

# Packaging and Storage-Excursion Qualification for Photoresins: Container Material, Headspace Oxygen, Light Transmission and Excursion Disposition

**Juan Seguro**

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Seguro. All Rights Reserved.

Correspondence: [info@3Dresyns.com](mailto:info@3Dresyns.com) · [www.3Dresyns.com](http://www.3Dresyns.com)

**ER-179 · Engineering Review · Version 0.2 · 12 September 2026**

## Statement of Significance

A photoresin does not stop evolving when it leaves the mixing vessel. The production package remains part of the material state because its polymer grade, wall, colour, closure, liner, gasket, headspace, gas transport, light transmission and thermal history can alter the liquid that later reaches the vat. A storage or transport excursion therefore cannot be disposed by a calendar rule alone. The defensible question is whether the exact packaged resin still satisfies the state and performance evidence required for its intended process. ER-179 defines that qualification problem without prescribing one universal bottle, headspace, oxygen concentration, temperature limit or shelf-life correction factor.

**Keywords:** photoresin packaging; storage excursion; headspace oxygen; MEHQ; container compatibility; permeation; light transmission; thermal history; shelf life; excursion disposition; qualification

## Abstract

Photoresin packaging is often treated as passive logistics, yet the controlled evidence shows that package construction and storage history can become active process variables. Direct VPP evidence demonstrates chemical and mechanical evolution during sealed high-temperature storage of a specific volumetric-additive-manufacturing resin [1]. Controlled photopolymer evidence also establishes that temperature, unintended light exposure, dissolved gases and inhibitor chemistry belong to resin state rather than to administrative storage metadata [1,2,12]. Adjacent packaging evidence shows that HDPE sorption, diffusion, permeation and swelling depend on the liquid and temperature [7], while chemical-resistance and environmental-stress-cracking standards define useful screening methods without qualifying a filled production package by themselves [4-6]. Phenolic inhibition adds a second complication: oxygen can participate in the inhibition pathway, so oxygen exclusion cannot be assumed to be the conservative storage state for every inhibited formulation [2,3]. Transport studies further show that closed containers can experience thermal histories that differ materially from nominal ambient conditions [11]. This review treats the exact package as a controlled material-contact system and separates four decisions: package qualification, storage-history capture, post-excursion state measurement and final disposition. No universal headspace fraction, oxygen window, container polymer, wall thickness, light-transmission limit, temperature excursion or shelf-life conversion is proposed. Acceptance after an excursion requires evidence that the formulation and its intended cure/process response remain inside a predefined qualified state.

## 1. Purpose and scope

ER-179 addresses packaged liquid photoresins between filling and release to a production process. Its question is not merely whether a bottle leaks or whether a nominal storage temperature was exceeded. It asks whether the production package and the history accumulated inside it preserve the defined liquid state and the performance evidence needed for printing or another radiation-curing operation.

The controlled Gate 1 decision assigns ER-179 ownership of container and headspace as process variables: oxygen permeability, headspace volume and phenolic-inhibitor function, light transmission and storage-

excursion disposition. ER-032 retains the open-vat and repeated-use state after the package has been opened [12]. ER-080 retains mechanism-led in-can stability chemistry, ER-081 retains in-can latency, and ER-054 retains permeability of printed parts. ER-170 retains accelerated-life inference and the validity of acceleration factors. ER-176 retains reactive process safety and runaway/fire risk. ER-179 therefore begins with an unopened or controlled package and ends with a documented accept, quarantine, re-test or reject decision.

The evidence architecture is deliberately mixed but bounded. Hedayati et al. provide direct photoresin storage evidence [1]. Pozdeeva and Denisov provide mechanistic evidence for hydroquinone-inhibited oxidation [2]. Producer-group guidance provides adjacent but safety-critical information on oxygen-dependent MEHQ inhibition in bulk acrylic monomers [3]. Aminabhavi and Naik provide adjacent direct polymer/liquid transport evidence for HDPE [7]. Standards provide test-method boundaries [4-6,8-10]. Endo and co-workers provide adjacent transport-container thermal evidence [11]. None of those sources alone defines a universal photoresin package.

## **2. The package is part of the material state**

A package has at least six controlled layers of identity: the primary container material; its grade, colour or masterbatch and conversion history; wall geometry; closure/liner/gasket construction; fill level and headspace; and accumulated environment. Treating only the resin formulation code as material identity loses variables that can change the liquid before use.

