

ER-99

Dispersant Chemistry for Photo-Curable Resins, Oligomers and Monomers in 2D, 2.5D and 3D Photopolymerisation
Historical Evolution, Molecular Architecture and Engineering Performance

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Document type	Scope	Commercial products	Proprietary formulation data	Primary application
Engineering Review	Provider-neutral chemistry and engineering review	Not identified or compared	Excluded	Photo-curable resins, oligomers and monomers; 2D and 3D evidence; 2.5D engineering-inference extension; VPP; pigmented and particle-filled systems

Statement of Significance

Dispersants are often treated as secondary formulation additives, yet in pigmented, ceramic-, metal- and filler-loaded photo-curable systems they can determine whether the formulation can be manufactured, stored, recoated, exposed and resolved at all. The useful design variable is not simply “molecular weight” or “surfactant strength”. It is the coupled architecture of particle-affine anchoring groups, resin-compatible solvating segments, molecular topology and, where relevant, reactive or renewable functionality. This review reconstructs the historical evolution from small-molecule wetting agents and hydroxy-fatty-acid oligomers to branched, grafted, block, comb-like and reactive polymeric dispersants, then translates that evolution into an engineering framework spanning 2D and 3D photopolymerisation, with particular attention to vat photopolymerisation (VPP); extension to 2.5D processes is treated as engineering inference rather than direct source coverage. Commercial supplier identities and product-to-product comparisons are intentionally outside scope; the discussion is based on public chemistry, primary literature and patent disclosures.

Abstract

High-solids photopolymer formulations require simultaneous control of wetting, particle-particle attraction, suspension rheology, sedimentation, optical transport and photopolymerisation. Historically, dispersant chemistry progressed from low-molecular-weight amphiphiles to oligomeric hydroxy-fatty-acid structures, polymeric anchoring agents, and increasingly defined block, grafted, branched and comb-like architectures. Public patent literature from the 1970s onward documents an important route based on ricinoleic acid and 12-hydroxystearic-acid polyesters, including polyester-polyamine and polyester-polyethyleneimine structures. Later approaches used polylactone, polyester or polyether solvating chains attached to multi-amine backbones, while controlled radical polymerisation enabled systematic AB, ABA and comb architectures. For VPP, these structural changes matter because dispersant adsorption changes agglomerate size, effective solids fraction, viscosity, yield stress, sedimentation, refractive-index contrast and absorption/scattering, thereby shifting exposure latitude, cure depth and feature fidelity. The review proposes an architecture-surface-resin-process framework for selecting and qualifying dispersants without reliance on commercial product identities. Bio-derived content is treated as an orthogonal design dimension: castor-oil-

derived ricinoleate and 12-hydroxystearate chemistry provides a historically important renewable route, but renewable origin alone does not predict dispersion or printing performance.

Keywords: dispersant; wetting agent; polymeric dispersant; pigment; ceramic slurry; metal slurry; photo-curable resin; oligomer; monomer; photopolymerisation; vat photopolymerisation; steric stabilisation; block copolymer; graft copolymer; comb polymer; polyhydroxystearic acid; ricinoleic acid; castor oil; bio-based additives.

1. Scope and evidence boundary

ER-99 addresses the molecular and interfacial design of dispersants used in non-aqueous photo-curable resins, oligomers and monomers across 2D and 3D photopolymerisation, with particular attention to particle-filled VPP. The same architecture-to-performance reasoning is extended to 2.5D photopolymerisation only as an engineering inference requiring process-specific validation; no source retained in this review directly studies 2.5D processing. Representative reactive matrices include acrylate/methacrylate, epoxy, vinyl-ether, thiol-ene/thiol-yne and other photo-reactive chemistries. ER-99 does not assume that adsorption, solvation, rheology or cure interactions transfer quantitatively between these chemistries; chemistry-specific behaviour requires formulation-specific validation. The same architecture principles are relevant to photo-curable inks, coatings, filled adhesives and radiation-curable composites, while the process constraints of VPP are treated explicitly. The review does not identify the suppliers used in any proprietary formulation, does not map commercial trade names onto 3Dresyns products, and does not disclose internal dosage, compatibility, screening, sourcing or processing know-how. When patents are cited, they are used as historical evidence of disclosed chemical architectures rather than as endorsements or evidence of present commercial composition.

