

In-Can Stability and Premature Polymerisation in Radiation-Curable Formulations

Inhibitor Mechanisms, Residual Acidity, Thiol Chemistry, Pigment/Filler Effects, Metallic-Ink Instability, Packaging Redox and Thermal Transport Risk

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Table 1. Document identity and review status.

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Abstract

Premature in-can polymerisation is a multivariable failure in which a radical-curable liquid formulation loses its induction period during manufacture, filling, storage or transport. The decisive event is not simply the presence of a polymerisable acrylate, methacrylate, thiol or photoinitiator, but a rate imbalance: radical generation becomes equal to or greater than the combined rates of radical scavenging and termination. Hydroperoxides generated during prior oxidation can remain latent until activated by heat, light, redox-active metals, reducing agents or an unsuitable inhibitor environment.

Residual acrylic acid or methacrylic acid can increase corrosion and alter inhibitor or amine speciation, whereas residual 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) primarily increase the pool of reactive unsaturation and must not be treated as equivalent to acid number. Thiol-containing resins add distinct routes involving thiolate formation, thiyl radicals, disulfides, radical thiol-ene propagation and base-catalysed thiol-Michael addition.

Pigments, dyes, graphene, graphite and metallic or mineral fillers can either suppress or promote instability through grade-specific combinations of inhibitor adsorption, surface redox chemistry, extractable metals, residual acids, water, dispersants and photochemical activity. UV metallic inks and coatings are a particularly demanding case: high-area aluminium, copper or copper-alloy flakes, passivation defects, adsorptive loss of soluble inhibitor, photoinitiator/co-initiator compatibility, hydroperoxide burden, heat and shear can converge to shorten induction time. Packaging and thermal history are therefore part of the formulation: qualified HDPE, PP or other thermoplastic containers, or metal containers with continuous internal can coatings and sealed/overcoated welds and seams, reduce direct resin-metal contact.

This review compares MEHQ, BHT, aluminium N-nitrosophenylhydroxylamine-type salts and generic copper dithiocarbamates, with explicit separation of established mechanisms from adjacent evidence and proposed pathways. It concludes with a source-attribution test matrix covering clear resins, thiol systems, pigmented formulations, carbon-filled materials, packaging contacts and summer or maritime transport profiles.

Keywords: *in-can polymerisation; storage stability; MEHQ; BHT; aluminium inhibitor; copper dithiocarbamate; hydroperoxide; acid number; HEA; HEMA; thiol-ene; thiol-Michael; pigment; copper phthalocyanine; rhodamine; titanium dioxide; metallic ink; aluminium flake; graphene; graphite; can coating; HDPE; PP; maritime transport.*

Highlights

- A low Acid Number is a useful quality-control indicator within a fixed resin family and method, but it does not identify the acid or replace peroxide, metal and inhibitor measurements.
- Acrylic acid and methacrylic acid are the most relevant residual acidic monomers in many acrylate and methacrylate streams; HEA and HEMA are reactive hydroxyalkyl monomers and should be controlled separately.
- Copper dithiocarbamates can plausibly shift from radical-control to redox-initiation behaviour when hydroperoxides, heat, reductants, thiols, acidity or accessible metals increase.
- Thiol resins require separate control of radical thiol-ene chemistry and dark base-catalysed thiol-Michael chemistry.
- Pigment or filler identity alone is insufficient: extractable metals, acidity, water, surface treatment, dispersant and inhibitor adsorption must be measured.
- Metallic UV inks and coatings often require a stronger and sometimes higher-active stabiliser package than matched nonmetallic systems, but passivation, acid/water control, amine selection, trace-metal control and temperature management are more fundamental than indiscriminate inhibitor addition.
- Package construction and shipment temperature are experimental factors, not logistics details.

0. Evidence terminology

The labels are applied at the point of use: Established is reserved for chemically comparable evidence; Adjacent for mechanistically informative but non-equivalent systems; Proposed for pathways requiring direct confirmation; and Industrial observation for practical behaviour not isolated in a controlled study.

Table 2. Evidence labels used in this review.

Label	Meaning in this review
Established	Supported directly in a chemically comparable system by primary literature or authoritative technical guidance.
Adjacent	Mechanistically informative but obtained with a different metal, ligand, substrate, temperature or reaction class.
Proposed	Chemically plausible pathway that requires direct confirmation in the exact formulation.
Industrial observation	Repeated practical behaviour that has not yet been isolated from confounding variables by a controlled study.

1. Scope and boundary

ER-80 addresses liquid formulations that cure by free-radical polymerisation after exposure to UV, visible light, electron beam or a deliberately activated redox system. The relevant product classes include 3D-printing resins, UV and EB inks, UV inkjet fluids, clear and pigmented coatings, overprint varnishes, tint media, metallic inks, filled composites, adhesives and related multifunctional acrylate, methacrylate, thiol-ene and thiol-acrylate systems. EB formulations may contain no conventional photoinitiator, but their acrylate functionality, oxidation products and redox-active contaminants can still support dark polymerisation before irradiation [1, 2, 3, 4].

The review is restricted to stability before intended cure. It does not attempt to rank commercial products without matched experiments, disclose proprietary compositions, or infer the identity of a proprietary stabiliser from performance. “In-can” is used as a functional term and includes bottles, jerrycans, pails, cartridges, drums, intermediate bulk containers, printer reservoirs and recirculation systems.

2. Rate-balance model of premature polymerisation

Polymerisation remains suppressed while the instantaneous rate of radical generation, R_{gen} , is lower than the combined rates of radical scavenging and termination. The induction period ends when the effective inhibitor reserve, oxygen condition, phase distribution or redox environment can no longer maintain this inequality. Because hydroperoxides and microgel can accumulate before a large bulk-viscosity change is measurable, a resin can appear normal and then deteriorate rapidly [1, 4]. The coupled rate-balance network is summarised in Figure 1.

$$R_{gen} < R_{scav} + R_{term} \cdot \text{stable induction period}$$

$$R_{gen} \cdot R_{scav} + R_{term} \cdot \text{radical accumulation} \cdot \text{microgel} \cdot \text{viscosity rise} \cdot \text{gelation}$$

Autoacceleration is especially important in multifunctional systems. Once branching and microgel reduce radical mobility, bimolecular termination becomes diffusion-limited while propagation continues. The resulting Trommsdorff-Norrish-type acceleration converts a slow storage drift into a rapid exothermic event. Package geometry, fill mass and heat-transfer conditions then affect severity, even when the initiating chemistry is identical.

Figure 1. Integrated reaction network for dark in-can polymerisation

Generic chemistry. No pathway is assigned to a proprietary stabiliser.

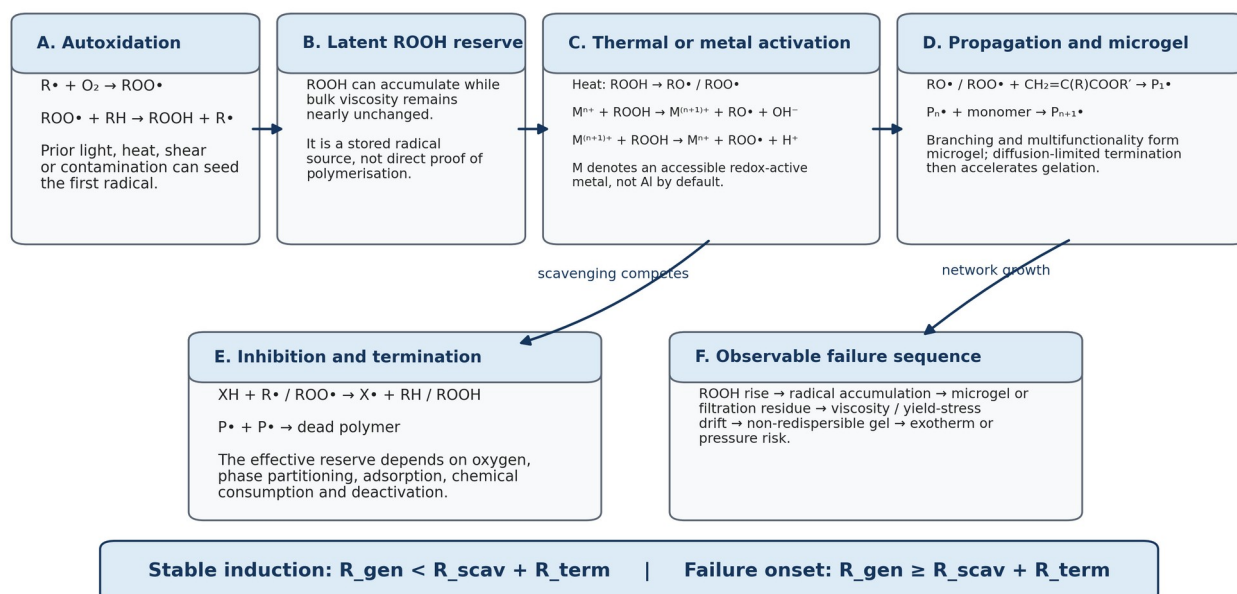


Figure 1. Integrated reaction network for dark in-can polymerisation. Hydroperoxides may accumulate during an apparently quiescent induction period. Heat or accessible redox-active metals can convert them into alkoxy and peroxy radicals; once radical generation equals or exceeds scavenging plus termination, multifunctional monomers form microgel and then a bulk network. The equations are generic and do not assign a mechanism to a specific proprietary stabiliser.

3. Sources of initiating species during dark storage

3.1 Hydroperoxides as latent radical reservoirs

Autoxidation converts carbon-centred radicals into peroxy radicals and then hydroperoxides. The initial radical can arise from trace initiator decomposition, previous light exposure, thermal decomposition of impurities, mechanical processing, oxidised monomers or oligomers, or catalytic surfaces. ROOH accumulation is therefore both a history marker and a potential source of future radical flux. An inhibitor that captures $ROO\cdot$ may delay chain propagation without removing the accumulated ROOH inventory; a subsequent increase in temperature or metal availability can then shorten the remaining induction period.

3.2 Photoinitiators, stray light and thermal history

Photoinitiator loading can increase storage sensitivity when the initiator or a sensitizer absorbs stray process light, forms long-lived charge-transfer states, or contains thermally labile impurities. This does not mean that a higher photoinitiator concentration universally reduces shelf life. The relevant variables are spectral exposure, extinction coefficient, quantum yield, thermal stability, oxygen condition and the inhibitor system. Manufacturing and filling operations should therefore control both illumination and time-temperature history rather than rely only on opaque final packaging.

3.3 Metal-mediated redox initiation

Fe(II)/Fe(III) and Cu(I)/Cu(II) couples can activate hydroperoxides by Fenton or Fenton-like pathways. The rate depends on ligand field, solvent polarity, water activity, pH or acidity, reducing agents and whether the metal is dissolved, colloidal, surface-bound or physically isolated. Total elemental metal is consequently an incomplete predictor; the extractable or catalytically available fraction is more informative. Metal contamination can originate from raw materials, pigments, fillers, dispersing equipment, pumps, valves, closures or exposed package seams.

4. Residual acidity, reactive residual monomers and Acid Number

4.1 Acrylic acid and methacrylic acid

In acrylate and methacrylate raw materials, residual acidic monomer is often dominated by acrylic acid or methacrylic acid, although oligomer end groups, catalyst residues and oxidation products may also contribute. The acids are not described here as autonomous radical initiators. Their principal destabilising roles are indirect: they can promote corrosion where resin reaches exposed metal; increase the mobility of metal ions; change amine protonation; alter

dithiocarbamate or other ligand stability; and redistribute water or ionic impurities. The effect is strongest when hydroperoxides are already present.

4.2 HEA, HEMA and the corresponding residual free acids in urethane (meth)acrylates

2-Hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) may remain after oligomer synthesis or be deliberately used as reactive diluents or hydroxyl-functional end-capping reagents. Public distributor and manufacturer documentation illustrates why four analytically distinct quantities must be separated: HEA content, HEMA content, free acrylic acid and free methacrylic acid. A distributor listing for HEA states free acid explicitly as acrylic acid, while a high-purity HEMA manufacturer specification states acidity as methacrylic acid and also controls water, inhibitor and diester impurities [39, 40, 41]. These documents are examples of industrial impurity control, not universal limits for every supplier or grade.

