

Waterborne UV-Curable Dispersions: Water Removal, Coalescence, Photocure and Film-Formation Coupling

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Statement of Significance

A waterborne radiation-curable coating does not pass directly from liquid formulation to cured network in one step. Water must be redistributed and removed to the degree required by the system, dispersed polymer particles or domains must approach and consolidate, mobile hydrophilic species can redistribute, and reactive groups must then reach a sufficient photochemical state. These events can overlap, compete or arrest one another. A film may look dry while remaining weakly consolidated, may reach substantial chemical conversion while retaining water or morphology defects, or may develop a surface conversion state different from its interior. ER-189 treats the process as a coupled state trajectory and defines the evidence needed to qualify that trajectory without prescribing a universal flash-off or UV recipe.

Keywords: waterborne UV curing; polyurethane dispersion; polyurethane acrylate; latex film formation; water evaporation; coalescence; photopolymerisation; oxygen inhibition; surfactant migration; film continuity; qualification

Abstract

Waterborne UV-curable dispersions combine at least two distinct transformations: formation of a coherent film from an aqueous colloidal state and photochemical conversion of reactive functionality into a network. Direct studies of waterborne polyurethane and polyurethane-acrylate dispersions show that polymer architecture, functionality, drying history and irradiation conditions affect conversion and final properties [1-7]. General latex-film studies independently show that evaporation, particle packing, deformation and interparticle consolidation depend on temperature, evaporation rate and particle mechanics, while mobile surfactants can redistribute during film formation [8-10]. These mechanisms cannot be collapsed into a single variable called cure.

ER-189 reviews the engineering coupling among water removal, colloidal consolidation, coalescence where applicable, migration of mobile species, oxygen inhibition and photochemical network formation. It distinguishes a visually dry film from a sufficiently consolidated film and both from a chemically converted network. It also separates incident UV conditions from the local reaction state and treats the order of drying and irradiation as a process variable that must be declared and qualified. No universal flash-off time, drying temperature, residual-water threshold, minimum film-formation temperature, UV dose, irradiance, wavelength, photoinitiator loading or film thickness is proposed.

1. Scope, terminology and ownership

ER-189 addresses radiation-curable dispersions in which water is a continuous or major carrier phase before application and a photoreactive polymer or oligomer becomes part of the final film. Waterborne polyurethane dispersions and polyurethane-acrylate dispersions are prominent examples, but the engineering framework is not restricted to one backbone chemistry.

Within the named sub-series *Radiation Curing Beyond Additive Manufacturing*, the same photochemistry, oxygen-inhibition, attenuation, interfacial and qualification principles are examined in films, coatings, inks

and bulk-applied materials rather than only in printed layers. ER-189 focuses specifically on the aqueous dispersion-to-film trajectory in waterborne coatings.

The term **drying** is used here for removal or redistribution of water and any other volatile carrier. **Consolidation** denotes the transition from separated or closely packed dispersed particles or domains toward a mechanically continuous film. **Coalescence** is used only where particle deformation, interfacial disappearance and molecular interpenetration are mechanistically appropriate. **Photocure** denotes radiation-driven conversion and network formation. These states can be coupled without being equivalent.

ER-189 owns the aqueous dispersion-to-film trajectory. ER-066 retains high-molecular-weight latexes as VPP feedstocks. ER-103 retains generic polyurethane chemistry. ER-168 retains coating and encapsulation qualification on reactive printed photopolymer substrates. ER-196 owns the thin pigmented graphic-ink surface-cure problem. These boundaries prevent ER-189 from becoming a general polyurethane synthesis review, a VPP-printability review or a graphic-ink review.

2. A waterborne UV film is created by more than one transformation

A conventional 100%-solids radiation-curable formulation can often be analysed primarily as an optical and reaction problem: photons are delivered, initiating species are created, reactive groups are consumed and a network develops. A waterborne dispersion adds a colloidal transport problem before and during that chemistry. The wet layer contains water, polymer particles or dispersed domains, ionic or nonionic stabilising groups, photoreactive functionality, photoinitiator and potentially pigments, fillers, rheology modifiers, defoamers and other mobile species.

As water leaves, the local solids fraction increases. Particles approach each other, capillary and interfacial forces change, viscosity rises and the optical path can change. If irradiation begins before the aqueous structure has reached the intended state, crosslinking can reduce mobility that would otherwise assist deformation or interdiffusion. Conversely, delaying irradiation can permit more complete physical film formation but also allows more time for migration, oxidation, contamination or substrate interaction. There is therefore no single scalar variable that describes the transition from wet dispersion to qualified film.