The scope is separated from neighbouring reviews. ER-36 controls the rheology of highly filled suspensions as a subject in its own right; ER-99 treats rheology as a consequence of dispersant architecture and stops at the interface. ER-44 controls optical attenuation and cure-depth physics; ER-99 records the optical consequences of dispersion state without developing that physics. ER-80 controls in-can stability and premature polymerisation; sedimentation and viscosity drift appear here only as dispersant-screening endpoints. ER-83 controls photocuring pathway taxonomy. ER-85 controls CIM/MIM feedstock questions; debinding and sintering appear here only as downstream consequences of green-body organic content. ER-95 controls photoinitiator migration and substitution; the reactive-dispersant and interfacial-environment discussions here do not inherit its conclusions. ER-96, ER-97 and ER-98 control thermomechanical dimensional stability, wettability and capillary flow, and charge-transfer-complex photoinitiation, respectively; ER-99 does not re-enter those measurement or mechanism domains. ER-99 owns the dispersant-specific chain from molecular architecture through colloidal state, rheology and optical transport to printed and sintered performance.

Three evidence classes are distinguished. “Established” denotes mechanisms supported by primary colloid/polymer literature in chemically comparable systems. “Adjacent” denotes evidence from coatings, inks or aqueous dispersions that is mechanistically useful but not directly transferable to 100% solids VPP. “Engineering inference” denotes a consequence that follows from accepted interfacial or photopolymer physics but still requires formulation-specific validation.

2. Why dispersion is a molecular-architecture problem

Particle dispersion requires two distinct operations: initial wetting/deagglomeration and subsequent stabilisation against reflocculation. A molecule may be an effective wetting agent but a weak long-term stabiliser, or vice versa. Polymeric dispersants became important because a macromolecule can use one part of its structure to adsorb to a particle while another part remains solvated in the continuous phase and generates steric repulsion. Reviews of polymeric titania stabilisation emphasise that adsorption depends strongly on functional-group type and density and that performance cannot be predicted from a generic “polymeric dispersant” label alone. [1, 2]

The minimum useful architecture therefore contains two functions: (i) an anchoring domain with sufficient affinity for the specific surface, and (ii) a stabilising domain that remains well solvated in the resin. Multidentate or multipoint adsorption can improve resistance to displacement, while sufficiently extended solvated chains increase the steric barrier. Too much surface affinity can be counterproductive if the polymer bridges particles; too little affinity leaves the stabilising chain free in solution. Molecular weight is therefore a design parameter, not a quality ranking.

Architecture-to-performance chain for dispersants in photo-curable particulate resins

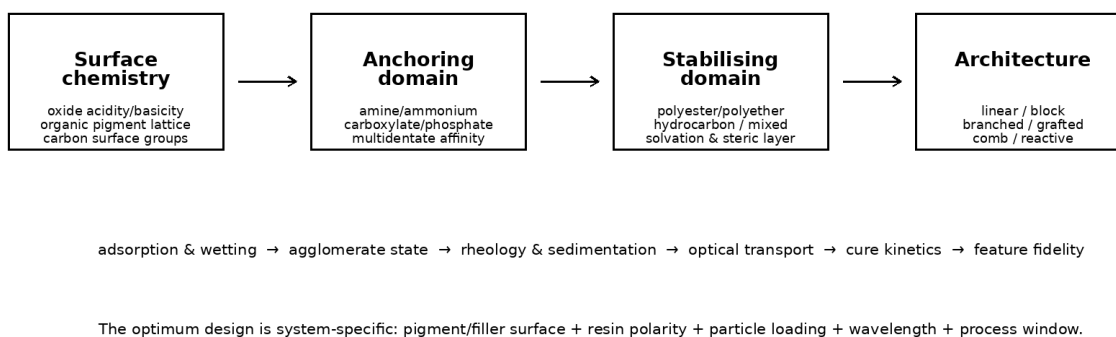


Figure 1. Architecture-to-performance chain used throughout ER-99.