When HEA- or HEMA-containing feed is used to prepare a urethane acrylate or urethane methacrylate, the corresponding free acid may be carried into the oligomer, consumed in side reactions, concentrated by subsequent processing, or regenerated later by hydrolysis or oxidative ageing. The final oligomer must therefore be assayed rather than inferred from the nominal monomer certificate. Acid Number detects titratable acidity but does not identify its molecular source; chromatographic or otherwise validated compound-specific analysis is required to distinguish acrylic acid from methacrylic acid and from other acidic residues.

HEA and HEMA themselves are reactive hydroxyalkyl monomers, not the acidic species measured as acrylic acid or methacrylic acid. Their hydroxyl groups increase polarity, hydrogen bonding and potential water uptake, while their polymerisable double bonds increase the available propagation pool. HEA is an acrylate and generally undergoes faster radical propagation and homopolymerisation than HEMA because HEMA carries an α -methyl substituent. Neither monomer initiates radical polymerisation merely by being present, but once $RO\cdot$, $ROO\cdot$, thiyl or carbon-centred radicals are generated, residual HEA can contribute particularly rapid chain growth and cross-linking in multifunctional mixtures.

The destabilising contribution of the free acid is principally indirect. Acrylic acid or methacrylic acid can protonate amine co-initiators, alter inhibitor or dithiocarbamate speciation, adsorb on oxide surfaces, attack defective metal passivation, mobilise trace Fe/Cu and change water distribution. The resulting combination of acid, accessible metal and pre-existing hydroperoxide can initiate polymerisation in complete darkness. Prior light exposure may increase the hydroperoxide inventory, but it should not be assumed to be the universal origin of the free acid.

4.3 Acid Number as a quality-control indicator

Within a fixed product family, sampling protocol and validated analytical method, a lower Acid Number generally indicates less titratable acidic material and therefore a lower probability of acid-assisted corrosion or speciation changes. 3Dresyns uses Acid Number as one of the quality-control indicators relevant to in-can stability. ISO 2114:2000 is directly applicable to polyester resins and paint or varnish binders, while ASTM D4662-25 covers acidic and basic constituents in certain soluble polyester polyols and other high-acidity or high-alkalinity materials; that standard's own scope further excludes polyether polyols, and neither method was written for acrylate, methacrylate, thiol or filled radiation-curable systems; A matrix-specific recovery, precision and endpoint study is required. Acid Number is not an absolute safety threshold, does not identify acrylic acid versus methacrylic acid, does not quantify HEA or HEMA, and does not reveal hydroperoxides, metal extractables or inhibitor reserve [18, 19]. The coupled acid, residual-monomer and package-metal pathway is summarised in Figure 2.

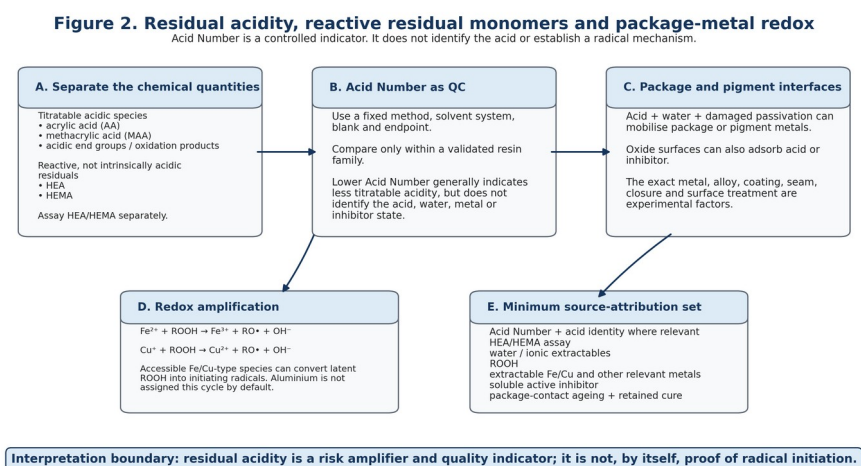


Figure 2. Coupling of residual acidity, reactive residual monomers and package-metal redox chemistry. Acrylic and methacrylic acid contribute to Acid Number; HEA and HEMA are separately controlled reactive monomers. The proposed acid/water-assisted package-metal pathway can activate hydroperoxides and initiate acrylate chains. Acid Number is an indicator, not a complete mechanistic assay. Panel D is reproduced in machine-readable form in Table 9.

5. Comparison of inhibitor families

5.1 MEHQ

Established in oxygen-containing acrylic-acid service, 4-methoxyphenol (MEHQ, p-hydroxyanisole) is widely used to inhibit acrylic and methacrylic monomers. Carbon-centred radicals are converted to peroxy radicals, and MEHQ transfers a hydrogen atom to $\text{ROO}\cdot$ to form ROOH and a resonance-stabilised phenoxyl radical. Subsequent radical coupling or disproportionation yields non-propagating products. Effective protection therefore depends on MEHQ concentration, dissolved oxygen, mass transfer and temperature. Oxygen starvation can sharply reduce performance, whereas uncontrolled oxygen ingress can also sustain autooxidation and ROOH formation; the required oxygen window is application-specific. Industry safe-handling guidance for acrylic acid, issued jointly by the European and North American monomer producer groups, states that the inhibitor system relies on a controlled dissolved-oxygen concentration and that oxygen exclusion is treated as a loss of inhibition rather than as a protective measure [5, 6, 1]. That guidance is written for bulk monomer storage and distribution; it should not be read as prescribing an optimum oxygen concentration for a formulated, pigmented or filled radiation-curable product. The family-level comparison is summarised in Figure 3.

5.2 BHT

Established chain-breaking mechanism: Butylated hydroxytoluene (BHT) is a hindered phenolic chain-breaking antioxidant. It donates a phenolic hydrogen atom, particularly to peroxy radicals, and forms a sterically protected phenoxyl radical. BHT can delay oxidative radical propagation and viscosity drift, but it does not guarantee control of a large flux of primary radicals generated directly from photoinitiator decomposition, a redox pair or a high hydroperoxide burden. Solubility, colour, cure interference and residual BHT after ageing must be evaluated in the final formulation.

5.3 Aluminium N-nitrosophenylhydroxylamine-type salts

One defined member of this family, aluminium tris(N-nitroso-N-phenylhydroxylamine), CAS 15305-07-4, is documented in patents and manufacturer literature as a polymerisation inhibitor for free-radical and radiation-curable formulations. US 6,018,078 describes the aluminium N-nitroso-N-phenylhydroxylamine complex as preventing premature polymerisation and the associated viscosity increase or gelation; WO 2007/035692 identifies the same CAS substance as an inhibitor for photocurable formulations; US 9,487,665 reports its use in an active-energy-ray-curable inkjet formulation; and FUJIFILM Wako lists monomers, UV inks, UV paints and photosensitive resins among its applications [62-65]. These sources establish publicly documented industrial practice, not a peer-reviewed compound-specific mechanism. The manufacturer proposes ligand-centred radical interception; this review therefore classifies the industrial use as an Industrial observation and the detailed elementary mechanism as Proposed. Al(III) itself is normally redox-inert under storage conditions and should not be represented as a Fenton-like centre. Exact identity, stoichiometry, active content, carrier, solubility and hydrolytic stability remain formulation-specific; the broader term "Al-NPHA-type salt" is retained when a commercial grade has not been fixed.

5.4 Generic copper dithiocarbamates, Cu(DTC)_2

Adjacent evidence underpins this section: Cu(DTC)_2 denotes a family, not a single substance. Dialkyl, cyclic, aryl and mixed-substituent dithiocarbamates differ in redox potential, ligand dissociation, colour, solubility, thermal stability and response to acid or peroxide. Cu(II)-DTC complexes can undergo oxidation, reduction, ligand-centred chemistry and photolysis. Literature on zinc dithiocarbamates shows that metal-DTC compounds can promote hydroperoxide decomposition, while copper-DTC studies demonstrate accessible Cu(I)/Cu(II) chemistry and ligand loss. These observations support a dual-function model but do not establish a universal in-can mechanism for every Cu(DTC)_2 [13, 14, 15, 16].

In the proposed stabilising regime, a low concentration of the copper complex may intercept radicals, bind reactive sulfur-centred species or control a small hydroperoxide burden. In the proposed pro-initiating regime, Cu(I)/Cu(II) cycling activates ROOH to $\text{RO}\cdot$ and $\text{ROO}\cdot$. Heat, high ROOH , acid-assisted ligand change, thiols, amines, reducing species or exposed metal can shift the balance. This is a testable rate-balance hypothesis, not a claim that copper dithiocarbamates invariably destabilise resin. The condition-dependent crossover is illustrated in Figure 4.

5.5 Practical safety and optical constraints

Dry copper dithiocarbamate powders require compound-specific SDS review and appropriate powder-handling controls [17]. Safety, appearance and optical constraints are ligand-specific within the Cu-DTC family. Copper(II) dimethyldithiocarbamate (CAS 137-29-1) is supplied by TCI as an orange-to-amber-to-dark-red powder or crystalline solid, whereas copper(II) dibutyldithiocarbamate (CAS 13927-71-4) is dark green to dark blue to black [72, 73]. The prior generic attribution of dark green or black colour must therefore not be transferred to the dimethyl compound. TCI lists the dimethyl compound with H410 and the signal word Warning. By contrast, PubChem's ECHA C&L Notifications Summary reports H330 in 99.5% of 562 company reports aggregated from 9 notifications and displays the aggregated signal word Danger [72, 74]. Both are self-classification data, not a harmonised classification, and the

current ECHA record should be checked before regulatory use. TRGS 552, Anhang 4, Tabelle 1, identifies copper dimethyldithiocarbamate as a precursor associated with NDMA formation under nitrosating conditions [70]. IARC's Group 1 evaluation applies to occupational exposures in the rubber-manufacturing industry, not to copper dithiocarbamates as an individual chemical class [71]. No universal carcinogenicity or reproductive-toxicity classification is inferred for Cu(DTC)2.

The aluminium family carries a separate toxicological constraint. The FUJIFILM Wako SDS for the defined aluminium salt (CAS 15305-07-4) self-classifies it as Acute Tox. 4 oral (H302), Skin Sens. 1 (H317), Muta. 2 (H341) and Aquatic Chronic 1 (H410), with the signal word Warning; it records a positive bacterial reverse-mutation assay and states that carcinogenicity data are unavailable [66]. The parent ligand cupferron (CAS 135-20-6), not the aluminium salt, is classified by IARC as Group 2B, is listed by the US National Toxicology Program as reasonably anticipated to be a human carcinogen, and has been listed by California Proposition 65 for cancer since 1988, with a 3 microgram/day NSRL [67-69]. Those entries are read-across context only and must not be presented as classifications of the aluminium salt. The chemistry is an N-nitroso hydroxylamine, not an N-nitrosamine; the two must not be conflated. A lower transition-metal redox risk is not a lower toxicological risk, and Figure 3 compares only the former.

Figure 3. Mechanistic comparison of four inhibitor families
Qualitative comparison only. Exact identity, active content, medium and stress state control performance.

MEHQ	BHT	Al-NPHA-type salt identity and grade specific	Cu(DTC)2 ligand and grade specific
Primary chemistry ROO• + ArOH → ROOH + ArO• Oxygen dependence High in acrylic-acid service; oxygen starvation can collapse protection. ROOH boundary Traps ROO• but does not remove the bulk ROOH reservoir. Evidence Established in oxygen-containing acrylic monomer service.	Primary chemistry ROO• + ArOH → ROOH + ArO• Oxygen dependence H transfer does not require O2, but ROO• arises from oxidation. ROOH boundary Chain-breaking antioxidant, not a bulk hydroperoxide remover. Evidence Established antioxidant chemistry; application-specific transfer.	Primary chemistry Ligand-centred radical interception and coordination are Proposed. Redox boundary Al(III) is normally redox-inert; no Fenton cycle is assigned. Failure constraints Identity, solubility, ligand exchange and toxicology are compound-specific. Evidence Industrial observation plus Proposed mechanism.	Primary chemistry Radical control and Cu(II)/Cu(I)-ROOH chemistry depend on ligand and medium. Role inversion High ROOH, heat, acidity, reductants, thiols/amines or exposed Fe/Cu can shift control toward radical generation. Failure constraints Potentially non-monotonic dose and stress response. Evidence Adjacent DTC evidence plus a Proposed model.

Comparison boundary: no universal ranking is implied. Measure active soluble inhibitor, ROOH, oxygen state, cure penalty and complete-formulation induction time.