ER-032 defines usable photoresin state as multidimensional: composition, physical state, optical state, reactive state and operational history. It also warns that a resin can remain visually uniform while one or more dimensions has drifted [12]. ER-179 transfers that state discipline to the sealed package. The package does not become equivalent merely because two containers share the label “HDPE”, “PP” or “coated metal”.

For a qualification record, the resin lot and package lot should therefore be linked. The record identifies resin version, fill date, exact primary-package construction, closure system, nominal fill, relevant transport/storage exposure and any package damage or opening. This is a traceability requirement, not a claim that every listed variable will be significant in every formulation.

## **3. Establishing the packaged-resin baseline**

Excursion disposition requires a baseline against which the returned or exposed package can be compared. A nominal certificate or appearance check is insufficient because different failure paths can preserve colour and clarity while altering inhibitor reserve, oxygen state, viscosity, optical response or cure behaviour.

The baseline is formulation- and application-specific. Candidate measurements include package mass and seal condition, resin appearance, viscosity or rheological state, water or other controlled impurity markers, inhibitor or residual-monomer assays where they are part of the material specification, optical response at the process wavelength, and a defined cure/process response. ER-032 explicitly requires paired state and performance measurements rather than a single appearance check [12].

The baseline also records the package state itself. The exact polymer grade, colour/masterbatch, wall, moulding or conversion process, closure, gasket and fill level are retained as candidate package variables because equivalence cannot be inferred from a generic material designation. Their significance must be established for the actual package-formulation system.

## **4. Container material and construction**

Container choice is a compatibility problem, not a polymer-name lookup. Aminabhavi and Naik demonstrated with hazardous organic liquids that sorption/desorption, diffusion, permeation and swelling of HDPE depend on the contacting liquid [7]. That study is adjacent to photoresins and cannot prove compatibility with a particular acrylate, methacrylate, thiol, epoxy-acrylate or filled formulation. Its

transferable lesson is narrower: package transport and dimensional response depend on both sides of the contact pair and on conditions such as temperature.

ISO 175 provides an immersion framework for effects of liquid chemicals on plastics [4]. ASTM D543 provides practices for evaluating plastic resistance to chemical reagents [5]. ISO 22088-1 provides general guidance for environmental stress cracking [6]. The methods answer different questions. An unconstrained immersion result does not establish resistance under closure stress, moulded residual stress, drop impact, thermal cycling or long-term permeation. Conversely, a package that shows no macroscopic swelling can still require permeation, extractables or seal assessment.

ER-179 requires the actual production package rather than a generic material coupon to close final qualification. Screening coupons can identify failure modes and rank candidate constructions; the released package requires the exact container/closure system and the intended formulation.

## **5. Closures, gaskets, seams and internally coated metal**

The package wall is only one material contact. Closures, liners, gaskets, valves, bungs, seams, welds, dip tubes and any exposed edge can create distinct contact chemistries and leak paths. A package qualified by wall immersion alone can therefore remain unqualified as an assembly.

For internally coated metal, the relevant object is the coating system and its continuity, not the metal name alone. Qualification therefore considers coating cure, film continuity, flex damage, closure contact and compatibility with the formulation. Filling, denting, seaming or transport can create defects that were absent in a flat coating coupon. ER-179 therefore treats intentionally defected coating or seam/weld challenge coupons as diagnostic tools, while final release still requires the production package.

The closure system also controls headspace exchange. However, ER-179 does not infer a quantitative leak, oxygen-transfer rate or headspace-composition trajectory from closure type. Those quantities require measurement or a validated package model.

## **6. Sorption, permeation, swelling, extractables and environmental stress cracking**

Sorption, permeation and swelling are distinct from gross leakage. A container can remain mechanically intact while molecules partition into the wall, traverse it or extract package constituents. The HDPE study in [7] establishes this distinction for its tested organic liquids. It does not establish a universal ranking of package plastics for photoresins.

The qualification question is consequently functional. If oxygen or moisture transport is relevant to stability, the package test must address the relevant gas or vapour under the intended temperature history. If monomer or oligomer sorption can shift formulation composition, mass balance and analytical comparison may be needed. If extractables could affect cure, colour or stability, the analytical target follows the actual package and formulation. If the container is mechanically stressed, environmental stress cracking cannot be inferred from immersion alone [4-6].