3. Historical evolution of dispersant chemistry

3.1 Small-molecule wetting agents and ionic stabilisers

Early dispersion practice relied heavily on low-molecular-weight amphiphiles: fatty acids and their salts, fatty amines, phosphate esters, sulfonates, soaps, lecithin-like phospholipids and related surfactants. Their principal strengths are rapid interfacial orientation, reduced wetting energy and low viscosity contribution. Their limitations are equally fundamental: a molecular monolayer usually provides less steric thickness than a solvated polymer chain, desorption can occur when the medium polarity changes, and ionic stabilisation can be weakened by counterions, acidity, water or changes in dielectric environment. In VPP, low-molecular-weight amphiphiles remain useful where viscosity and rapid wetting dominate, but they should not be assumed to provide the storage robustness of a deliberately anchored polymeric architecture.

3.2 Hydroxy-fatty-acid oligomers: the castor-oil route

A major historical step was the use of long-chain hydroxycarboxylic acids as self-condensing polyester building blocks. Public patents from the 1970s describe dispersants based on ricinoleic acid, 12-hydroxystearic acid and related hydroxy-fatty acids. One disclosed synthesis heated ricinoleic acid at approximately 190–200 °C while removing water to form polyricinoleic acid; another preferred route used commercial hydrogenated castor-oil fatty acid rich in 12-hydroxystearic acid. The resulting polyester provided a long, resin-compatible aliphatic stabilising segment while terminal acid functionality could be coupled to amine-containing anchoring structures. [3, 4]

This chemistry is historically important for bio-derived dispersant design because ricinoleic acid is the defining fatty acid of castor oil, a seed-derived feedstock. Hydrogenation converts the unsaturated ricinoleate motif into 12-hydroxystearate chemistry while retaining the secondary hydroxyl group needed for polyester formation. The engineering lesson is broader than the feedstock: a hydroxy-fatty-acid polyester combines a highly solvophilic organic segment with a terminal function that can be converted into a stronger anchoring architecture.

3.3 Polyester-polyamine and branched polyimine architectures

The next important development coupled carboxyl-terminated polyesters to polyamines or polyalkyleneimines. A 1980 patent disclosed dispersing agents formed by reacting a poly(lower alkylene)imine, preferably branched polyethyleneimine (PEI), with a carboxyl-terminated polyester so that at least two polyester chains were attached to each polyimine chain. The disclosure explicitly includes ricinoleic acid, 12-hydroxystearic acid and hydrogenated castor-oil fatty acid as polyester precursors. [4]

This architecture is conceptually powerful. The amine-rich branched core can provide multiple adsorption sites, while several polyester chains extend into the organic phase to supply steric stabilisation. It is therefore an early example of what would now be described generically as a branched or grafted polymeric dispersant with a multidentate anchoring domain and multiple solvating arms.

3.4 Polylactone, polyester and polyether grafts

Later patent literature broadened the solvating arms beyond self-condensed hydroxy-fatty-acid polyesters. Disclosed structures include PEI backbones carrying polylactone chains grown by ring-opening polymerisation, particularly caprolactone and valerolactone, followed by modification with fatty-acid, hydroxy-fatty-acid, polyhydroxystearate or acid-terminated polyether

residues. These disclosures explicitly separate the functions: the polyimine segment supplies pigment affinity, while grafted polyester chains interact with the resin phase and form the steric stabilising environment. [5]

This marks a transition from “a dispersing molecule” to deliberate modular architecture. Anchor density, arm number, arm length, polyester identity and end-group chemistry become separately tuneable parameters. The same design logic can be implemented with polyester, polyether or mixed stabilising segments selected to match the polarity and hydrogen-bonding characteristics of the continuous phase.

3.5 Block, grafted and comb architectures from controlled polymerisation

From the late 1980s onward, block-copolymer approaches increasingly separated pigment-affine and medium-compatible segments. Patent literature described AB/BAB structures in which a polar or ionic segment adsorbs at the pigment and a second block provides steric stabilisation. [6]

Controlled/living radical polymerisation then made this architecture experimentally systematic. Fang et al. prepared AB diblock, ABA triblock and comb dispersants by RAFT polymerisation and directly compared molecular weight, composition, anchoring-chain length and stabilising-chain length for silica dispersion in organic media. Their results show that topology itself changes particle size and viscosity; “comb” is not automatically superior to a well-balanced diblock or triblock. [7]

Related structured-polymer work uses ATRP, RAFT, NMP, catalytic-chain-transfer/macromonomer routes and other controlled methods to position anchoring groups in selected blocks and maintain a separately solvated stabilising block. [7, 8]