Figure 3. Qualitative comparison of MEHQ, BHT, an aluminium N-nitrosophenylhydroxylamine-type inhibitor and generic Cu(DTC)2. The figure separates elementary radical-control chemistry, oxygen dependence, hydroperoxide response, expected kinetic behaviour, failure modes and required analytics. It is not a commercial ranking and does not imply equivalence among different aluminium or copper complexes. A machine-readable companion is provided in Table 10.

Conceptual rate model; curves are not fitted experimental data.

Figure 4. Condition-dependent role inversion of Cu(DTC)2

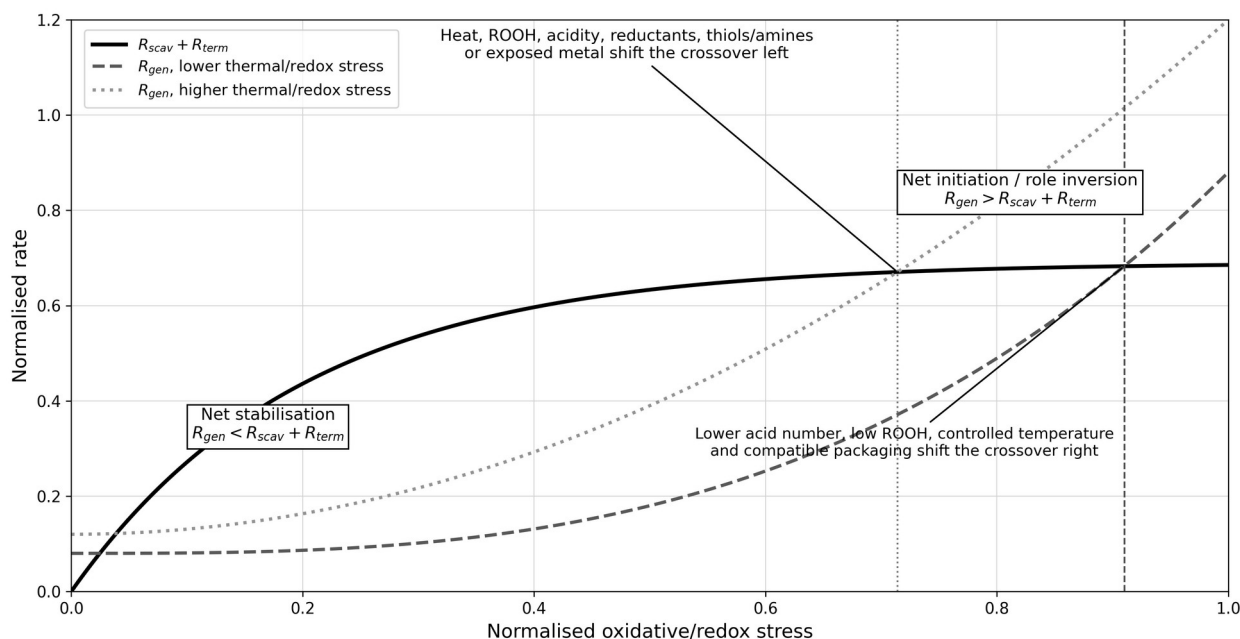


Figure 4. Conceptual rate model for condition-dependent role inversion of Cu(DTC)2. The stabilising regime exists while radical scavenging plus termination exceeds radical generation. Hydroperoxides, heat, acidity, reducing agents, thiols/amines or exposed metal can move the crossover to lower overall stress. Curves are conceptual and are not fitted data.

6. Thiol-containing resins

6.1 Why thiol systems require a separate stability model

Thiol-ene and thiol-acrylate formulations contain S-H bonds that can participate in radical chain transfer and, after deprotonation, nucleophilic addition. A storage model based only on acrylate homopolymerisation therefore misses two major pathways: radical thiol propagation and dark base-catalysed thiol-Michael addition. Multifunctional thiols convert small extents of either reaction into branching and gel formation [7, 8, 9, 10]. The parallel destabilisation routes are summarised in Figure 5.

6.2 Thiol oxidation, disulfides and hydroperoxides

Thiols can be oxidised to disulfides and higher sulfur-oxygen products. The route is strongly affected by oxygen, ROOH, transition metals, light and base. Thiyl radicals form by hydrogen abstraction or redox chemistry and add rapidly to electron-rich or electron-poor double bonds. Disulfide formation may initially reduce free-thiol concentration, but it also records oxidative stress and can coexist with hydroperoxide formation. Odour change, colour drift or loss of free thiol can therefore precede measurable viscosity increase.

6.3 Dark thiol-Michael addition

Amines, phosphines and other nucleophiles can generate thiolate anions. Thiolate adds to an activated acrylate double bond, and proton transfer regenerates thiolate, enabling catalytic propagation without light. Residual base, basic pigments, amine synergists, contaminated surfaces or decomposition products can therefore produce dark conversion even when radical inhibitors are adequate. Increasing acidity can suppress thiolate concentration by protonation, but the same acidity may worsen metal corrosion or destabilise other additives; the net effect is formulation-specific.

6.4 Dithiocarbamates in sulfur-rich environments

The ZDMC literature demonstrates a genuine environment-dependent change of function: zinc dimethyldithiocarbamate activates sulfur, forms active sulfurating species and promotes perthiol or polythiothiol cross-link precursors in rubber vulcanisation. This is adjacent evidence, not direct proof that Cu(DTC)2 initiates an acrylate resin in storage. It nevertheless shows why a metal dithiocarbamate cannot be assumed to remain a passive antioxidant in the presence of thiols, sulfur species and elevated temperature [11, 12].

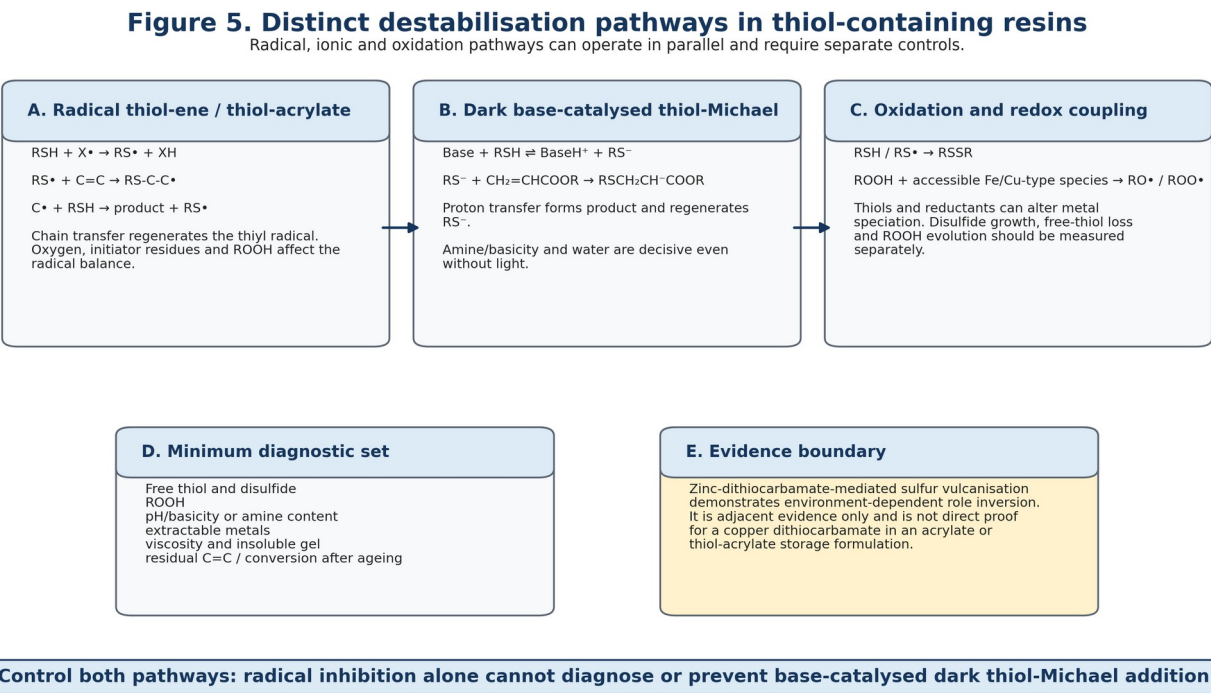


Figure 5. Distinct destabilisation pathways in thiol-containing resins. Radical thiol-ene/thiol-acrylate propagation, base-catalysed thiol-Michael addition, thiol oxidation and metal/peroxide redox chemistry can occur in parallel. Zinc-dithiocarbamate vulcanisation is included only as adjacent evidence for environment-dependent role inversion.

7. Pigments, dyes and metallic effect materials

7.1 The complete commercial grade is the experimental unit

A pigment is not only its ideal crystal formula. Commercial grades include crystal form, particle-size distribution, specific surface area, surface treatment, wetting agent, dispersant, salts, residual reagents, water and trace metals. In-can instability can arise from catalytic extractables, residual acrylic acid, methacrylic acid or mineral-acid synthesis residues, incomplete washing, adsorptive loss of inhibitor, local oxygen gradients, light absorption or photoinduced electron transfer. Low-purity pigments and dyes that retain synthesis reagents therefore present higher uncertainty, but neither colour nor nominal metal content alone predicts failure. The grade-specific source-attribution logic is summarised in Figure 6.

7.2 Representative pigment panel for UV flexographic and lithographic ink bases

The public 3Dresyns UV flexographic and UV lithographic portfolios describe fourteen concentrated single-pigment bases, four-colour process inks, expanded-gamut systems and high-lustre gold and silver metallics [27, 28]. The public pages do not disclose the exact fourteen pigment identities. Table 3 is therefore a representative screening panel assembled from public printing-ink practice and radiation-curable ink examples; it is not presented as a proprietary 3Dresyns recipe or a definitive list for every printer [42, 29, 30]. The stability-relevant experimental unit remains the complete commercial pigment grade, including its treatment, salts, water, dispersant demand and extractables.

Table 3. Representative pigment screening panel for UV flexographic and lithographic ink bases. The panel is assembled from public printing-ink practice and is not a proprietary 3Dresyns recipe.

No.	Representative pigment	Typical colour/chemistry	Principal in-can questions
1	C.I. Pigment Yellow 13	Diarylide yellow; common process/spot yellow	Residual coupling reagents or salts, acidic extractables, dispersant demand and inhibitor adsorption
2	C.I. Pigment Yellow 74	Monoazo yellow; modern process yellow option	Purity, ionic residues, particle-size distribution and dispersion stability
3	C.I. Pigment Yellow 83	Diarylide yellow-orange shade	Residual synthesis reagents, thermal history and surface acidity
4	C.I. Pigment Orange 34	Diarylide orange	Extractable salts/metals, incomplete washing and dispersion compatibility
5	C.I. Pigment Red 57:1	Calcium-lake azo red; common lithographic magenta/red	Lake metal/counterions, residual acid, soluble salts and water

No.	Representative pigment	Typical colour/chemistry	Principal in-can questions
6	C.I. Pigment Red 112	Naphthol AS red	Residual coupling reagents, surface acidity and inhibitor adsorption
7	C.I. Pigment Red 122	Quinacridone magenta	Particle treatment, dispersant coverage, residual ionic species and optical screening
8	C.I. Pigment Red 170	Naphthol AS red	Grade purity, crystal form, residual reagents and thermal stability
9	C.I. Pigment Violet 23	Dioxazine violet	Trace metal/ionic residues, high colour strength and possible inhibitor adsorption
10	C.I. Pigment Blue 15:1	Alpha copper phthalocyanine blue	Crystal-form stability, extractable Cu/Fe, acidic residues and dispersant chemistry
11	C.I. Pigment Blue 15:3	Beta copper phthalocyanine cyan; frequent CMYK cyan	Extractable rather than total Cu, residual acid/water, agglomerate microenvironments
12	C.I. Pigment Green 7	Halogenated copper phthalocyanine green	Extractable Cu/Fe, halide/ionic residues, washing quality and surface treatment
13	C.I. Pigment Black 7	Carbon black	Surface oxygen groups, ash/metals, inhibitor adsorption, oxygen transport and heat absorption
14	C.I. Pigment White 6	Titanium dioxide; preferably surface-treated pigmentary rutile	Crystal phase, alumina/silica coating, photoactivity, trace metals, moisture and dispersant demand

A representative CMYK set is PB15:3 or PB15:4 for cyan, PR57:1 or PR122 for magenta, PY13, PY74 or a more modern yellow such as PY155/PY180 for yellow, and PBk7 for black. Selection varies with printing process, migration requirements, lightfastness, rheology, colour standard and regional restrictions. Every incoming pigment should therefore be controlled by commercial grade and lot, not only by C.I. designation.