A package equivalence claim therefore needs more than equal resin-contact polymer names. Grade, additives/masterbatch, conversion route, wall and closure can change the system. A supplier change in any of these elements can reopen qualification even when the nominal package volume and resin formulation remain unchanged.

## **7. Headspace volume, dissolved oxygen and gas exchange**

Headspace belongs to the package state because it is part of the gas reservoir coupled to the liquid. The Gate 1 ownership explicitly requires headspace volume and oxygen permeability to be treated as process variables. ER-179 records them but does not prescribe a universal fill ratio or oxygen concentration.

The controlled evidence gives a strong reason for that restraint. Pozdeeva and Denisov describe hydroquinone-inhibited oxidation of acrylic acid and methyl methacrylate through oxygen/peroxyl chemistry [2]. ER-032 therefore records that dissolved oxygen can act as a co-reactant in phenolic-inhibitor function [12]. The EBAM and BMM guidance likewise treats oxygen exclusion as unsafe for MEHQ-inhibited bulk acrylic monomers [3]. Those sources are not formulation-specific photoresin specifications. A filled, pigmented, multifunctional photoresin can have different oxygen transport, radical generation and inhibitor demand.

Accordingly, ER-179 prohibits a simplistic “more oxygen is better” or “less oxygen is better” rule. The qualified state defines what package atmosphere, permeability and fill condition were actually validated. A deliberate change in headspace, closure permeability, inerting practice or repeated opening requires evidence that the inhibitor and cure system remain controlled.

## **8. Phenolic inhibitor function and the oxygen ambiguity**

MEHQ and hydroquinone illustrate why package qualification cannot be separated from formulation chemistry. MEHQ performance depends on concentration, dissolved oxygen, mass transfer and temperature. Oxygen starvation can reduce the intended phenolic inhibition pathway, while uncontrolled oxygen exposure can also participate in oxidation and hydroperoxide formation. The required balance is system-specific [2,3].

ER-179 therefore uses inhibitor chemistry as a decision variable, not as a universal package recipe. Where a phenolic inhibitor is load-bearing for storage stability, the package study should preserve the validated oxygen/headspace condition and should verify the relevant inhibitor or stability response after significant excursions or package changes. Where another inhibitor family is used, its own mechanism and analytical control apply.

No concentration from bulk acrylic-acid or acrylic-ester guidance is transferred into a formulated photoresin. The role of those guidance documents is to block the unsafe inference that oxygen-free storage is automatically conservative.

## **9. Light transmission and unintended exposure**

A dark-looking package is not automatically an optically qualified package. What matters is transmission over the spectral region capable of changing the formulation, together with exposure duration and intensity. Pigment, masterbatch, wall thickness and package ageing can change transmission even within one nominal polymer family.

ER-032 identifies unintended light exposure as a mechanism that can consume photoinitiator, generate radicals and create soluble oligomers, microgels or cured particles [12]. ER-179 therefore requires package light protection to be expressed as a measured property where it is load-bearing. The relevant test is spectral or wavelength-resolved transmission of the actual package construction, not a colour description alone.

This requirement does not create one universal transmission limit. A resin with strong absorption or a different photoinitiator package can respond differently from another formulation. Qualification links the measured package transmission to the tested storage/light challenge and the retained resin state.

## **10. Temperature excursions and transport histories**

A storage excursion is a time-temperature history, not a single maximum label. Hedayati et al. directly demonstrated chemical and mechanical evolution of a specific VAM resin under sealed high-temperature storage [1]. The result establishes that photoresin state can change during elevated-temperature storage, while its exact conditions and outcomes remain formulation-specific.

Endo, Kimura and Imaeda studied temperature distribution in a dry freight container and showed that solar load and container conditions can create thermal histories not represented by nominal ambient temperature [11]. ER-179 transfers no universal drum-core temperature from that study.

ER-179 therefore treats measured package temperature history as preferable evidence after significant transport or storage exposure. When direct measurement is unavailable, a conservative simulation or justified bounding history may support an investigation, but it does not become a universal shelf-life rule. Package size, fill, position and thermal inertia can separate liquid temperature from external air temperature.

### **11. Thermal acceleration and limits of shelf-life models**

ISO 11357-5 defines DSC measurement of reaction-curve temperatures, times, enthalpy and conversion for applicable materials [8]. ASTM E537 provides a DSC thermal-stability screening method [9]. ASTM E698 provides kinetic-parameter methodology under stated assumptions [10]. These methods can support investigation, but they do not authorise a generic time-temperature conversion for an inhibited photoresin.