3.6 Reactive and network-integrating dispersants

A later design objective is to reduce the amount of permanently mobile dispersant after cure. Public block-copolymer literature describes dispersants carrying functional groups capable of reacting with film-forming components, so that the dispersant can become part of the final network rather than remain fully extractable. [8]

For photo-curable reactive matrices, the analogous engineering strategy is a dispersant bearing acrylate, methacrylate, allylic, vinyl, epoxide, thiol or other polymerisable/crosslinkable functionality positioned so that it does not destroy adsorption or solvation before exposure. Such functionality can reduce migration and extractability when it becomes incorporated into the network, but it introduces new constraints: the reactive group may change viscosity, storage stability, cure kinetics, network heterogeneity and interfacial stress. Reactive dispersants should therefore be treated as resin components, not simply process aids, and their behaviour must be validated in the specific cure chemistry.

Historical evolution of dispersant molecular design

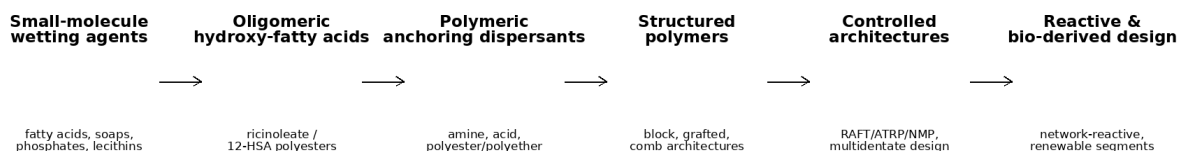


Figure 2. Simplified historical progression from molecular wetting agents to structured, reactive and bio-derived dispersant architectures. The stages overlap; later approaches do not universally replace earlier ones.

4. Architecture taxonomy for provider-neutral formulation design

Family	Typical architecture	Primary stabilisation	Strength	Principal risk
Small-molecule amphiphile	single head + tail	wetting; electrostatic/limited steric	low viscosity, fast wetting	desorption; weak steric layer
Oligomeric fatty polyester	short polyester + terminal anchor	steric + adsorption	organic-phase compatibility	insufficient anchor density
Linear polymeric	anchor groups along/backbone end	steric/electrosteric	simple, tunable MW	bridging or weak adsorption
Branched/grafted	multifunctional core + solvating arms	multi-point adsorption + steric	strong retention, high efficiency	over-adsorption; viscosity
Block copolymer	distinct anchor and solvating blocks	selective adsorption + steric	precise function separation	synthesis/compatibility sensitivity
Comb-like	backbone with many side chains	multi-anchor or multi-arm steric	high interfacial coverage	topology not universally optimal
Reactive polymeric	above + polymerisable function	steric + network integration	lower migration potential	cure/stability coupling

Table 1. Provider-neutral classification used in this review.

5. Anchoring chemistry: match the surface, not the trade name

The preferred anchor is determined by surface chemistry. Oxide surfaces such as TiO₂, Al₂O₃, ZrO₂ and native metal oxides expose hydroxylated and acid/base sites whose density depends on crystal face, treatment, water history and pH. Carboxylates, phosphates/phosphonates, polyacids, amines and other polar groups can adsorb through acid-base, coordination, hydrogen-bonding or ionic interactions. The strongest anchor in one oxide/resin system may be excessive or poorly solvated in another. Farrokhpay's review of titania emphasises that functional-group type and density govern adsorption and stabilisation and that the lessons extend qualitatively to alumina and zirconia. [1]

Organic pigments present a different problem. Their surfaces may contain aromatic, heterocyclic, acidic or basic sites and are frequently surface-treated. Anchoring can exploit acid-base pairing, aromatic affinity, hydrogen bonding or pigment-derivative interactions. Carbon black introduces graphitic surface domains plus oxygenated groups, ash and trace metals; its effective surface chemistry varies strongly by grade. Metals in VPP are commonly oxide-covered, so the relevant interface is often dispersant/native-oxide/resin rather than dispersant/bulk metal.

For this reason, a useful provider-neutral formulation rule is: select the anchor from surface chemistry first, then select the stabilising segment from resin compatibility, and only then tune molecular weight/topology.