Banan's 2025 WPUA study provides a clear system-specific example of process separation: the cast films were dried before UV irradiation, and the UV step then changed mechanical, surface and water-resistance properties [1]. That sequence demonstrates separability of physical drying and photochemical crosslinking. It does not establish a universal 24-hour or room-temperature drying requirement.

3. The deposited dispersion is already a structured material state

The starting point is not simply polymer plus water. A dispersion has a particle-size distribution, interfacial chemistry, surface charge or steric stabilisation, continuous-phase composition, pH, ionic strength, solids content and rheological state. Duan et al. reported UV-curable WPUA dispersions with measured particle size and zeta potential before preparing cured coatings, illustrating that colloidal state is a measurable precursor to final film behaviour [2]. Banan likewise measured dispersion particle-size distributions and stability before assessing the corresponding films [1].

Those properties matter because the drying film inherits them. Particle size influences packing length scale and interfacial area. Hydrophilic groups that stabilise the dispersion may later contribute to water uptake or remain mobile. Neutralisers and surfactants can partition differently as water disappears. Reactive acrylate groups may be located on particle surfaces, within particles, on separate oligomeric species or in interpenetrating components, so chemical conversion need not begin from a spatially homogeneous molecular state.

Qualification should therefore preserve the liquid-state identity that created the film: formulation version, solids content, particle-size distribution or another justified dispersion-state metric, pH where relevant,

viscosity/rheology, age, storage history, mixing history and any dilution or additive introduced immediately before application. A cured-film test without a controlled precursor state cannot distinguish an inherent formulation property from a shifted dispersion state.

4. Water removal creates concentration and transport gradients

Evaporation is spatial. The air-facing surface usually exchanges water with the environment more directly than the substrate-facing region. Substrate permeability, wet-film thickness, air velocity, temperature, humidity and boundary-layer conditions can therefore produce a water-content gradient through the film. Heating may accelerate evaporation, but it can also change polymer mobility, surface skin formation and reaction kinetics.

General latex research shows that drying rate cannot always be reduced to an external evaporation constant. Routh and Russel described competing deformation mechanisms during consolidation [8]. Keddie's film-formation framework similarly treats evaporation, particle packing, deformation and interdiffusion as linked but separable stages [10]. These studies are not UV-PUD qualification data; they provide the physical basis for expecting water distribution to depend on both environment and particle mechanics.

A mass-loss plateau can be useful evidence of volatile removal, but it does not automatically prove a uniform through-film water state. The same total mass can be distributed differently through thickness or trapped at interfaces. For critical qualification, gravimetry may need to be combined with spatial or spectroscopic evidence, especially when film thickness, substrate impermeability or rapid surface drying creates a plausible gradient.

5. Particle packing, deformation and coalescence are conditional mechanisms

As water leaves a colloidal film, particles become concentrated and can approach close packing. A continuous film then requires sufficient deformation or other consolidation to eliminate mechanically significant voids and weak boundaries. Routh and Russel showed that capillary and interfacial driving forces can dominate in different regions of a film-formation map [8]. The implication is not that every UV-curable dispersion follows one canonical path, but that particle modulus, temperature, drying rate and interfacial conditions can change how the film consolidates.

This matters especially when photochemical crosslinking changes mobility. Before network formation, a sufficiently soft polymer domain may deform or interdiffuse. After crosslinking, the same domain can become less able to rearrange. Irradiation that arrives too early for one formulation can therefore freeze a discontinuous morphology. For another formulation, reactive species may be distributed so that early irradiation reinforces already established contacts without preventing continuity. The sequence has to be measured rather than inferred from the label waterborne UV.

Coalescence should also not be demanded when the actual system forms a coherent film by another architecture. Some dispersions contain interpenetrating components, reactive oligomers or particles whose interfaces are modified during cure. The qualification question is whether the final film is continuous and fit for duty and whether the process route creating that state is controlled, not whether it conforms linguistically to a textbook latex mechanism.

6. Drying and photocure order is a process variable

The most common industrial logic for many UV-curable polyurethane dispersions is physical water removal followed by UV exposure. Direct literature examples follow that sequence [1], and waterborne UV systems are often valued precisely because they can acquire handling strength or tack-free character through physical drying before radiation creates the final chemical-resistance and mechanical state.

The engineering error is to turn that common sequence into a universal law. The relevant state is not elapsed flash-off time but the degree and spatial uniformity of water removal and consolidation reached before irradiation. Two ovens with the same residence time can deliver different film states if air temperature, substrate temperature, humidity, wet-film thickness or airflow differs. A laboratory film dried overnight and an industrial film flashed for minutes therefore cannot be called equivalent from time alone.