7.2.1 Relative screening priority by pigment family and commercial grade

The following hierarchy is a risk-based screening priority, not a universal order of dark-polymerisation activity. A purified pigment crystal can be benign while a lower-purity grade of the same Colour Index destabilises the formulation through residual synthesis reagents, soluble salts, water, ash, catalyst residues, trace metals, surface treatment or dispersant demand. Conversely, a nominally metal-containing pigment can remain stable if the metal is structurally inaccessible and the grade is well purified and passivated. The correct unit of qualification is therefore pigment manufacturer × commercial grade × lot × dispersant package × resin matrix.

Table 4. Relative screening priority by pigment family and commercial grade. The hierarchy is a risk-based screening order, not a universal order of dark-polymerisation activity.

Screening priority	Representative families	Why the complete grade can be problematic	Minimum source-attribution controls
Very high, conditional	Metallic aluminium; copper, brass or bronze effects; damaged/passivation-deficient metal flakes	Accessible metal or alloy interface, oxide/hydroxide defects, large surface area, settling, inhibitor adsorption, acid/water attack and Fe/Cu contamination can converge with ROOH and heat. Aluminium is not assigned a Fenton cycle.	Pigment architecture and treatment; Acid Number; water; ROOH; soluble inhibitor recovery; extractable Fe/Cu/Mn/Ni; dark induction; microgel; retained cure and appearance
High when ionic or poorly washed	Azo lake reds and oranges; diarylide, monoazo and disazo grades; rhodamine or xanthene dye lakes	Diazotisation, coupling and laking can leave mineral acid or base, nitrite-derived residues, chloride, sulfate, alkali salts, aromatic amine/coupler traces, lake counterions, water and finishing aids. Xanthene chromophores also require a separate stray-light photoredox assessment.	Aqueous-extract pH/conductivity; soluble halide/sulfate and nitrite where relevant; residual amine/coupler where feasible; water; extractable metals; dark-versus-light induction; inhibitor recovery
High interfacial/contamination priority	Carbon black, graphite, graphene, reduced graphene oxide and very fine high-area grades	Surface oxygen groups, defects, ash, metal residues and high area can adsorb phenolic inhibitors, photoinitiators or dispersants, alter oxygen transport and concentrate species at interfaces. Heat absorption and shipment temperature can increase the kinetic	Ash; Fe/Cu/Mn/Ni/Co/Cr extractables; surface oxygen/defect metrics; inhibitor and photoinitiator recovery; ROOH; rheology; microgel; matched filled/unfilled thermal ageing

Screening priority	Representative families	Why the complete grade can be problematic	Minimum source-attribution controls
		stress.	
High under light; conditional in darkness	Cu-phthalocyanine blues/greens; rhodamine/xanthene colorants; photoactive or incompletely treated TiO ₂	Specific phthalocyanine and xanthene derivatives can undergo photoinduced electron transfer under suitable illumination, and TiO ₂ can generate electron-hole chemistry. This does not prove dark initiation. Dark risk is more credibly linked to extractable metals, ionic residues, water, surface defects, adsorption and prior light history.	Strict dark control; defined spectral exposure; extractable rather than total metal; photoactivity/ROS screen; water/ions; inhibitor recovery; equal loading and equal optical-density comparisons
Usually lower intrinsic redox priority, but not inert	High-purity quinacridone, DPP, benzimidazolone and isoindolinone grades; well-coated pigmentary rutile	These families generally introduce fewer deliberately incorporated redox-active metals, but particle size, residual catalyst or salts, surface treatment and dispersant demand can still lower the free inhibitor reserve or alter cure.	Commercial-grade comparison; extractables; water; inhibitor recovery; dispersion stability; dark induction; cure depth and conversion

A release or development panel for pigment concentrates should include, where chemically relevant, aqueous-extract pH and conductivity, Acid Number of the concentrate and final formulation, Karl Fischer water, soluble chloride and sulfate, residual nitrite or aromatic synthesis intermediates, ash, extractable Cu/Fe/Mn/Ni/Co/Cr, particle-size distribution or a surface-area surrogate, inhibitor and photoinitiator recovery after controlled pigment contact, ROOH, dark induction time, defined-light induction time, viscosity drift, insoluble microgel and retained cure. Supplier name or Colour Index alone is not an adequate in-can stability specification [54, 55, 56, 57].

7.3 Copper phthalocyanine blue and green

Copper phthalocyanine pigments, including PB15 and PG7 families, are highly conjugated and contain a Cu centre, but the Cu is strongly coordinated in the macrocycle and is not automatically equivalent to soluble Cu(I)/Cu(II). Pure CuPc should not be described as a universal dark initiator. Visible-light resonance-Raman work on a specific sulfonated CuPc derivative demonstrated ligand-centred radical formation only under defined irradiation and aggregation conditions, with strong dependence on molecular stacking and medium; this is direct evidence for possible phthalocyanine photoredox chemistry but not for dark gelation by pigmentary PB15 or PG7 [52]. A problematic blue or green resin may instead reflect soluble or surface-accessible Cu/Fe, residual acidic synthesis species, halides, water, dispersant chemistry, inhibitor adsorption, agglomerate microenvironments or previous light exposure. Dispersion studies also show that carbon black and CuPc agglomerates respond differently to morphology, medium infiltration and chemical interaction, reinforcing the need for grade-specific testing [54, 55]. A controlled study should compare several grades at equal pigment volume and, where optical effects matter, equal optical density; measure extractable rather than only total metal; and separate dark ageing from illuminated ageing.

7.4 Rhodamine dyes and lake pigments

Rhodamine and related xanthene chromophores can participate in visible-light absorption, intersystem crossing, photoinduced electron transfer and photoredox initiation when paired with suitable donors or acceptors. A controlled photopolymerisation study showed that heavy halogen substitution increases the photoredox initiating performance of xanthene dyes; among the pairs examined, brominated rhodamine 6G outperformed the parent dye under visible light, although the halogenated fluoresceins were the strongest initiators in that series [53]. That result establishes a light-dependent mechanistic possibility, not dark in-can initiation by every rhodamine pigment. For rhodamine pigments or lakes, the investigation must distinguish the organic dye from the lake metal, counterions, residual acid, salts and unreacted synthesis reagents. Dark thermal ageing, controlled illumination, oxygen dependence, ROS or spin-trapping measurements and ionic/metal extraction are required before assigning causality to the chromophore.

7.5 Titanium dioxide in white UV inks and coatings

Pigment White 6 is not a single kinetic entity. Anatase, untreated or weakly treated high-surface-area TiO₂ and photocatalytic grades can generate electron-hole pairs under suitable irradiation, followed by reactive oxygen species such as hydroxyl radicals. By contrast, durable pigmentary rutile grades are commonly coated with alumina, silica, zirconia or related layers to occupy reactive surface sites and suppress binder oxidation. Indexed peer-reviewed studies show that photocatalytic activity and pigment behaviour depend on crystal phase, particle size, surface area and treatment density [31, 32]. A concordant report in a non-indexed journal describes marked suppression after alumina treatment [49]. Because that journal is non-indexed, the report is retained only for traceability of the observation and is not used as evidentiary support for any conclusion.

Therefore, a white UV ink that destabilises in complete darkness should not be attributed automatically to the rutile crystal itself. More plausible variables include incomplete or damaged surface treatment, anatase contamination,

trace Fe/Cu, residual sulfate/chloride or acidic processing residues, moisture, dispersant interactions, inhibitor adsorption and prior light exposure. The release specification should include crystal phase, treatment chemistry and level, moisture, soluble ionic extractables, photoactivity screening and inhibitor recovery after pigment contact.

White opacity also changes cure physics. Pigmented UV systems can require photoinitiator re-optimisation because scattering and absorption reduce local photon availability; published photo-DSC work shows that pigment loading can change photoinitiator efficiency and conversion [47]. This is a cure-depth issue and a possible reason for a larger latent cure package, not evidence that surface-treated rutile initiates dark polymerisation by itself.

Figure 6. Source-attribution map for pigments, fillers and carbonaceous grades

The complete commercial grade, not nominal colour or elemental identity, is the experimental unit.

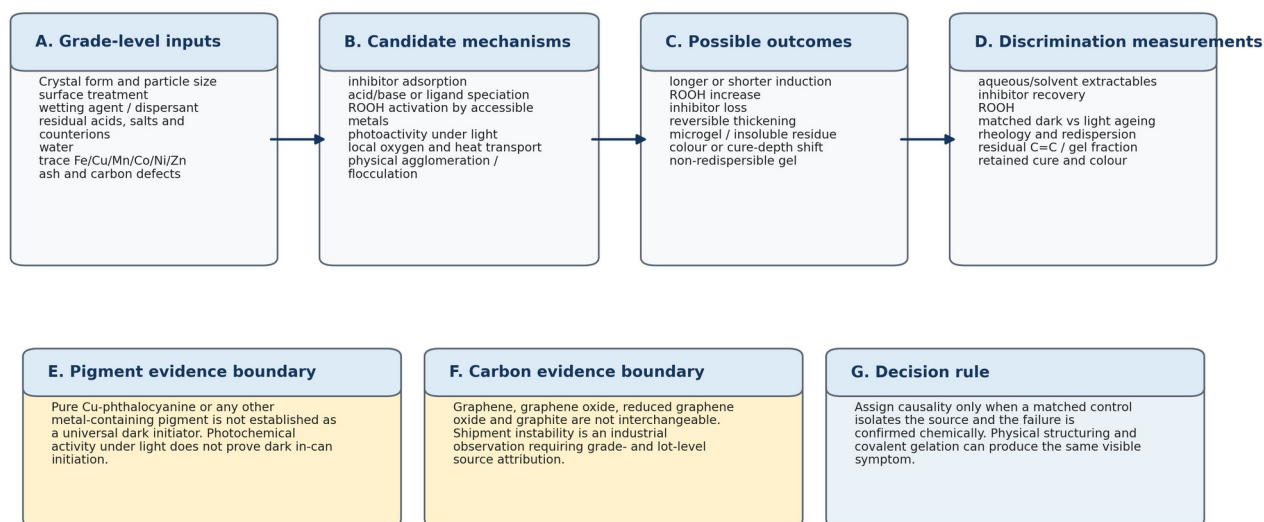


Figure 6. Grade-specific pigment, dye and carbon-filler mechanisms that may amplify in-can instability. Cu-phthalocyanine and rhodamine systems must be separated into chromophore, impurities, counterions or lake metal, dispersant and surface effects. Graphene/graphite risk is similarly controlled by surface area, defects, oxygenated groups, ash, metals and inhibitor adsorption. Transport heat amplifies all kinetic pathways. A machine-readable companion is provided in Table 11.

7.6 Why UV metallic inks and coatings can gel unusually rapidly

UV metallic inks and coatings combine a highly reactive multifunctional binder with a large solid-liquid interface and a cure package designed to overcome reflection, scattering and optical screening. Their rapid storage failure is not explained by one universal reaction, and aluminium should not be described as a Fenton metal. The practical risk comes from the convergence of interfacial adsorption, passivation quality, hydroperoxide chemistry, accessible redox-active impurities or alloy components, residual acid and water, co-initiator compatibility, temperature and shear. The coupled mechanism network is summarised in Figure 7.

7.6.1 Direct evidence that formulation details control shelf stability

Public patent literature specifically reports that metal flakes in UV-curable inks and coatings can promote premature initiation and short-time gelation, and that surface treatment and the way a protective component is associated with the flake can change storage stability [35]. A separate aluminium-metallic UV study reported a comparative formulation that gelled within 48 hours in an amber bottle at room temperature, whereas related formulations remained stable for more than three months. In that system, methyldiethanolamine reduced brilliance and shelf stability; the same patent warns that MDEA, triethanolamine and certain amine acrylates can gel aluminium- or copper-containing compositions immediately or within days [36]. These are formulation-specific examples, not universal numerical shelf-life claims.

Peer-reviewed formulations confirm the coexistence of urethane methacrylate or acrylate oligomers, multifunctional reactive diluents, photoinitiators, amine co-initiators and leafing or non-leafing aluminium pigments in practical UV-metallic systems [33]. Recent flexographic work with leafing vacuum-metallised aluminium pigments also shows that these very thin flakes require treatment for compatibility with UV-ink chemistry and that dwell time and temperature strongly affect viscosity-controlled migration, orientation and gloss [34].

