not interchangeable

The literature supports several route classes with different governing variables. Li et al. incorporated laser-activatable functionality into SLA resin and selectively metallized printed circuitry [1]. Daegon Lee et al. embedded ZnO nanoparticles in a photocurable DLP resin and used 355 nm UV laser activation before electroless Cu plating [2]. Andreatta et al. instead modified already printed ultra-smooth SLA polymer surfaces with grafted interfacial chemistry before Cu deposition [3]. Gerges et al. used ordinary vat-printed substrates, localized catalyst in designed tracks and sandblasting to improve Cu adhesion [4]. Dongmin Lee et al. designed a thiol-ene-acrylate photocurable resin with surface thiols that bind metal ions and enable Cu, Ag and NiP deposition [5]. Bernasconi et al. more recently reported DLP resins containing NiCl<sub>2</sub> or CuSO<sub>4</sub> precursors that become catalytically active after reduction [6].

**Table 1. Metallization route classes and their primary qualification risks**

| Route class                              | Primary enabling step                                                          | Primary failure risk                                                                |
|------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| External activation of printed polymer   | Roughening, grafting, primer/catalyst or other post-print surface treatment.   | Incomplete activation, weak interfacial anchoring, geometry-dependent coverage.     |
| Catalyst/precursor in photocurable resin | Catalytically active species incorporated before printing and activated later. | Cure-depth/dispersion trade-off, catalyst burial, loss of selectivity.              |
| Laser-selective activation               | Local energy input exposes or converts catalytic sites before plating.         | Activation-window drift, heat/ablation damage, edge broadening.                     |
| Chemically functional surface            | Network chemistry provides binding sites for metal ions/catalyst.              | Surface-group depletion, cure-state dependence, ageing sensitivity.                 |
| Conductive coating or seed layer         | A separate conductive film is deposited before electroplating/electroforming.  | Pinholes, thickness non-uniformity, poor adhesion, inaccessible recesses.           |
| Conductive sacrificial mandrel           | Printed mandrel is itself conductive enough to enter the deposition process.   | Nonuniform current distribution, insufficient surface conductivity, removal damage. |

## 3. The printed polymer surface is the first process state

A resin formulation that prints successfully does not automatically present a surface suitable for metallization. Surface conversion, residual cleaning solvent, low-molecular-weight species, oxygen-inhibited material, roughness and post-cure history can alter wetting and chemical activation. Gerges et al. deliberately changed roughness and contact angle by sandblasting before selective electroless Cu deposition [4]. Andreatta et al. demonstrated a contrasting strategy in which high adhesion was obtained on ultra-smooth SLA substrates through grafted chemistry rather than relying on roughness alone [3]. These two approaches show why a single roughness target cannot be universal.

Qualification should therefore record the exact printed/post-processed surface state before any activation step. If the surface is polished, plasma-treated, sandblasted, chemically etched, grafted or coated, the treatment becomes part of the metallization specification rather than an optional preparation detail.

#### **4. Catalyst and seed-layer continuity are different from bulk conductivity**

Electroless deposition requires catalytic nucleation but does not require the whole polymer substrate to be a bulk electrical conductor. Conversely, electroforming or electrolytic thickening requires a conductive path connected to the external circuit. This distinction matters when comparing catalyst-loaded VPP resins with conductive coatings or conductive sacrificial mandrels.

In catalyst-containing resins, loading and dispersion are coupled to VPP optics. The 2021 ZnO-DLP study explicitly balanced nanoparticle content against photocuring behaviour and electroless-plating efficiency [2], while the 2026 self-activating-resin study reports that precursor optical properties affect curing depth, printability and mechanical behaviour [6]. A metallization formulation must therefore be evaluated in both printing state and activation/plating state; successful metal deposition cannot retroactively establish adequate VPP fidelity.

#### **5. Selectivity requires spatial control of activation**

For plastronics and patterned conductors, complete surface metallization may be a failure rather than a success. The relevant endpoint is the contrast between intentionally active and inactive regions. Laser activation, localized catalyst placement and multimaterial printing are three distinct ways to create that contrast [1,2,4,6].

Minimum evidence should include the designed conductor width, plated width, edge broadening, bridging between nominally isolated features, unplated voids and continuity around bends or vias. Optical inspection alone is insufficient when small metallic bridges can electrically short adjacent tracks.