6. Stabilising segment: solvation in photo-curable media

Steric stabilisation fails if the arm or block collapses in the continuous phase. In solvent-free photo-curable systems, "solvent compatibility" becomes compatibility with reactive diluents, oligomers and other network-forming components. Polyester-rich arms can be attractive in ester-rich reactive matrices, including many acrylate/methacrylate systems; polyether segments may improve compatibility with more polar monomers but can increase water affinity; hydrocarbon/fatty segments favour hydrophobic reactive media but may be mismatched to highly polar systems. Mixed polyester/polyether or compositionally graded structures can broaden the solvation window. These trends are formulation dependent and are not assumed to transfer quantitatively between acrylate/methacrylate, epoxy, vinyl-ether, thiol-ene/thiol-yne or other photo-curable chemistries.

The arm must also be long enough to generate a steric barrier but not so long or numerous that the free dispersant fraction raises viscosity or plasticises the cured network. The optimum therefore depends on particle surface area as well as particle mass. Nanoparticles and high-BET ceramics can require far more interfacial polymer per unit mass than coarse powders.

7. Molecular architecture versus molecular weight

"High-molecular-weight dispersant" is an incomplete descriptor. Two dispersants with identical Mn can differ radically if one is a random linear polymer and the other is an AB block or branched graft polymer. Architecture controls how much of the chain is sacrificed to adsorption and how much remains available for steric stabilisation. Structured polymer studies show that AB, ABA and comb topologies can produce different particle size and viscosity even at broadly comparable chemistry. [7]

The useful variables are therefore: (i) number and strength of anchors per molecule; (ii) anchor distribution; (iii) solvating-arm length; (iv) arm density; (v) backbone flexibility; (vi) total molecular-weight distribution; and (vii) the ratio of adsorbed to unadsorbed polymer. A high molecular weight with poor topology can bridge particles and increase yield stress; a lower molecular weight with correctly segregated anchor and solvating domains can outperform it.

8. Translation to vat photopolymerisation

8.1 Rheology and solid loading

Ceramic VPP requires unusually high solid loading while retaining sufficient flow for recoating. Reviews of ceramic VPP identify dispersant type and concentration as major determinants of viscosity, shear behaviour, yield stress and achievable solid fraction. [9, 10]

The molecular explanation is straightforward: poor dispersion creates agglomerates and immobilised resin, increasing the effective hydrodynamic volume fraction. Effective adsorption breaks or prevents agglomerate networks and releases trapped continuous phase, often lowering viscosity dramatically. At excessive dosage, unadsorbed polymer or multilayer adsorption can increase viscosity, cause depletion effects, alter cure chemistry or change sedimentation behaviour. In the cited VPP systems, optimisation is expressed through system-specific minimum-viscosity or maximum-stability windows; no universal dosage rule follows from those results.

8.2 Optical transport and cure

Recent VPP reviews report that dispersant choice can affect slurry transmittance: as the absorption coefficient of the dispersant increases, slurry light transmittance decreases [11]. Dispersant type and content are separately reported as major determinants of slurry rheology [9, 10]. These are review-level syntheses of primary studies rather than primary measurements.

As an engineering inference requiring formulation-specific validation, adsorption at particle surfaces may also alter the local distribution of photoinitiator or inhibitor species. ER-99 does not treat such partitioning as established without direct chemical or interfacial evidence.

Accordingly, a dispersant cannot be qualified only by viscosity. A formulation that gives the lowest viscosity may still be inferior if it increases optical attenuation, shifts working-curve parameters, broadens lateral cure or interferes with conversion. For high-resolution printing the correct objective is a coupled optimum: stable dispersion + acceptable recoating rheology + controlled optical penetration + sufficient radical generation.

8.3 Surface area, sedimentation and green-body uniformity

Sedimentation is controlled by density contrast, particle size/agglomeration, continuous-phase viscosity and interparticle structure. A dispersant that reduces agglomerate size can paradoxically slow or accelerate settling depending on whether it simultaneously changes viscosity and yield stress. In high-density metal and ceramic slurries, storage and vat residence should therefore be assessed separately from short rheology measurements. Spatial variation in solids loading translates directly into dimensional, cure and debinding heterogeneity.