7.6.2 Metal-flake architecture, surface area and passivation

Aluminium “silver” effects may use conventional cornflake or silver-dollar pigments or much thinner vacuum-metallised pigments. As flake thickness decreases and specific interfacial area rises, more formulation is brought into contact with the pigment surface. Soluble inhibitor, photoinitiator, amine, dispersant, acidic species and

hydroperoxides can partition to that interface. The effective inhibitor reserve may therefore be substantially lower than the nominal analytical concentration:

$$I_{eff} = I_{total} - I_{adsorbed} - I_{consumed} - I_{inactive}$$

The native Al₂O₃ layer and any fatty-acid, phosphate, silane, amine, polymeric or silica-based treatment determine whether the metal remains isolated from the liquid phase. Incomplete coverage, mechanical damage, aggressive grinding, incompatible dispersants or chemical attack can expose new sites. Silica encapsulation studies in other coating media show that homogeneous coverage and appropriate shell thickness are decisive for aluminium-pigment stability, although such aqueous evidence must be treated as adjacent rather than directly transferable to a 100% solids UV ink [38, 50].

Adsorptive depletion of the inhibitor reserve is a mechanistically credible but grade-specific contributor. Alumina is used industrially to remove tert-butylcatechol from monomer streams by adsorption, and acrylic acid itself shows strong, pH-dependent adsorption on alumina [43, 44]. These studies do not prove that a particular aluminium flake removes MEHQ, BHT or a proprietary stabiliser from a UV ink. They do demonstrate that oxide surface chemistry can partition both inhibitor-like phenols and acrylic acid. The relevant experiment is therefore direct: assay soluble active inhibitor before pigment addition and after controlled contact with the exact flake grade.

7.6.3 Residual acid, water and metal mobilisation

Residual acrylic acid or methacrylic acid, water and ionic contaminants can alter the oxide or surface-treatment equilibrium, increase soluble aluminium species and mobilise trace transition metals. Aluminium-pigment studies in aqueous alkaline media show that acid functionality and polymer Acid Number correlate with hydrogen evolution in the tested systems, with lower Acid Number associated with lower corrosion in those copolymer series [37, 51]. This is adjacent evidence: a dry 100% solids UV ink may contain far less water and need not evolve measurable hydrogen. It nevertheless supports controlling Acid Number, water and extractable metals rather than treating the metallic pigment as chemically inert.

For waterborne, water-reducible or hybrid UV metallic inks, aluminium-water corrosion is an additional and potentially pressurising failure mode. Peer-reviewed work confirms hydrogen evolution and loss of metallic lustre from unprotected aluminium pigment in water, and shows that adsorbed surfactant layers can inhibit that corrosion, a phosphate surfactant being the most effective of those tested [45]. Hydrogen evolution must not be transferred automatically to an anhydrous UV system, but water introduced with pigment paste, hygroscopic monomers or humid storage can move a nominally 100% solids formulation toward that regime.

Aluminium itself is not assigned an Fe- or Cu-like Fenton cycle. Where alkoxy or peroxy radicals are detected, candidate redox sources include extractable Fe or Cu contamination, copper-containing gold pigments, brass or bronze alloys, exposed package metal, mixed-metal wear particles, and metal-ligand complexes generated by the formulation. “Gold” metallic inks based on copper or copper-zinc bronze therefore require a different redox assessment from aluminium “silver” inks.

7.6.4 Cure-package loading and amine compatibility

Metal flakes are highly reflective and can scatter or shield actinic radiation. Flake orientation measurably changes optical reflectance, and pigment loading can reduce photoinitiator efficiency in UV-curable films [48, 47]. Formulators may therefore compensate with a stronger or broader photoinitiator package, sensitiser, amine synergist or higher total initiator loading. That cure strategy enlarges the latent inventory of species able to undergo thermal decomposition, electron transfer or side reactions during storage.

Co-initiator identity is critical. Public metallic-UV formulation evidence shows that closely related amines can have sharply different effects on brilliance and shelf stability [36]. In adjacent aqueous work, ethanolamines promoted dissolution of aluminium oxide, plausibly through soluble Al(III) complexes, whereas sodium dodecyl phosphate stopped the dissolution and sodium dodecyl sulphate only retarded it [46]. This does not prove the same dissolution mechanism in a dry UV ink, but it explains why MDEA, TEOA and amine acrylates cannot be treated as interchangeable cure accelerators around aluminium. The correct comparison is pigment grade × surface treatment × photoinitiator × co-initiator × inhibitor, not pigment alone.

7.6.5 Leafing, oxygen gradients and local microenvironments

Leafing pigments migrate toward the ink-air interface, whereas non-leafing pigments remain more uniformly distributed. During bulk storage, settling, flocculation, platelet stacking and wall accumulation can create local differences in oxygen transport, inhibitor concentration and thermal conductivity. MEHQ protection is particularly vulnerable to oxygen-poor microenvironments. Dense flake-rich zones can also concentrate adsorbed or extractable species, so polymerisation may begin at the wall, bottom, closure or pigment agglomerate before bulk viscosity changes.

7.6.6 Heat, shear and the transition from microgel to bulk gel

Grinding, high-speed mixing, recirculation, pumping, press rollers and summer transport add heat and shear. Heat accelerates hydroperoxide decomposition and inhibitor consumption; shear can damage fragile flakes or their treatment and generate fresh interface. Once a small fraction of a multifunctional acrylate polymerises at that interface, the resulting microgel adsorbs additional pigment and raises local viscosity. Reduced diffusion then suppresses termination and promotes autoacceleration. A filled system can therefore move abruptly from a small insoluble fraction to a non-redispersible bulk gel.

7.6.7 Why higher stabiliser demand does not mean “more is always better”

Compared with a matched nonmetallic ink, a metallic formulation often requires a stronger multi-mechanism stabiliser package and sometimes a higher nominal addition because the *effective soluble reserve* can be lower while the radical challenge is higher. The reserve is reduced by adsorption on oxide or treatment layers, irreversible consumption by hydroperoxides, deactivation through acid/base or ligand exchange, partition into pigment-rich zones, and loss during prior thermal or light exposure. Simultaneously, trace Fe/Cu, copper-alloy pigments, a larger photoinitiator/co-initiator package, high functionality and transport heat can increase radical generation. The practical target is therefore not merely total stabiliser concentration but left after pigment contact and ageing.

The required level cannot be specified generically and a high-dose strategy is not intrinsically safer. Excess inhibitor can reduce cure speed, conversion, adhesion, gloss, transfer, jetting or low-migration performance; it may also alter colour, metallic brilliance or interfacial wetting. A strongly coloured copper complex is especially constrained in high-lustre silver, pale and white systems, while powder handling of hazardous copper-containing additives can add occupational exposure concerns during manufacture. Stabiliser optimisation must be performed on active-content and soluble-reserve bases, with induction time, retained cure and appearance as co-primary endpoints.

The preferred hierarchy is: select a properly passivated pigment grade; minimise Acid Number, water, ROOH and extractable Fe/Cu; choose compatible dispersant, photoinitiator and co-initiator chemistry; limit unnecessary heat and shear; qualify the production package and transport profile; and only then optimise the inhibitor combination and concentration. Bulk stabiliser addition cannot reliably compensate for a defective flake treatment or an incompatible amine.

7.6.8 Distinguishing physical thickening from chemical gelation

Metallic inks can thicken through reversible platelet flocculation, leafing, settling or loss of steric stabilisation without covalent polymerisation. Chemical gelation should be demonstrated by loss of residual C=C, insoluble gel, exotherm, molecular-weight growth or persistent non-redispersibility. Physical structuring is more likely when viscosity and yield stress recover after controlled shear or dilution without a change in conversion. Both phenomena can coexist, and physical flocculation may concentrate reactants sufficiently to accelerate subsequent chemical gelation.

7.6.9 Metallic-ink release and stability controls

- Exact metal or alloy, pigment morphology, leafing/non-leafing character, particle-size distribution, metal content and surface-treatment identity or supplier declaration.
- Acid Number, residual acrylic or methacrylic acid where relevant, water, conductivity or ionic extractables, and initial ROOH burden.
- Total and extractable Fe, Cu, Ni, Mn, Co, Zn and other process-relevant metals rather than total aluminium alone.
- Soluble/active inhibitor before pigment addition and after defined pigment-contact time; adsorption isotherm where the stability margin is small.
- Dark induction and viscosity/microgel monitoring at 25, 40 and 50 °C or at temperatures justified by the actual shipping profile.
- Residual C=C, insoluble gel, filtration residue, isothermal heat flow and redispersion response to distinguish chemical from physical failure.
- Retained cure dose, conversion, adhesion, tack, transfer, gloss, colour, tarnish and metallic brilliance after ageing.
- Actual package contact, including HDPE/PP, intact lined metal, coating defect, seam/weld and closure coupons.

7.6.10 Source-attribution matrix by metallic-effect family

Table 5 separates the dominant questions and minimum controls for each metallic-effect family; it should be used as a source-attribution matrix rather than a ranking of inherent instability.

Table 5. Source-attribution matrix by metallic-effect family.

Metallic-effect material	Dominant stability questions	Evidence boundary and minimum controls
Passivated aluminium, leafing or non-leafing	Inhibitor adsorption; oxide/treatment integrity; acid, water and amine compatibility; optical screening; physical platelet structuring	AI is not assigned a Fenton cycle. Verify treatment, left, ROOH, Acid Number, water, extractable Fe/Cu, residual C=C, microgel and retained brilliance.
Very thin vacuum-metallised aluminium or damaged flakes	Very high interface per mass; treatment damage by shear; rapid inhibitor partition; strong leafing and oxygen gradients	Compare intact/stressed pigment and low/high-shear processing; verify inhibitor recovery, rheology reversibility and induction.

Metallic-effect material	Dominant stability questions	Evidence boundary and minimum controls
Copper, brass or bronze gold pigments	Accessible Cu chemistry, Zn/Fe impurities, amine sensitivity, tarnish and hydroperoxide activation	Measure extractable Cu/Zn/Fe, Cu speciation where feasible, ROOH, amine challenge, colour/tarnish, microgel and induction time.
Zinc-containing metallic pigment in waterborne or hybrid UV system	Corrosion, hydrogen evolution, oxide/passivation breakdown and pH sensitivity	Hydrogen-pressure testing belongs only to water-containing systems. Measure water, pH, gas evolution, metal dissolution and passivation retention.
Mica-, alumina- or TiO2-based pearlescent effect pigment	No metallic core redox by default; surface treatment, trace metals, photoactivity, inhibitor adsorption and optical cure effects remain relevant	Identify layer architecture and TiO2 phase/treatment; measure extractables, photoactivity, inhibitor recovery, cure depth and dark control.

Figure 7. Mechanistic network for rapid in-can instability of UV metallic inks and coatings
Chemical polymerisation and reversible platelet structuring are separate pathways that can reinforce one another.

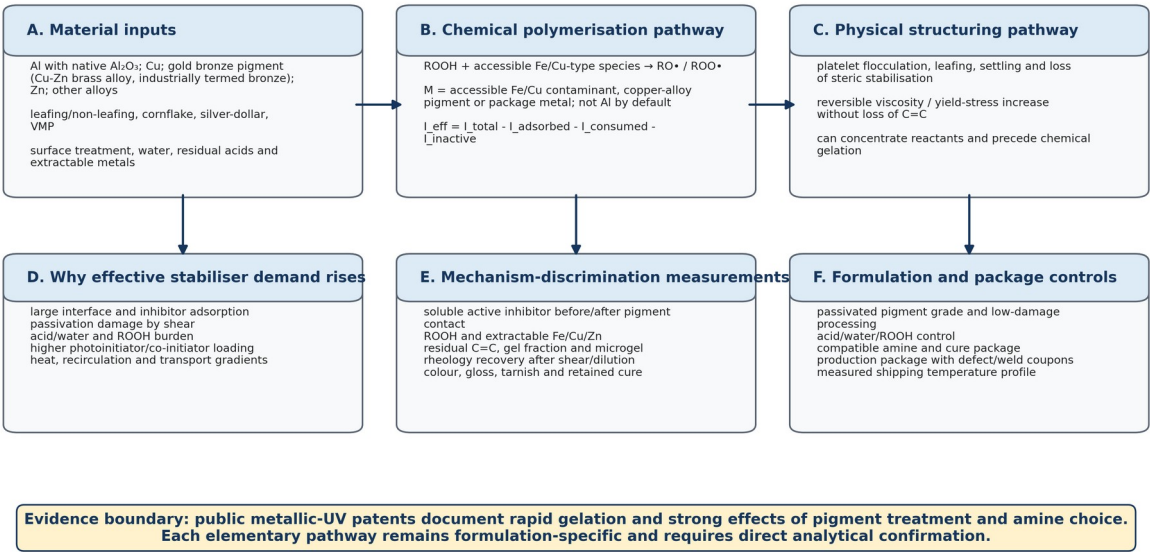


Figure 7. Coupled destabilisation network for UV-curable metallic inks and coatings. Flake architecture, passivation, acid/water, hydroperoxides, accessible redox-active metals, cure-package compatibility, heat and shear can increase radical demand or reduce soluble inhibitor reserve. Aluminium is not assigned a Fenton-like cycle, and reversible platelet structuring is separated from covalent microgel and bulk gelation.