#### **6. Adhesion is an interface property, not a synonym for coverage**

A continuous-looking film can delaminate under tape, bending, thermal cycling or service loads. Andreatta et al. focused specifically on highly adhesive electroless Cu layers on SLA polymer surfaces [3], while both the ZnO/laser route and thiol-mediated route included adhesion evidence for the deposited metal [2,5]. Gerges et al. likewise treated surface preparation as a means to increase Cu adhesion [4].

Adhesion testing must state what is actually measured. ISO 2409:2020 is a cross-cut resistance-to-separation classification for paint/varnish coatings and explicitly states that it is not a measurement of adhesion; it points to ISO 4624 when adhesion measurement is required [S1]. ASTM D3359-23 is a tape-test rating method with important substrate and sensitivity limitations [S2]. These methods may be useful screening tools only when their scope fits the coating/substrate system. Quantitative pull-off, peel or custom interface tests may be necessary for thick metal shells, curved parts or flexible devices.

#### **7. Electrical performance requires geometry and thickness**

Resistance, sheet resistance, resistivity and conductivity are not interchangeable. A plated track can show low resistance because it is thick or short while the deposited metal itself has a higher resistivity than bulk metal. The 2021 ZnO route reported Cu-layer resistivity after deposition [2], and later VPP metallization work demonstrated high-conductivity selective Cu tracks and flexible conductors [4,9]. These values are route-specific and should not be transferred across plating baths, thicknesses or geometries.

For metallic conductor material where its scope is appropriate, ASTM B193-25 defines a resistivity method and dimensional/resistance requirements [S3]. For patterned thin films or microscale tracks, the actual test geometry and contact method should be declared even if a different dedicated method is used. A qualification report should provide deposited thickness or cross-sectional area together with the electrical measurand.

## 8. Three-dimensional coverage is a transport problem

Complex VPP geometry creates recesses, internal channels, sharp corners and changes in local orientation that can affect activation, wetting, bubble retention, reagent replenishment and deposition. Conformal coverage on an accessible coupon therefore does not prove coverage inside a complex part. Electroforming adds current-distribution effects after the surface is conductive; deposition thickness can vary with geometry, current density and mass transport.

The original SLA-mandrel electroforming work by Rennie et al. identified practical problems from uneven conductive-paint application, including holes in later electroforms, and used improved spraying to reach deep recesses [7]. The general lesson remains current: the seed layer and subsequent metal thickness should be mapped on the actual geometric risk locations, not only on a planar witness coupon.

## 9. Electroforming is a downstream manufacturing state, not merely thick electroplating

Electroforming deliberately grows a self-supporting metallic body on a mandrel and subsequently separates or removes the mandrel. Rennie et al. used stereolithography photopolymer mandrels with a conductive silver-loaded coating for copper electroforming [7]. Matsuzaki et al. later combined additive polymer sacrificial molds with electroforming in a multimaterial manufacturing route [8].

The qualification endpoint is therefore the recovered metal component, not only the plated mandrel. Required outputs can include shell continuity, thickness distribution, dimensional replication, surface transfer, residual mandrel material, distortion after release and any damage introduced by the removal chemistry or thermal route.

## 10. Sacrificial removal introduces a second compatibility problem

A removable mandrel can simplify complex internal or closed geometries, but its removal medium must be compatible with the deposited metal and with any later process. Water-soluble, solvent-soluble, thermally removable and mechanically separable mandrels therefore create different risk sets. ER-79 does not rank those routes. It requires evidence that removal is complete enough for the intended use and does not measurably compromise the metal shell.

For soluble mandrels, residual polymer or ionic contamination may remain in blind cavities; for thermal removal, gas evolution and thermal mismatch may distort thin shells; for mechanical release, undercuts can prevent separation. The removal route must be designed together with the mandrel geometry and electroform thickness rather than selected after deposition.