The opposite sequence also cannot be dismissed without evidence. A formulation deliberately designed to tolerate irradiation before complete water removal may follow a different coupled path. The burden is then to show that irradiation does not trap a harmful water distribution, arrest necessary particle deformation, create voids, generate a weak interface or produce unacceptable conversion gradients. ER-189 therefore treats sequence as a declared variable: apply, dry or flash, irradiate, post-dry or condition, and any overlap between those stages must be recorded.

7. Residual water can be a state variable rather than a binary defect

Water in a nominally dry film can occupy different environments: free or weakly bound water in voids, water associated with ionic groups, water near hydrophilic domains or water retained at an interface. These states can affect optical properties, local mobility, hydrogen bonding, surface energy and subsequent water uptake. The effect depends on chemistry and cannot be replaced by a universal residual-water percentage.

The practical consequence is that acceptance should be linked to function. If residual water affects adhesion, chemical resistance, electrical behaviour, optical clarity or dimensional stability, the qualification plan should measure the relevant state and property after a controlled conditioning interval. A film that reaches constant mass under one laboratory condition is not automatically stable under a different humidity or thermal history.

Banan's study showed that hydrophilic/hydrophobic balance and UV crosslinking influenced water absorption in the investigated WPUA system [1]. The transferable conclusion is that aqueous-process history and network state can remain visible in later water interaction. The numerical water-absorption values are specific to that formulation and test.

8. Photochemical conversion is a second state axis

Once the film is optically and physically ready for exposure, photochemical network formation introduces its own variables: action-spectrum overlap, photoinitiator distribution, irradiance, dose, film optical density, functionality, mobility and oxygen access. Hwang et al. showed that polyol molecular weight and end-group functionality affected cure rate, conversion and physical properties in waterborne UV-curable polycarbonate-based polyurethane dispersions [4]. Llorente et al. used photo-DSC, ATR-FTIR and thermal analysis to resolve reaction rate, UV penetration and crosslink state [5]. Xu et al. likewise combined FT-IR and photo-DSC to analyse WPUA photopolymerisation kinetics [6].

These methods answer different questions. FT-IR can follow consumption of a selected functional group. Photo-DSC measures heat-flow response associated with reaction. Mechanical tests describe later material response. None alone proves that the film is dry, continuous, uniformly cured and fit for service.

The distinction becomes especially important when water removal has already created gradients. A local conversion measurement at the top surface may not describe the substrate interface. A bulk calorimetric response can conceal a thin weak surface layer. A hardness measurement can respond strongly to surface crosslinking while under-reporting internal defects. Qualification therefore needs measurements that correspond spatially and physically to the claim being made.

9. Oxygen inhibition creates a location-specific surface state

Free-radical acrylate photopolymerisation can be inhibited by oxygen at an air-exposed boundary. In waterborne UV-curable films this effect is superimposed on the drying and consolidation history. Zhang and

Wu measured lower top-surface acrylate conversion than bottom conversion in their open-air UV-WPUA films under selected conditions and showed that the difference changed with photoinitiator concentration and irradiance [7].

The result demonstrates two principles. First, film conversion can be spatially nonuniform even when the wet-film preparation is nominally uniform. Second, the air-facing surface is a distinct boundary condition. It does not justify a universal inerting requirement, because oxygen sensitivity varies with chemistry, source, film thickness and reaction pathway. Nor should oxygen-response behaviour be transferred between thiol-ene and ordinary acrylate chain-growth systems merely because both are UV-cured.

A qualification plan should decide whether surface conversion itself is a critical quality attribute or whether its consequence, such as tack, abrasion, adhesion to a subsequent layer or extractables, is the relevant acceptance variable. When surface state matters, measurement should be deliberately surface-sensitive and should record atmosphere and time between drying and exposure.

10. Mobile hydrophilic species can redistribute during film formation

Waterborne dispersions commonly contain ionic groups, neutralisers, surfactants or other hydrophilic species that support colloidal stability. As water evaporates, those species do not necessarily remain uniformly distributed. General latex evidence shows that surfactant can migrate toward film-air and film-substrate regions and that the degree of migration can affect water uptake and adhesion [9].

Amalvy et al. demonstrated that a polymerisable surfactant reduced migration and altered water-absorption behaviour relative to a conventional surfactant in the studied latex systems [9]. This is useful mechanistic evidence but not a universal prescription. A waterborne UV-PUD may use internal ionic groups rather than a freely mobile surfactant, a mixture of stabilisation mechanisms or no analogous additive at all.