ASTM E698 is not a default shelf-life model for partially inhibited or multistep systems when its assumptions do not hold. Multiple coupled processes can change with temperature, including inhibitor consumption, peroxide chemistry, package permeation, extraction, corrosion or secondary reactions. ER-170 separately owns the validity of accelerated-life inference.

ER-179 therefore uses accelerated testing only inside a declared mechanistic and validation boundary. A rule such as “shelf life halves for each temperature increment” is not admitted unless the exact formulation and package have independently established such behaviour over the relevant range.

### **12. Package contact as a source of chemical change**

The package can change the resin through more than gas transport. Sorption can remove constituents from the liquid; extractables can enter it; metal exposure at coating defects can introduce new chemistry; gasket or liner components can swell or leach; water can enter; and thermal cycling can change both contact and seal state. The evidence base is uneven across those mechanisms, so ER-179 treats them as hypotheses to test rather than guaranteed failure modes.

A staged package matrix can compare an inert control, HDPE, PP, other thermoplastics, intact coated metal and defect/weld challenges, with responses including metal release, permeation, package change and induction behaviour. ER-179 adopts that architecture as a qualification design, not as proof that every package class will fail by the same route.

The strongest investigation compares the exposed production package with a retained control from the same resin lot under a defined reference package/history. That comparison helps separate formulation-lot variation from package/history effects.

### **13. Sampling after an excursion**

Sampling can erase the very gradient an investigation needs to detect. A package may have wall-contact, headspace-proximal or bulk differences. Complete homogenisation before the first sample can destroy evidence of stratification, local gel formation, sedimentation or interface-related contamination.

ER-179 therefore distinguishes forensic sampling from release sampling. Forensic sampling records package orientation and condition, then obtains position-resolved samples when the failure hypothesis requires them. Release sampling may subsequently use a defined homogenisation procedure if the qualified workflow requires a homogeneous state before use.

The analytical panel follows the suspected mechanism and the normal release controls. Candidate comparisons include viscosity/rheology, optical response, water, inhibitor or residual species where

controlled, filtration/microgel evidence, and cure/process response. No single panel is mandatory across all photoresins.

#### 14. Excursion disposition: quarantine, investigate, re-test, decide

A storage-temperature alarm or damaged carton is not itself the final material disposition. ER-179 separates the decision into four stages.

First, quarantine the affected package population and preserve identity and history. Second, reconstruct the excursion: affected lots/packages, package construction, duration, measured or bounded temperature/light exposure, physical damage, orientation, opening state and deviations. Third, select tests from plausible failure mechanisms and the normal material specification. Fourth, compare results against predefined acceptance criteria and representative process performance.

This architecture permits four outcomes: accept within the existing qualification; accept with a documented restricted condition if such a condition has been pre-authorised by evidence; hold for additional testing; or reject. ER-179 does not permit an ad hoc “looks fine” release or an automatic discard rule presented as science.

#### 15. Requalification against cure and process performance

Chemical stability that destroys process performance is not acceptable stability. Conversely, a package may show a measurable analytical change that is irrelevant to the intended process if the qualified decision rule has demonstrated adequate margin. The link between state and function must therefore be explicit.

For VPP materials, candidate response variables can include working-response or cure-rate measures, dimensional/process witnesses and final state tests appropriate to the application. ER-179 does not take ownership of those methods; it uses them as endpoints defined by the surrounding ER corpus and the product-specific qualification plan.

A post-excursion pass should therefore demonstrate retained performance across the attributes that the package history could plausibly affect. A single cured coupon cannot prove preserved viscosity, optical response, storage induction or contamination state, just as an unchanged viscosity cannot prove preserved cure chemistry.

#### 16. Package equivalence and change control

A new package is not equivalent because it has the same nominal polymer and volume. Equivalence evidence should address the variables that materially define the old qualified state: exact resin-contact materials, wall and geometry, masterbatch/colour, closure and gasket, fill/headspace, relevant gas/light transport, extractables, stress-cracking behaviour, seal performance and thermal response.

The amount of bridging evidence depends on the change. A supplier change to a nominally identical HDPE bottle may require less evidence than a move from opaque HDPE to a translucent fluoropolymer or from plastic to internally coated metal, but neither is automatically minor. A closure-liner substitution can reopen package qualification even when the bottle remains unchanged.