## 11. Qualification architecture

**Table 2. Minimum qualification architecture for metallized VPP parts and electroforms**

| State           | Minimum record                                                                               | Release question                                          |
|-----------------|----------------------------------------------------------------------------------------------|-----------------------------------------------------------|
| Printed polymer | Resin lot/version, printer, exposure, orientation, wash, post-cure, surface roughness/state. | Is the substrate state reproducible before metallization? |

| State           | Minimum record                                                                                            | Release question                                                              |
|-----------------|-----------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Activation      | Treatment chemistry/energy, catalyst or precursor identity, concentration/loading, time and geometry.     | Are intended regions reproducibly activated without damaging print fidelity?  |
| Seed/nucleation | Coverage, pinholes, local continuity, edge selectivity and access to recesses.                            | Is there a continuous path for the next deposition step?                      |
| Deposited metal | Metal identity, bath state, temperature, time/current where applicable, thickness map and microstructure. | Is the metallic layer continuous and dimensionally controlled?                |
| Interface       | Adhesion test, failure locus, conditioning and geometry.                                                  | Does the metal remain bonded under the intended process/service load?         |
| Electrical      | Resistance/resistivity/conductivity with track dimensions, thickness, contacts and temperature.           | Does the conductor meet the actual electrical endpoint?                       |
| Electroform     | Shell thickness distribution, dimensional replication, defects and free-standing integrity.               | Does the recovered metal body meet geometry/mechanical requirements?          |
| Mandrel removal | Removal medium/temperature/time, completeness, residues and metal compatibility.                          | Can the tooling be removed without damaging or contaminating the electroform? |

## 12. 3Dresyns implementation boundary

Controlled 3Dresyns product documentation includes GrapSEK1-GNP as a water-soluble graphene-based conductive sacrificial photopolymer positioned for electroforming and advanced manufacturing [M1]. The public 3Dresyns corpus also documents AgEK1 and CuEK1 as silver- and copper-based conductive additive routes [M2-M3]. The AgEK1 source is a current public product/TDS implementation page that identifies 3D-ADD AgEK1 as the silver-powder component of the AgSEK1 system; CuEK1 is retained only as historically documented manufacturer/publication context because no current standalone product page was located during the 27 August 2026 independent review. These are relevant implementation examples because they map onto two different ER-79 route classes: intrinsically conductive/removable mandrels and conductive seed/coating routes.

No universal electroforming performance is inferred from that positioning. In particular, catalogue conductivity or solubility does not establish seed-layer continuity on an arbitrary geometry, metal adhesion after electrodeposition, electroform thickness uniformity, compatibility with a specific plating bath, complete sacrificial removal or service durability. Those endpoints require route-specific validation on the actual printed and metallized geometry.

## 13. Minimum reporting checklist

- photopolymer identity, batch/lot, printer, wavelength, exposure, layer thickness and build orientation;
- washing, drying and post-curing before activation or coating;
- surface preparation: roughness, polishing, blasting, plasma, etch, grafting or primer as applicable;
- activation/catalyst/precursor chemistry, loading, reduction or laser parameters and spatial selectivity;
- plating bath identity, metal deposited, temperature, time, agitation/flow and bath age or control state;
- for electrolytic deposition/electroforming: electrical connection strategy, current/current density and deposition time;
- seed-layer and final-metal thickness, including mapping at geometric risk locations;
- coverage defects, pinholes, bridges, unplated zones and internal/recess accessibility;
- adhesion method, specimen geometry, conditioning, failure locus and test limitations;
- electrical measurand with conductor dimensions, contact method and measurement temperature;

- dimensional change from CAD to printed polymer to metallized state and, for electroforming, to recovered metal shell;
- sacrificial-removal method, completeness, residues and evidence of metal compatibility;
- replicate count and within-part/between-part variability;
- application-specific acceptance criteria defined before testing.

## 14. Failure-mode and discrimination matrix

**Table 3. Common metallization failures and discriminating evidence**

| Observation                                | Competing explanations                                                                  | Discriminating evidence                                                                    |
|--------------------------------------------|-----------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Patchy metal coverage                      | Insufficient activation; poor wetting; catalyst depletion; trapped gas; bath transport. | Activation map + contact/wetting evidence + cross-section/SEM of unplated regions.         |
| Metal deposits outside tracks              | Activation spread; laser overexposure; catalyst contamination; bridging during growth.  | Pre-plating activation map + plated-edge metrology + electrical isolation test.            |
| Good coverage, poor adhesion               | Weak polymer/seed interface; contamination; over-cure/under-cure; residual stress.      | Interface-specific adhesion test + failure-locus microscopy + surface chemistry/state.     |
| Low resistance but poor reproducibility    | Variable thickness; contact geometry; local cracks; inconsistent bath state.            | Thickness/cross-section map + four-terminal or declared resistance method + bath controls. |
| Electroform has holes                      | Seed-layer pinholes; inaccessible recesses; loss of electrical continuity.              | Seed continuity test before electroforming + defect mapping after deposition.              |
| Shell thickness varies strongly            | Current-density distribution; shielding; mass-transfer differences; seed resistance.    | Position-resolved thickness + current/geometry model or controlled witness locations.      |
| Mandrel will not release                   | Undercuts; insufficient solubility/swelling; metal penetration; removal-medium access.  | Removal kinetics on representative geometry + residue inspection + design review.          |
| Metal cracks after bending/thermal cycling | Metal ductility limit; interface failure; polymer strain mismatch; residual stress.     | Strain/temperature cycling with resistance + microscopy + adhesion retest.                 |