The engineering implication is to track mobile species when they plausibly control failure. Surface bloom, poor intercoat adhesion, water sensitivity or a weak substrate interface may arise from chemical redistribution rather than inadequate UV conversion. Increasing UV dose cannot be assumed to correct a migration-created interface. Conversely, a migration signal is not proof of cure deficiency. The diagnosis must keep physical transport and photochemistry separate.

11. Film thickness, substrate and drying environment alter the same formulation

Wet-film thickness changes the distance over which water must move and the volume of water removed per unit area. It can also change internal temperature and the optical path presented during UV exposure. A thicker film may therefore require a different drying history before it reaches the same water and consolidation state as a thinner film. No single wet-film-thickness limit transfers across formulations.

The substrate is another boundary condition. A porous substrate can remove some water through absorption or vapour transport; an impermeable metal, glass or polymer cannot. Substrate temperature changes evaporation and particle mobility. Surface energy influences wetting and can affect how the consolidating film contacts the substrate. If adhesion is a release criterion, the substrate preparation and environmental history are part of the qualification identity.

Drying temperature should likewise be interpreted relative to particle mechanics and chemistry, not as an isolated setpoint. Heating can accelerate water loss and lower polymer viscosity, assisting deformation in some systems. Excessively rapid surface drying can also generate gradients or skinning. A thermal schedule therefore needs evidence of the resulting film state rather than justification from temperature alone.

12. Pigments, fillers and matting agents add transport and optical coupling

Pigments and fillers can modify water transport, rheology, particle packing, optical attenuation and heat flow. A pigment may also compete with the photoinitiator for photons or scatter light away from reactive regions. In a waterborne system, these optical effects are added to the evolving morphology created by drying.

ER-189 treats such additives only insofar as they affect the aqueous dispersion-to-film sequence. It does not own graphic-ink transfer, dot gain or security-feature design. Those subjects belong elsewhere in the corpus. The key qualification question is whether the additive changes the time or conditions needed to reach a reproducible dry/consolidated state and whether it changes the spatial cure state under the declared UV process.

A clear coating and a pigmented coating based on the same binder should therefore not automatically share one process window. Nor should a matting-agent change be treated as purely optical. It can alter wet-film rheology, interfacial area, water release and UV delivery simultaneously.

13. A useful measurement stack separates the coupled states

A strong qualification plan uses orthogonal measurements instead of asking one proxy to represent the complete film.

For the liquid dispersion, relevant observations can include solids content, particle size or another dispersion-state descriptor, pH, viscosity/rheology and storage history. During drying, mass loss, film temperature, environmental temperature/humidity and time can define the external process. Where water gradients are plausible, spatial or spectroscopic methods can add direct evidence.

For consolidation, microscopy, optical clarity, porosity, mechanical integrity before UV, tack, or another validated structural measure can be appropriate depending on film type. For photocure, FT-IR, Raman or another conversion-sensitive method can be used at representative locations, while photo-DSC or related methods can characterise kinetic response during development [5,6]. Final mechanical, adhesion, chemical-resistance, barrier or appearance tests then establish service-relevant outcomes.

No element of this stack is mandatory in every system. The method set follows the claim and failure modes. The critical rule is correspondence: a test for water removal cannot substitute for conversion; a conversion test cannot substitute for film continuity; a final hardness result cannot reconstruct which earlier state variable caused a failure.

14. Qualification should be written as a state trajectory

A defensible process record for a waterborne UV-curable coating should connect at least five states:

1. **received or prepared dispersion**, with controlled formulation and colloidal identity;
2. **applied wet film**, with wet thickness, substrate and application method;
3. **pre-UV film**, with declared drying environment and evidence of the intended water/consolidation state;
4. **irradiated film**, with source spectrum, irradiance or dose descriptor, geometry, atmosphere and local cure evidence;
5. **conditioned final film**, with service-relevant properties after a declared post-cure, post-dry or conditioning interval.

The acceptance criterion can be different at each state. A pre-UV film may need to be sufficiently nonblocking for handling without yet possessing chemical resistance. A post-UV film may need a minimum conversion or surface state. A conditioned film may need adhesion and water resistance. The states should not be back-projected onto one another.

This architecture also makes failures diagnosable. If a final film has poor chemical resistance but the pre-UV water state and film continuity were acceptable, the investigation can focus on cure chemistry or irradiation.

If adhesion fails while bulk conversion is acceptable, the substrate interface, surfactant migration and drying history remain live hypotheses.