8.4 Downstream debinding and sintering

For ceramic and metal feedstocks, dispersant chemistry remains present in the green body and therefore contributes to organic content, decomposition profile, gas evolution and possible residue. The dispersant is therefore not a pre-print-only variable: its architecture propagates through colloidal state and rheology into the printed body and the sintered result.

9. Bio-derived dispersant chemistry as an orthogonal design dimension

Renewable origin does not define dispersant performance. A bio-derived fatty segment can be incorporated into a weak small-molecule surfactant, an effective oligomeric polyester or a sophisticated graft polymer. Conversely, a high-performance structured polymer may contain only a limited renewable fraction. Bio-derived content should therefore be reported separately from architecture and performance.

The most historically established renewable route in organic dispersants is castor-oil chemistry. Ricinoleic acid provides both a long C18 hydrophobic chain and a secondary hydroxyl group, enabling self-polycondensation to polyricinoleate. Hydrogenation gives 12-hydroxystearic-acid chemistry, which likewise forms polyhydroxystearate segments. The 1970s–1980s patent record documents both routes in dispersants for organic pigment systems. [3, 4]

Other plausible renewable building blocks include fatty-acid polyesters from other plant oils, polyglycerol-derived segments, cardanol-derived aromatic/alkyl structures, rosin-derived groups and bio-derived polyesters/polyethers. Their usefulness must be established by the same tests as fossil-derived architectures. “Natural” or “bio-based” is not evidence of miscibility in a photo-curable reactive matrix, low colour, low water uptake, photochemical inertness or adequate shelf stability.

10. Selection matrix by dispersed phase

Dispersed phase	Likely anchor emphasis	Stabilising-domain emphasis	VPP-specific risk	Evidence status
TiO ₂ / oxide pigment	carboxylate, phosphate/phosphonate, polyacid, selected amines	polyester/polyether matched to resin	strong scattering; surface treatment variability	Established/adjacent
Organic pigments	acid-base and aromatic affinity; multidentate adsorption	organic-soluble polyester/acrylic block	colour strength vs cure absorption	Adjacent
Carbon black / graphite	amine/aromatic affinity; grade-specific polar sites	strongly solvated organic block	possible PI/inhibitor interfacial interaction; optical opacity	Engineering inference / adjacent optics
Al ₂ O ₃ / ZrO ₂ / SiO ₂	oxide-affine acid/base or coupling chemistry	steric polymer arm	high BET; viscosity; scattering	Established VPP
Metal powders	native-oxide affinity; robust multidentate anchor	resin-compatible organic arm	density; oxide variability; trace metals	Engineering + VPP
Nano-fillers	high anchor density, strong adsorption	sufficient arm thickness	very high surface demand; viscosity	Established/adjacent

Table 2. Architecture-first selection matrix. “Likely” indicates screening direction, not universal compatibility.

11. Qualification workflow for photo-curable resins, oligomers and monomers

A provider-neutral dispersant screen should use the same base resin, solid grade, milling protocol and solids loading. The minimum useful sequence is:

- Compatibility before solids: clarity/haze, phase separation and viscosity of dispersant in the reactive resin.
- Adsorption/wetting screen: grind time, agglomerate size, surface coverage proxy and minimum-viscosity dosage curve.

- Rheology: viscosity over process-relevant shear rates, yield stress where relevant, thixotropic recovery and temperature dependence.
- Stability: accelerated and room-temperature sedimentation, redispersibility, viscosity drift and any colour/odour change.
- Optics: UV-Vis at the actual exposure wavelength, scattering/transmittance and working-curve shift.
- Photochemistry: Ec/Dp or equivalent exposure response, conversion, oxygen sensitivity and post-cure behaviour.
- Print fidelity: lateral cure, fine-feature retention, trapped-resin clearing and dimensional accuracy.
- Downstream performance: green strength, debinding residue/gas evolution for ceramic/metal systems, and final densification where applicable.
- Ageing interaction: repeat critical measurements after thermal/light storage to detect adsorption changes, hydrolysis, oxidation and any formulation-specific evidence consistent with altered photoinitiator/inhibitor distribution; do not assume surface partitioning without direct evidence.

The outcome should be an architecture-performance map, not a single ranked list. A dispersant that is optimal for a low-BET organic pigment may be inappropriate for a high-BET oxide nanopowder, even in the same photo-curable reactive matrix.