8. Graphene- and graphite-containing resins

Graphene, graphene oxide, reduced graphene oxide and graphite are not mechanistically interchangeable. Their defect density, oxygenated edge groups, ash, metal contamination, surface area and dispersion chemistry vary widely. Carbon surfaces may scavenge radicals, adsorb phenolic or metal-complex inhibitors, catalyse peroxide transformation through impurities, alter local oxygen transport and change heat transfer. Adsorption studies on activated carbon and carbon-black surfaces provide adjacent evidence that phenolic molecules and polymeric or ionic species can partition strongly to carbonaceous interfaces, although these aqueous systems do not quantify inhibitor loss in a UV resin [56, 57]. The same nominal loading can therefore increase or decrease induction time depending on grade and surface treatment.

3Dresyns has observed that some graphene- and graphite-filled resins are more prone to destabilisation during shipment, particularly under summer conditions. This is treated as an industrial observation requiring controlled attribution rather than a universal material property. The minimum test set is inhibitor-recovery or adsorption, ROOH evolution, ash and extractable-metal analysis, Raman/defect and oxygen-content characterisation, rheology, microgel filtration, and matched dark thermal ageing of filled and unfilled controls.

9. Packaging as part of the formulation

9.1 Plastic containers

Qualified HDPE and PP containers are commonly used by 3Dresyns because they prevent direct contact between the liquid formulation and redox-active structural metal. Other thermoplastics may also be suitable after compatibility testing. Plastic is not automatically inert: oxygen or moisture permeation, monomer and oligomer sorption, swelling, environmental stress cracking, extractables from resin/additive packages or colour masterbatches, light transmission,

closure-liner or gasket incompatibility and thermal cycling can all change the formulation or the seal. Published HDPE work with organic liquids demonstrates that sorption, diffusion, permeation and swelling are strongly dependent on liquid identity and temperature, so polymer name alone is not a package qualification [23]. ISO 175:2010 covers unconstrained immersion and explicitly does not address environmental stress cracking; ISO 22088-1:2006, currently under revision as ISO/AWI 22088-1, gives method-selection guidance for ESC, while ASTM D543-21 includes immersion and a mechanical-stress/reagent practice. These methods are screening frameworks, not substitutes for the actual production pack [20, 22, 21]. The final study should record the exact polymer grade, colour/masterbatch, wall thickness, moulding process, closure, gasket and fill level; measure mass and dimensional change, visible damage, extractables, seal loss or permeation where relevant, response to thermal cycling and the formulation induction time after package contact.

9.2 Metal containers with internal can coatings

Metal pails or drums can be suitable when a continuous, chemically compatible internal can coating isolates the formulation from the substrate. Coating type, cure, film continuity, flex resistance, closure contact and compatibility with monomers, pigments and additives must be validated. A nominally coated container should not be assumed safe if filling, denting, seaming or transport damages the coating.

9.3 Welds, seams and closures

Welds and seams are high-priority inspection points because local coating discontinuities, heat-affected metal and crevices can create a chemically different interface. Welds, seams and exposed cut edges should be sealed or overcoated so that resin cannot contact bare metal. Closure springs, bungs, valves, foil liners and metallic dip tubes require the same review. A package-contact study should compare intact coating, intentionally defected coating, seam/weld coupons and an inert control.

Table 6. Package classes, principal in-can risks and minimum validation.

Package class	Potential advantage	Principal in-can risks	Minimum validation
HDPE	No deliberate metal-wall redox source; widely available	O ₂ /H ₂ O permeation, resin sorption, swelling, ESC, masterbatch/additive extractables, light transmission and closure/gasket compatibility	Exact grade/colour/wall/moulding; mass and dimensions; extractables/permeation or seal loss; thermal cycle; final-pack induction time
PP	No deliberate metal-wall redox source; useful chemical resistance for many formulations	Permeation, resin sorption, low-temperature brittleness, ESC, masterbatch/additive extractables and closure/gasket fit	Exact grade/colour/wall/moulding; immersion plus stress; extractables; closure; thermal cycle; final-pack induction time
Other qualified thermoplastics	Possible barrier or mechanical advantages without deliberate metal-wall contact	Unknown monomer/oligomer compatibility, permeation, swelling, ESC, plasticiser/additive migration, light transmission and seal compatibility	Full grade, conversion-process, closure/gasket and filled-package qualification with the actual formulation
Coated steel/tinplate	Mechanical strength and low permeation	Coating defects, seams, welds, corrosion and metal release	Holiday/continuity test, defect coupon, extractable Fe/Cu and ageing
Coated aluminium	Low mass and good barrier	Coating damage, acid/water attack at defects, closure compatibility	Coating continuity, defect coupon, metal extraction and ageing

10. Summer and maritime transport

Unconditioned road, port and maritime transport can expose packages to temperatures substantially above the recommended storage condition, even in complete darkness. A July-to-September transit study of a loaded 20-foot dry container specifically examined cargo heating under direct summer solar radiation [58]. Separately, summer field measurements in a refrigerated-container yard demonstrated solar-driven surface-temperature stratification among stacked containers, with differences of several degrees between upper and lower surfaces at solar intensities approaching 900 W m⁻² [59]. Only the external, inter-container stratification finding is carried across here: the internal thermal regime of an actively cooled reefer is not transferable to an unpowered dry container or drum. These studies establish the relevance of solar load, container position and thermal stratification; they do not define a universal drum-core temperature. Solar heating of a closed freight container, hot deck or terminal residence, long transit time and limited ventilation can create a thermal history that is not represented by a laboratory shelf held at 25 °C. The core temperature of a filled drum may lag the air temperature but remain elevated for longer. The correct input for stability assessment is therefore the measured package-temperature profile or a justified conservative simulation, not the nominal ambient temperature.

Arrhenius acceleration affects hydroperoxide decomposition, inhibitor consumption, corrosion, ligand exchange, thiol oxidation and propagation. A formulation with a long induction margin near room temperature can fail much earlier after a high-temperature excursion if the process is strongly autocatalytic. ISO 11357-5:2025 provides DSC reaction-curve temperatures, times, enthalpy and conversion for monomers, prepolymers and polymers, including materials containing fillers or initiators; ASTM E537-24 provides a thermal-stability screening framework for solids, liquids and slurries, with sealed high-pressure containers relevant to volatile or pressure-generating samples [24, 25]. ASTM E698-23 may be used only when its kinetic assumptions are met: its scope specifically excludes partially inhibited reactions and warns that simultaneous or consecutive reactions can invalidate the method. It should therefore not be the default shelf-life model for an inhibited, pigment-filled resin with multiple coupled pathways [26]. Isothermal ageing, appropriate calorimetry and package-level temperature histories must be used to challenge any extrapolation.

Packaging and thermal stress interact. Heat can increase permeation through thermoplastics, soften or stress a coating, accelerate extraction from pigments/fillers, and mobilise corrosion products at defects. Shipping qualification should therefore use the production container and closure, not only a glass vial.

11. Application-specific implications

The application matrix in Table 7 translates the mechanism-led controls above into process-specific screening priorities; it does not establish universal failure rankings or acceptance limits.

Table 7. Application-specific in-can risk and critical controls.

Application	Why in-can risk can be elevated	Critical controls
3D-printing resins	Multifunctional monomers, high photoinitiator/sensitiser loading, pigments/fillers, repeated vat exposure and recirculation	Dark package ageing, stray-light control, working curve after ageing, vat-life and filter/microgel checks
UV inks and coatings	High pigment loading, dispersants, large interfacial area and on-press heat	Pigment-grade screening, press/recirculation temperature, inhibitor reserve, cure retention
EB inks/coatings	Highly functional acrylates without a conventional photoinitiator can still autoxidise or respond to redox contaminants	ROOH, metals, temperature, package contact and EB cure after ageing
UV inkjet	Low viscosity, fine pigment dispersions, recirculation, small channels and local heating	Sub-micron filtration, microgel, viscosity, jetting, printhead temperature and dark recirculation test
Clear/white/pastel systems	Colour limits exclude strongly coloured stabilisers; low additive levels may be required	Optical transmission, colour, cure depth and alternative low-colour inhibitor validation
Aluminium silver metallic inks/coatings	High-area Al flakes, inhibitor adsorption, passivation defects, high cure-package demand, heat/shear and oxygen gradients	Pigment morphology/treatment, Acid Number, water, ROOH, inhibitor recovery, extractable Fe/Cu, dark thermal ageing and retained gloss/cure
Copper/brass/bronze gold metallics	Cu-containing metal or alloy can add accessible redox chemistry, tarnish and amine sensitivity	Alloy identity, extractable Cu/Zn/Fe, ROOH, amine compatibility, colour/tarnish, dark induction and package contact
White TiO ₂ systems	High pigment loading, optical screening and grade-dependent photoactivity or inhibitor adsorption	Rutile/anatase phase, surface treatment, photoactivity, moisture, extractables, inhibitor recovery and dark-versus-light ageing
Thiol-ene/thiol-acrylate	Radical, oxidation and base-catalysed dark pathways coexist	Free thiol, disulfide, base/amine control, ROOH, metals, cure conversion

12. Quality-control strategy

No single test establishes in-can stability. Acid Number is valuable because it is simple, sensitive to acidic synthesis residues and suitable for lot control, but it must be interpreted with peroxide, inhibitor, metal and rheological data. A strong QC release panel should be chosen from the following measurements according to formulation risk: The corresponding condition-dependence and source-attribution matrix is shown in Figure 8.

- Acid Number using a fixed method, solvent system, endpoint and blank.
- ROOH or peroxide value with pigment, thiol and reducing-agent interference assessed.

- Inhibitor identity and concentration, including soluble/active fraction where relevant.
- Residual acrylic acid or methacrylic acid, and separate HEA/HEMA assay when relevant.
- Water content and conductivity or ionic extractables.
- Extractable Fe, Cu, Mn, Co and other relevant metals from raw materials and package contacts.
- For metallic pigments: exact metal/alloy, leafing character, morphology, surface treatment, metal content, extractable Fe/Cu/Ni/Mn/Co/Zn and inhibitor recovery after pigment contact.
- For metallic inks: residual C=C, insoluble gel, redispersion response, gloss/tarnish and retained cure to distinguish physical flocculation from chemical gelation.
- Viscosity at controlled temperature, full flow curve where non-Newtonian drift is possible, filtration residue and insoluble gel fraction.
- Isothermal heat flow, DSC induction or another validated accelerated-stability response.
- Cure performance after ageing: RT-FTIR, photo-DSC, working curve, print, coating or EB conversion test.
- Colour, transmission and spectral change for clear or colour-critical systems.

Figure 8. Condition-dependence and quality-control matrix

No single measurement identifies the initiating source. The companion table provides the complete machine-readable matrix.