## 15. Research and standardisation priorities

- VPP-specific round-robin studies separating printed-surface state from plating-bath variability;
- quantitative links between degree of conversion/surface chemistry and catalyst uptake or metal adhesion;
- spatial activation and plating-resolution metrology for curved tracks, vias and internal recesses;
- non-destructive mapping of conductive seed continuity before electroforming;
- geometry-aware electroforming thickness models validated on VPP mandrels with controlled curvature and cavities;
- paired adhesion/electrical durability datasets under humidity, thermal cycling and repeated flexing;
- controlled comparisons between externally seeded, catalyst-loaded and self-activating photopolymer routes;
- residue and contamination measurements after dissolution of sacrificial conductive mandrels;
- qualification of recycled or regenerated plating baths without conflating bath sustainability with part performance.

## 16. Conclusions

Metallization of vat-printed photopolymers is a chain of coupled transformations. Printing establishes the geometry and polymer surface state; activation establishes where metal can nucleate; seed continuity controls whether later deposition is complete; interfacial chemistry and roughness affect adhesion; plating conditions determine metal thickness and microstructure; and electroforming adds current distribution plus mandrel removal. No single conductivity, adhesion or coverage metric represents the complete route.

Independent studies now demonstrate several viable VPP-specific strategies, including laser-activatable SLA/DLP resins, grafted high-adhesion interfaces, localized catalyst tracks, thiol-mediated direct metallization and self-activating precursor-containing resins. Their process windows and performance are formulation- and geometry-specific. The appropriate engineering response is therefore route qualification, not extrapolation from one metallized coupon to another resin or device.

For 3Dresyns implementation, conductive soluble photopolymers and conductive Ag/Cu coating systems create useful electroforming and seed-layer options, but their manufacturer descriptions cannot establish deposited-metal adhesion, coverage, thickness uniformity or electroform integrity. Those claims require the full printed-surface → activation/seed → metal deposition → interface/electrical → recovered electroform evidence chain defined here.

## Limitations

The independent literature spans SLA/DLP as well as some transferable polymer-metallization and AM-electroforming studies outside VPP. Process chemistries differ substantially, and numerical conductivity, adhesion and deposition-rate values are therefore not pooled. Electroplating bath design, corrosion performance of finished metals and detailed electrochemical kinetics are outside scope except where they constrain the VPP-derived manufacturing chain. No new experimental metallization data are reported.

## Author contributions

Juan Seguro: conceptualisation, literature synthesis, metallization/electroforming qualification framework, writing and critical review.

## Competing interests

The author is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. Manufacturer documentation is included only as implementation context and is separated from independent scientific evidence.

## Data availability

No new experimental dataset was generated for this review. Scientific statements derive from the cited literature and standards; manufacturer examples derive from controlled 3Dresyns documentation.

## Company information

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## Standards and measurement references

- [S1] ISO 2409:2020, Paints and varnishes - Cross-cut test. Edition 5. The method rates resistance to separation and is not a direct adhesion measurement; see its stated scope and limitations.
- [S2] ASTM D3359-23, Standard Test Methods for Rating Adhesion by Tape Test. Active edition; applicability and sensitivity limitations must be respected.
- [S3] ASTM B193-25, Standard Test Method for Resistivity of Electrical Conductor Materials. Active edition; use only when specimen and measurement scope are applicable.

## Manufacturer implementation sources

- [M1] 3Dresyns by Resyner Technologies S.L., “3Dresyn GrapSEK1-GNP,” controlled product/TDS documentation, 2026. Manufacturer positioning: water-soluble graphene-based conductive sacrificial photopolymer for electroforming and advanced manufacturing. Public collection URL: <https://www.3dresyns.com/collections/3d-resins-for-electronics>
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the conductive resin system. Public URL: <https://www.3dresyns.com/products/3dresyn-agsek1-soluble-swellable-electrically-conductive-silver-based-3d-resin>

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