15. Scale-up and change control must follow causal variables

Scale-up changes more than residence time. A laboratory drawdown may dry under natural convection on a small thermally uniform substrate. An industrial line may use forced hot air, infrared heating, moving web or thick three-dimensional components. The same nominal air temperature can produce a different film temperature and evaporation rate.

Changes that can reopen qualification include solids content, particle size, neutralisation, stabiliser package, photoinitiator, pigment or filler, wet-film thickness, substrate, application method, flash-off environment, dryer air velocity, line speed, source spectrum, lamp ageing, atmosphere and final conditioning. The degree of requalification should follow the affected mechanism.

A change in dryer geometry primarily reopens water-removal and consolidation evidence. A photoinitiator substitution primarily reopens spectral overlap and conversion evidence but may also alter dispersion stability. A surfactant or neutraliser change can reopen colloidal stability, migration and final water resistance. A pigment change can reopen both drying and optical cure. Treating any of these as an administrative minor change without mechanism analysis can invalidate the transfer.

16. Common invalid shortcuts

Several statements are too weak to qualify a waterborne UV film.

The film is dry to the touch. Tactile dryness does not establish uniform residual water or complete consolidation.

The mass stopped changing. A mass plateau under one environment does not prove a uniform through-film water distribution or equilibrium under service conditions.

The film was UV-cured. Exposure is a process input, not evidence of local conversion or network state.

Conversion is high. High conversion of one reactive group does not establish water removal, film continuity, adhesion or chemical resistance.

The surface is hard. Surface hardness can coexist with an interfacial or internal defect.

The same binder worked in a clear film. Pigments, fillers, matting agents and film thickness can change both water transport and photon delivery.

The same flash-off time was used. Time is not transferable without the thermal, humidity, airflow, substrate and thickness conditions that determine the state reached in that time.

Water must always be completely removed before UV. Many practical systems are deliberately dried before UV, but the universal statement is stronger than the evidence. The actual sequence and residual-water state must be qualified for the declared formulation.

17. Research gaps

Direct literature on UV-curable waterborne dispersions is rich in synthesis and final-property comparisons but thinner in spatially resolved process studies that measure water concentration, particle morphology and photochemical conversion simultaneously. More useful engineering studies would combine time-resolved gravimetry or water profiling with microscopy and conversion mapping through the same film.

The interaction between crosslink onset and particle deformation deserves particular attention. The key practical question is not only how fast a formulation photopolymerises, but whether network formation occurs

before, during or after the particle-scale motions required for a defect-free film. This interaction should be studied across different particle architectures rather than inferred from one polyurethane-acrylate family.

Mobile-species mapping is another gap. Surfactant and neutraliser distributions are known to affect conventional latex films, but systematic studies linking their redistribution to UV exposure timing, conversion gradients and intercoat adhesion in modern UV-PUDs would improve diagnosis. Industrial studies should also report actual film temperature and water state rather than only oven setpoint and nominal flash-off time.

18. Conclusions

Waterborne UV-curable dispersions form useful films because physical film formation and photochemical crosslinking can be combined in one process. That combination is also the central qualification challenge. Water removal, particle consolidation, migration of mobile species and photochemical conversion are coupled but non-equivalent state variables. Their sequence and spatial distribution determine whether a film that appears dry and cured is actually continuous, sufficiently converted and fit for duty.

The engineering rule is therefore to qualify the trajectory rather than a recipe. Control the incoming dispersion, applied-film geometry and substrate; measure the drying state relevant to the failure modes; record the irradiation field and atmosphere; verify local chemical state where needed; and test the final conditioned film against its intended function. Literature values for drying time, temperature, UV dose, photoinitiator level, film thickness or conversion remain coordinates of the systems that produced them, not universal windows.

ER-189 consequently defines an evidence architecture for aqueous dispersion-to-film evolution. It does not replace polyurethane chemistry, VPP latex-feedstock science, reactive printed-substrate coating qualification or thin graphic-ink surface-cure analysis.

Related Engineering Review boundaries

- ER-066 retains high-molecular-weight latexes as printable VPP feedstocks.
- ER-103 retains generic polyurethane chemistry.
- ER-168 retains coating and encapsulation of reactive printed photopolymer substrates.
- ER-196 retains oxygen inhibition and photon competition in thin pigmented graphic-ink films.
- ER-189 owns water removal, consolidation and photocure coupling in aqueous radiation-curable dispersions.

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. The paper is an engineering review and qualification framework, not an independent product comparison. No proprietary formulation, product ranking or universal operating window is provided.

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Data availability

No new experimental dataset was generated for this review.