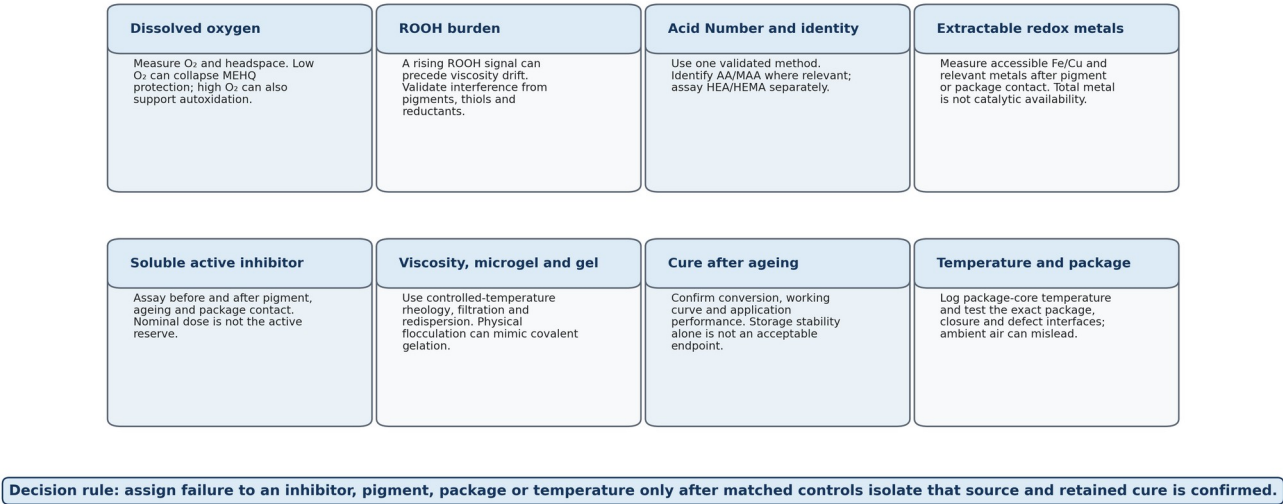


Figure 8. Quality-control and condition-dependence matrix. The purpose is source attribution: a stability failure should not be assigned to the inhibitor until oxygen, ROOH, acidity, metals, temperature, inhibitor assay, microgel and retained cure response have been measured. A machine-readable companion is provided in Table 12.

13. 3Dresyns in-can stabiliser implementations

3Dresyns offers two proprietary in-can stabiliser implementations, 3D-ADD STAB1 and 3D-ADD STAB2 Bio. Their exact compositions are not inferred in this review. According to the manufacturer-published product information, STAB1 is a clear stabiliser typically recommended at approximately 0.5-1% above resin solids, with 2-3% described for high-temperature environments; STAB2 Bio is described as biobased and biocompatible, typically at approximately 1-2%, with 3-4% described for high-temperature environments [60, 61]. These are manufacturer recommendations, not independently established universal doses, and they must not be transferred directly to metallic inks without cure, colour, migration and package validation.

These statements must be read as manufacturer-specific product positioning, not as an independent demonstration of universal toxicological superiority. “Safer”, “bio-based” and “eco-friendly” claims must remain limited to the wording, test basis and scope stated in the current TDS and SDS. Comparative performance should be established in each application against MEHQ, BHT, the exact aluminium inhibitor and the exact copper dithiocarbamate, using equivalent active content and a matched cure-response endpoint.

Occupational exposure during manufacture is governed by the physical form in which a stabiliser is charged, not only by its intrinsic hazard. The defined aluminium salt is supplied as a dry powder and its manufacturer SDS specifies dust-mask protection [66]; representative copper dimethyl- and dibutyldithiocarbamates are likewise supplied as powders [72, 73]. A liquid or otherwise controlled-delivery form eliminates the dry-powder dust-generation route attributable to that additive at the charging step. This is a statement about physical form and exposure route, not a comparative toxicological claim, and it does not establish that any particular product is intrinsically less hazardous. Because the exact compositions of STAB1 and STAB2 Bio are not disclosed, comparative toxicological superiority cannot be assessed and no such claim is made here. Each implementation must still be assessed for colour, solubility, migration, cure speed, extractables and compatibility with pigments, thiols, graphene/graphite and the selected package.

14. Recommended validation programme

The comparison should be performed as a staged factorial programme rather than a single accelerated-ageing vial. The first stage defines intrinsic resin stability; later stages introduce chemical stressors, solids, package contacts and transport conditions. This prevents a pigment impurity or coating defect from being misidentified as inhibitor failure. The staged architecture is shown in Figure 9.

The design must state whether it is full or fractional factorial; for a fractional design, report its resolution and alias structure. Randomise run order against oven position and time-to-test, use genuinely independent replicates rather than repeated measurements of one specimen, and include a positive-control formulation expected to fail so that a stable result can be distinguished from an insensitive test.

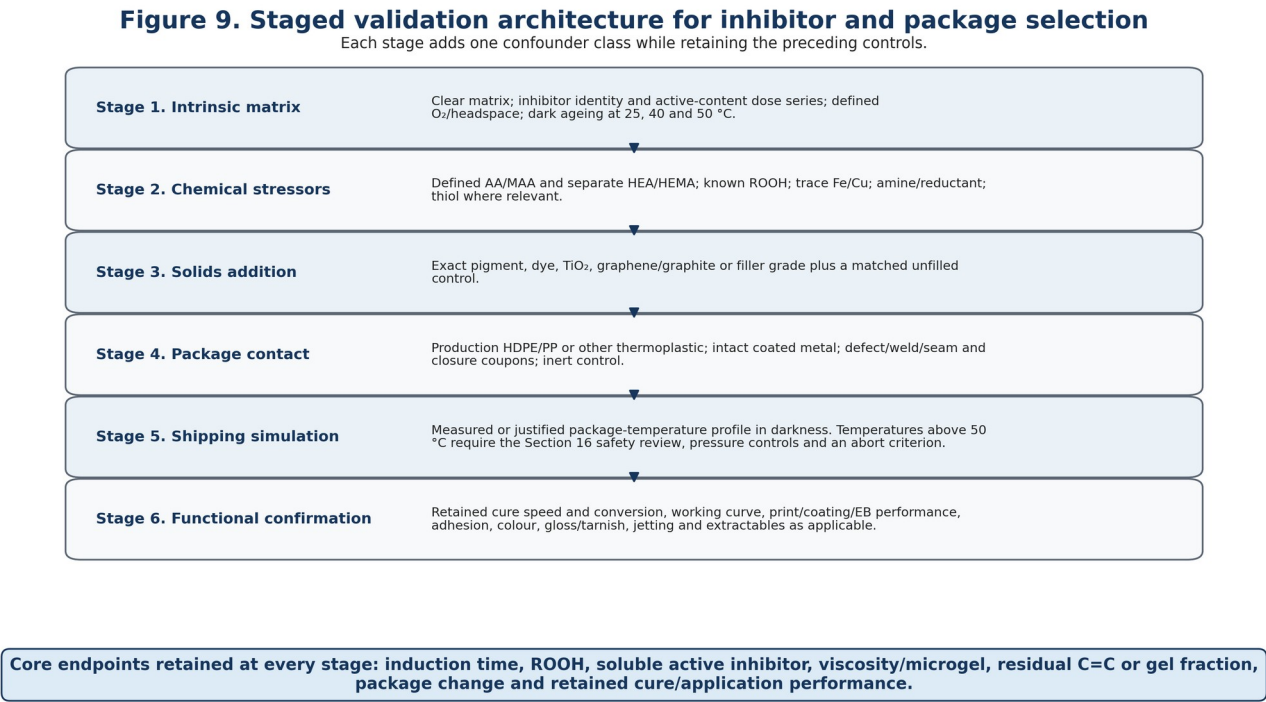


Figure 9. Staged validation architecture. Each stage introduces one class of confounder while retaining the previous controls. The final stage confirms that storage stabilisation has not unacceptably reduced intended cure or application performance.

Table 8. Staged factorial validation matrix: factor groups, levels and responses.

Factor group	Suggested levels or controls	Responses
Base matrix	Clear acrylate; urethane acrylate with measured HEA/HEMA; thiol-ene or thiol-acrylate	Baseline induction time, ROOH, viscosity, cure
Inhibitor	MEHQ, BHT, exact Al-NPHA salt, exact Cu(DTC)2, 3Dresyns implementations; dose series on active basis	Induction, inhibitor assay, colour, cure speed
Oxygen/headspace	Defined dissolved O2 and headspace; sealed and controlled-permeation conditions	O2, ROOH, induction, MEHQ response
Acid and residual monomer	Defined acrylic acid or methacrylic acid; independently varied HEA or HEMA	Acid number, corrosion/speciation, conversion
Redox stress	Known ROOH challenge; Fe/Cu additions at trace levels; amine/reductant; thiol	Radical generation, heat flow, microgel
Pigment/filler	PB15 grades, rhodamine dye/lake, TiO2 grades, graphene/graphite grades	Extractables, adsorption, ROOH, viscosity, colour
Metallic pigment	Al cornflake/silver-dollar/VMP; Cu or brass/bronze; leafing/non-leafing; intact and stressed surface treatment	Inhibitor recovery, ROOH, extractable metals, microgel, residual C=C, cure, gloss/tarnish
Cure package in metallic system	Photoinitiator and co-initiator identity/dose; MDEA/TEOA/amine-acrylate challenge only where justified and safely controlled	Induction, viscosity, appearance, inhibitor assay, cure dose and conversion
Package	Glass/inert control, HDPE, PP, other thermoplastic, intact coated metal, defect/weld coupon	Metal release, permeation, package change, induction
Temperature/light	Dark isothermal series; measured shipping cycle; controlled stray-light exposure	Kinetic model, role inversion, shelf-life estimate

Factor group	Suggested levels or controls	Responses
Design assurance	Full or fractional factorial; report resolution and alias structure; randomised run order; independent replicates; positive-control formulation expected to fail	Sensitivity, repeatability, interaction identifiability and uncertainty

15. Interpretation rules

1. Do not treat Acid Number as a complete stability test. Compare values only within a validated method and resin family.
2. Do not describe HEA or HEMA as the acidic species measured by Acid Number; assay them separately as reactive residual monomers.
3. Do not infer the behaviour of one copper dithiocarbamate from another ligand or transfer zinc-dithiocarbamate vulcanisation data as direct proof.
4. Do not assign a Fenton-like redox cycle to Al(III) without compound-specific evidence; focus on the coordinated ligand and speciation.
5. Do not classify Cu-phthalocyanine, rhodamine, graphene, graphite or any metal-containing pigment as universally destabilising. Test the commercial grade and its extractables.
6. Do not infer that aluminium itself performs a Fenton-like cycle in a metallic UV ink. Separate Al passivation/corrosion from Fe/Cu-type redox contaminants and copper-alloy pigment chemistry.
7. Do not solve metallic-ink instability by increasing inhibitor concentration alone; validate pigment treatment, acid/water/ROOH, amine compatibility, soluble inhibitor reserve, package and retained cure.
8. Do not use clear-vial accelerated ageing alone to qualify a plastic or coated-metal production package.
9. Do not apply ASTM E698 kinetics automatically to partially inhibited or multi-step formulations; verify the method assumptions and confirm predictions by isothermal ageing and an appropriate calorimetric screen.
10. Do not accept improved storage stability if it is achieved by unacceptable loss of cure speed, conversion, resolution, jetting or coating performance.
11. Report industrial observations as observations until a controlled source-attribution experiment has been completed.

16. Safety and scale-up boundary

Accelerated ageing of multifunctional acrylates, methacrylates and thiol systems can produce exothermic polymerisation, pressure rise and rigid gel. Tests should use small quantities, compatible vented or pressure-rated equipment, temperature limits, remote monitoring and a defined abort criterion. Vial results should not be extrapolated directly to drums or IBCs because heat-removal area, package material, headspace and oxygen transport change with scale.

The present review is mechanistic and does not replace the exact SDS, transport classification, reactive-chemical hazard assessment or package-compatibility qualification. Copper dithiocarbamate, aluminium-salt and proprietary stabiliser hazards must be assessed by exact identity and physical form. For unknown proprietary compositions, no toxicological or environmental mechanism is inferred.

Scope boundaries within the Engineering Review series

Shared measurement conventions, reporting rules and disclosure boundaries for this series are defined in RP-02, the Evidence-to-Decision Qualification Framework for Vat Photopolymerisation [R1]. ER-80 states only the topic-specific content.

ER-32 addresses photopolymer storage, reuse and the open-vat state, including light leakage, oxygen ingress, contamination and repeated printing [E1]. ER-80 is limited to mechanism-led in-can and package-contact chemistry before intended cure.

ER-44 addresses pigment-light interaction, photoabsorbing fillers, optical response and cure-depth control [E2]. ER-80 uses optical measurements only to distinguish light-driven storage effects from dark redox effects.