12. Failure modes and diagnostic signatures

Observed problem	Likely dispersant mechanism	Diagnostic	Corrective direction
High viscosity at low dosage	poor wetting/weak adsorption	large agglomerates; no viscosity minimum	change anchor chemistry or resin compatibility
Viscosity rises after optimum	free polymer/multilayer/bridging	minimum in dosage curve	reduce dose or change topology/MW
Good viscosity, fast settling	insufficient structural stability	low yield stress; clear supernatant	increase adsorption/steric layer or tune rheology
Stable slurry, poor cure depth	dispersant/filler optical absorption or scattering	UV-Vis/working curve shift	change optical profile or dosage
Good initial cure, ageing drift	chemical interaction or desorption	viscosity/Ec/Dp changes with ageing	screen stability/inhibitor interactions
Poor green/sintered uniformity	spatial solids segregation	density gradient; debinding defects	improve colloidal stability and vat handling

Table 3. Mechanism-oriented troubleshooting.

13. Research gaps

Several gaps remain despite decades of dispersant development. First, most industrial chemistry was developed for coatings and inks, while VPP imposes a unique requirement that the continuous phase must also remain optically and kinetically printable. Second, many ceramic VPP studies report trade names rather than molecular architecture, which makes cross-study transfer difficult. Third, dispersant concentration is often reported by total slurry mass rather than by particle surface area, obscuring comparison between powders of different BET area. Fourth, photochemical effects are frequently measured only as cure depth without separating absorption, scattering, possible interfacial redistribution of photoinitiator species and radical inhibition; the interfacial term remains an engineering hypothesis until measured directly. Fifth, the downstream role of dispersant in debinding and sintering remains under-integrated with pre-print rheology optimisation.

A useful future direction is to report dispersants by generic architecture descriptors: anchor family; stabilising-chain family; topology; approximate molecular-weight range; active fraction; bio-derived fraction if measured; and reactive functionality if present. Such descriptors preserve commercial neutrality while allowing scientifically meaningful comparison.

14. Conclusions

Dispersant chemistry has evolved from small-molecule wetting agents to deliberately structured macromolecules that separate anchoring and stabilising functions. Hydroxy-fatty-acid polyesters derived from ricinoleic acid and 12-hydroxystearic acid represent an important historical bridge between renewable feedstocks and polymeric dispersion technology. Coupling such polyester segments to polyamine/polyimine structures introduced multipoint adsorption and multiple solvating arms; subsequent polylactone, polyether, block, grafted and comb designs made those functions increasingly modular and controllable.

For photo-curable formulations across 2D, 2.5D and 3D processes, and especially for particle-filled VPP, this molecular evolution matters because the dispersant sits upstream of both rheology and photochemistry. It changes wetting, agglomeration, effective solids fraction, sedimentation and optical attenuation. It may also change the local interfacial environment experienced by photoinitiator and inhibitor species, but any specific surface-partitioning mechanism remains an engineering inference unless it is measured directly in the formulation of interest.

The engineering design rule emerging from the evidence is concise: match the anchoring domain to the particle surface, match the stabilising domain to the reactive resin, select topology to provide sufficient interfacial retention without bridging, then validate the resulting dispersion against both rheological and photochemical process windows. Bio-derived content can be added to this framework, but it is an independent axis rather than a substitute for molecular design.

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Version note

v0.6 incorporates the independent bibliography/patent gate corrections from the ER-99 v0.4 HOLD review and the author-requested scope generalisation from acrylate-specific wording to photo-curable resins, oligomers and monomers across 2D and 3D photopolymerisation, with the 2.5D extension explicitly labelled as engineering inference requiring process-specific validation. The unlocatable Zhou et al. reference has been withdrawn and its two load-bearing sentences rewritten without a replacement citation. EP0329873A1 no longer carries the false priority claim; the transmittance statement is assigned to [11] rather than [10]; patent date/status details and minor bibliographic fields are corrected. Chemistry-specific names such as acrylate/methacrylate, epoxy, vinyl ether and thiol-ene/thiol-yne are retained only where they identify representative or source-specific chemistries, and no quantitative transfer between cure chemistries is assumed. The nine declared ER boundaries, protected-know-how controls, system-specific dosage wording and engineering-inference labelling are preserved. The focused independent review and release controls were completed.