ER-61 addresses gelation, vitrification and mobility arrest during network formation [E3]. ER-80 uses gelation as a storage-failure endpoint and does not redefine the network physics.

ER-30 addresses oxygen inhibition and surface-cure effects [E4]. ER-80 treats oxygen and headspace as storage-state variables rather than as a printing-surface endpoint.

ER-36 addresses rheology, recoating and dispersion control of highly filled suspensions, including sedimentation and depth-dependent sampling [E5]. ER-80 addresses the chemical consequences of the pigment package. Colloidal instability and chemical destabilisation can produce the same visible symptom and must be separated by the discrimination experiments in Figure 6.

ER-27 addresses conversion metrology [E6]. ER-80 requires conversion measurements to quantify cure penalty but does not replace conversion-method validation.

17. Conclusions

12. Premature in-can polymerisation is best understood as a rate-balance failure involving radical generation, inhibitor reserve, termination and transport of heat and oxygen.
13. Hydroperoxides are the central latent reservoir that connects prior oxidation with later thermal or metal-mediated radical initiation.
14. Residual acrylic acid and methacrylic acid can amplify corrosion and additive-speciation risks. HEA and HEMA are distinct reactive residual monomers and require separate control.
15. A lower Acid Number generally indicates lower acid-assisted risk within a fixed chemistry and method, which supports its use as a 3Dresyns QC indicator, but it is not a universal threshold.
16. MEHQ, BHT, Al-NPHA-type salts and Cu(DTC)₂ operate through different and partly overlapping mechanisms. No family is universally optimal.
17. Cu(DTC)₂ requires an explicit role-inversion assessment because copper/peroxide redox chemistry can become pro-initiating under high ROOH, heat, acidity, reductant, thiol or exposed-metal stress.
18. Thiol formulations add radical thiol-ene and dark thiol-Michael pathways that cannot be controlled or diagnosed by acrylate-only models.
19. Pigment, dye, graphene and graphite effects are grade-specific. Metallic or alloy interfaces, poorly washed ionic or lake pigments, high-area carbonaceous grades and photoactive colorants warrant higher screening priority, but purity, residual reagents, extractable metals, water, surface chemistry and inhibitor adsorption are more informative than nominal colour or elemental identity.
20. UV metallic inks and coatings are high-risk formulations because metal-flake surface area, passivation, inhibitor adsorption, optical cure-package demand, amine compatibility, residual acid/water, redox-active impurities, heat and shear can converge. Aluminium silver, copper-alloy gold, zinc-containing and pearlescent systems require different source-attribution tests, and physical flocculation must be separated from covalent gelation.
21. Qualified HDPE, PP or other thermoplastics, or fully coated metal containers with sealed/overcoated welds and seams, reduce direct package-metal redox risk. Thermoplastic qualification must nevertheless include the exact grade, masterbatch, conversion process, closure/gasket, permeation/sorption, swelling, ESC, extractables, thermal cycling and final-pack induction time.
22. Summer and maritime transport can accelerate dark polymerisation solely through temperature; package-level thermal profiles must therefore be included in shelf-life validation.
23. The final stabiliser decision must preserve intended cure performance and be supported by a staged factorial programme in the complete formulation and production package.

Author contributions

Juan Segurola: conceptualisation, industrial observations, literature synthesis, engineering interpretation, manuscript preparation, review and final approval.

Competing interests

Juan Segurola is founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L., which supplies photopolymer resins, radiation-curable ink systems and the two in-can stabiliser additives discussed in Section 13. Manufacturer documentation is segregated from the scientific references and is used only to define public implementation context. No independent comparative performance data for those products are presented.

Data availability

No new experimental dataset was generated for this review. The proposed validation architecture, factor matrix and quality-control panels are methodological recommendations. Any future comparative data should report the exact inhibitor identity and active content, resin version, pigment grade and lot, package construction, temperature and light history, oxygen and headspace state, analytical methods and uncertainty.

Limitations

This review is literature-based and reports no new kinetic, calorimetric, corrosion, metal-leaching, peroxide or shelf-life measurement. No formulation-matched head-to-head study comparing an aluminium N-nitrosophenylhydroxylamine-type salt with a defined copper dialkyldithiocarbamate in a radiation-curable resin was located; the comparison in Section 5 and Figure 3 therefore reports mechanistic expectation, not measured ranking. Publicly documented use of the defined aluminium salt is supported by patents and manufacturer literature [62-65], but no peer-reviewed compound-specific mechanistic study was identified. The zinc-dithiocarbamate evidence is adjacent and is not proof of copper-dithiocarbamate behaviour in an acrylate. The metallic-ink evidence rests substantially on two patent disclosures, which are formulation-specific examples rather than controlled comparative studies. Several packaging, transport and adsorption sources were obtained in aqueous or non-radiation-curable systems and are labelled adjacent throughout. No published ISO or ASTM method was identified as a complete validation standard for in-can shelf life of a radiation-curable formulation; the descriptors and matrices proposed here are engineering aids, not standards. No comparative toxicological assessment of the proprietary implementations is made because their exact compositions are not disclosed. The C&L comparison for copper dimethyldithiocarbamate

reports aggregated company notifications rather than a harmonised classification and must be rechecked against the current ECHA record before regulatory use.

Appendix A. Machine-readable companion tables

The following tables reproduce substantive matrix content from Figures 2, 3, 6 and 8 in selectable, searchable form. The figures remain visual summaries; these tables are the machine-readable companions.

Table 9. Machine-readable companion to Figure 2, panel D: quality-control interpretation.

Control	What it measures	Interpretation	Limitation
Acid Number	Total titratable acidity	Lower values generally reduce acid-assisted risk within the same chemistry and method	Does not identify the acid and does not quantify HEA/HEMA
ROOH / peroxide value	Oxidised precursor burden	High values indicate reduced redox margin	Method response may be matrix-dependent
Extractable Fe/Cu	Catalytically available metal	Links package, pigment or filler to redox risk	Total metal alone may overstate availability

Table 10. Machine-readable companion to Figure 3: qualitative comparison of four in-can inhibitor families.

Mechanistic criterion	MEHQ 4-methoxyphenol	BHT hindered phenol	AI-NPHA-type salt identity and grade specific	Cu(DTC) ₂ ligand and formulation specific
Primary elementary step	POO• + ArOH → POOH + ArO•; phenoxy-mediated termination	ROO• + ArOH → ROOH + ArO•; chain-breaking H transfer	Predominantly ligand-centred radical interception; AI(III) is normally redox-inert	Radical interception may compete with Cu(I)/Cu(II)-mediated ROOH activation
Dependence on oxygen	High in acrylic-acid service; dissolved O ₂ supports effective inhibition	Indirect: H transfer does not require O ₂ , but ROO• radicals arise from oxidation	Must be determined for the exact complex and medium	O ₂ changes Cu state, ligand chemistry and ROOH formation; net effect is not monotonic
Response to hydroperoxide burden	Intercepts ROO• radicals rather than directly removing bulk ROOH; high burden can exceed reserve	Suppresses ROO•-chain propagation; high burden and heat consume reserve	Coordination or other deactivation of ROOH is a working hypothesis unless directly demonstrated	Low burden may be buffered; high burden can produce RO•/ROO• radicals by redox cycling
Expected kinetic signature	O ₂ - and concentration-dependent induction period; abrupt loss when reserve or O ₂ is depleted	Delayed autoxidation and viscosity rise; limited protection against a large non-oxidative initiator flux	Induction extension only while soluble, intact and correctly speciated	Potentially non-monotonic dose and stress response with a crossover from inhibition to initiation
Main failure or role-inversion regime	Low O ₂ , high temperature, depleted MEHQ or high radical flux	High ROOH, high temperature, depletion, insolubility or incompatibility	Wrong identity/ligand, hydrolysis, precipitation or ligand exchange	High ROOH, acid, heat, thiols/amines/reductants, exposed metal or ligand dissociation
Analytical validation	Dissolved O ₂ , MEHQ, ROOH, induction time, viscosity and cure conversion	BHT, ROOH, induction time, viscosity and cure conversion	Exact identity, ligand:AI ratio, solubility, speciation, ROOH and cure impact	Cu(I)/Cu(II), DTC integrity, ROOH, EPR/spin trapping, induction time, colour and cure impact

Table 11. Machine-readable companion to Figure 6: pigment-, filler- and transport-coupled source attribution.

Material class	Plausible destabilising attributes	Required discrimination experiment	Scientifically defensible conclusion
Cu-phthalocyanine blue (PB15 grades)	Soluble/extractable Cu or Fe; acidic or ionic synthesis residues; dispersant package; inhibitor adsorption; light absorption and grade-specific photochemistry	Compare several grades at equal pigment volume and optical density; measure extractable metals, acidity, water, ROOH and inhibitor recovery; age in darkness and under controlled light	Pure CuPc is not established as a universal dark initiator. Any effect must be assigned to the complete pigment grade and formulation.
Rhodamine dyes and lake pigments	Visible-light sensitisation; electron transfer with donors/acceptors; counterions, lake metal, residual acid, salts or unreacted synthesis reagents	Separate dye from lake pigment; dark versus illuminated ageing; oxygen dependence; ROS/spin-trapping tests; ionic and metal extractables	Photochemical activity under light does not prove dark in-can initiation. Dark risk is more plausibly linked to redox partners, impurities or residual reagents unless demonstrated otherwise.
Graphene, graphene oxide and graphite	High surface area; defect and oxygenated sites; metal/ash impurities; inhibitor adsorption; altered heat transfer; batch-dependent surface chemistry	Characterise BET area, Raman/defects, oxygen content, ash and ICP metals; inhibitor adsorption isotherm; ROOH evolution; matched thermal history	Carbon fillers can scavenge or promote radical chemistry depending on grade. Reported shipment instability is an industrial observation requiring controlled attribution.
Metallic, mixed-metal and low-purity pigments	Accessible Fe, Cu, Mn, Co or other redox-active ions; acidic washing residues; moisture; reactive surface treatments	Extractable rather than total metal; Acid Number; conductivity/ions; peroxide challenge; package-contact controls	Low purity and inadequate washing increase uncertainty, but metal-containing pigments are not automatically pro-initiating.

Transport amplification: unconditioned summer or maritime transport may expose drums to temperatures far above the recommended storage range; Arrhenius acceleration can shorten the induction period even in darkness. Use measured package-temperature profiles or justified thermal cycles, not nominal ambient temperature alone.

Table 12. Machine-readable companion to Figure 8: condition-dependence and quality-control matrix.

Control variable	Why it matters	Preferred measurement	Risk signal	Interpretive caution
Dissolved oxygen	Controls MEHQ performance and oxidation regime	Headspace and dissolved-O ₂ method validated for the matrix	O ₂ depletion, uncontrolled ingress or strong lot-to-lot variation	High O ₂ can also support autoxidation; optimum is system-specific
Hydroperoxide burden	Immediate precursor reservoir for redox radical generation	Peroxide value or selective ROOH method with matrix blank	Increasing ROOH before viscosity drift	Methods can respond differently to pigments, reductants and thiols

Control variable	Why it matters	Preferred measurement	Risk signal	Interpretive caution
Acid Number / acidity	Indicator of acidic residues and corrosion/speciation pressure	ISO/ASTM acid-number method applied consistently	Upward drift or value above validated family range	Does not identify the acid; HEA/HEMA are reactive residuals but not equivalent to Acid Number
Extractable Fe and Cu	Links package, pigment or filler to catalytic redox chemistry	Extraction protocol plus ICP-OES/ICP-MS; soluble fraction preferred	Increase after ageing or package contact	Total metal does not equal catalytic availability
Temperature history	Controls reaction rate and shipment acceleration	In-package logger or justified thermal cycle	Excursions above validated storage limit	Ambient air temperature may not represent drum-core temperature
Inhibitor identity and assay	Defines actual stabiliser reserve and speciation	HPLC/UV, elemental or speciation methods as appropriate	Loss, precipitation or colour/speciation change	Analytical response must distinguish parent additive from products
Viscosity / microgel / gel	Detects early network formation	Rheology, filtration, insoluble fraction and microscopy	Non-Newtonian drift, particles or rising gel fraction	Bulk viscosity can remain normal while local microgel forms
Cure response after ageing	Prevents over-stabilisation and confirms product utility	RT-FTIR, photo-DSC, working curve or application-specific cure test	Reduced conversion, slower cure or altered depth/profile	Storage stability alone is not an acceptable endpoint

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