Change control also applies to shipping configuration when it changes the thermal or light boundary: palletisation, outer cartons, route, container type, insulation, seasonal exposure or use of temperature-controlled transport can alter the evidence needed for equivalence.

#### 17. Qualification matrix, evidence gaps and reporting minimum

A defensible ER-179 qualification matrix contains at least five linked blocks:

| Gate             | Required evidence                                                     | Typical failure that prevents closure |
|------------------|-----------------------------------------------------------------------|---------------------------------------|
| Package identity | Exact container, closure, gasket, fill/headspace and lot traceability | Generic polymer name only             |

| Gate                  | Required evidence                                                                                  | Typical failure that prevents closure                             |
|-----------------------|----------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|
| Contact compatibility | Sorption/swelling/ESC/extractables/permeation as relevant in the actual formulation-package system | Coupon screening treated as production-package qualification      |
| Optical/gas boundary  | Measured light transmission where load-bearing; validated oxygen/headspace condition               | Colour or “airtight” description substituted for measurement      |
| Thermal history       | Measured or justified bounded excursion; appropriate thermal/stability methods                     | Nominal ambient temperature or universal acceleration factor      |
| Final disposition     | State measurements plus representative cure/process performance against predefined criteria        | Visual inspection or one unrelated property used as release proof |

Important evidence gaps remain. Direct, systematic studies comparing production photoresin packages across polymer grades, closures, headspace fractions and controlled oxygen-transfer rates are limited in the controlled corpus. Several package and transport anchors are intentionally adjacent rather than photoresin-specific. That limitation is a result, not a reason to replace the missing evidence with a universal recipe.

The minimum report therefore preserves evidence class. It identifies which findings are direct photoresin evidence, which are polymer/package evidence, which are bulk-monomer safety/mechanism guidance, which are standards and which are proposed qualification controls.

## 18. Conclusions

1. The production package is part of photoresin material state when container contact, gas exchange, light transmission or thermal history can change the liquid before use.
2. Package qualification is assembly-specific: container grade, wall, colour/masterbatch, closure, gasket, fill/headspace and actual formulation remain linked.
3. HDPE, PP, coated metal or another package class cannot be declared universally compatible from the material name alone.
4. Phenolic-inhibitor systems make oxygen management non-trivial; oxygen exclusion is not automatically conservative, and bulk-monomer oxygen guidance must not be converted into a universal formulated-photoresin oxygen specification.
5. Light protection should be measured when it is load-bearing; visual opacity alone is not a qualification datum.
6. Storage/transport excursions are time-temperature/light histories, not single administrative exceedances.
7. Thermal-analysis and kinetic methods provide bounded evidence; they do not create a universal shelf-life conversion for inhibited multicomponent photoresins.
8. Excursion disposition requires quarantine, history reconstruction, mechanism-selected testing and comparison against predefined state and process-performance criteria.
9. A package change can reopen qualification even when resin formulation and nominal container volume are unchanged.
10. The controlled corpus supports a critical qualification architecture but does not support universal package materials, headspace fractions, oxygen windows, temperature limits or shelf-life corrections.

## References

- [1] Hedayati, S. K.; Safari Mozajin, H.; Almdal, K.; Hansen, H. N.; Islam, A. Chemical and Mechanical Evolution of a Volumetric Additive Manufacturing (VAM) Resin Under High-Temperature Storage. *Polymers* 2026, 18(10), 1213. <https://doi.org/10.3390/polym18101213>
- [2] Pozdeeva, N. N.; Denisov, E. T. Mechanism of Hydroquinone-Inhibited Oxidation of Acrylic Acid and Methyl Methacrylate. *Kinetics and Catalysis* 2011, 52, 506-512. <https://doi.org/10.1134/S0023158411040136>
- [3] EBAM (European Basic Acrylic Monomer Group, a Cefic Sector Group). *Safe Handling and Storage of Acrylic Acid*, 4th ed., 2 December 2020; Basic Acrylic Monomer Manufacturers, Inc. (BAMM). *Acrylic Acid: A Summary of Safety and Handling*, 4th ed., 2013. Authoritative bulk-monomer handling guidance; used here only for the oxygen-dependent inhibitor boundary, not as a formulated-photoresin oxygen specification.

- [4] ISO 175:2010. *Plastics — Methods of test for the determination of the effects of immersion in liquid chemicals*. International Organization for Standardization.
- [5] ASTM D543-21. *Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents*. ASTM International. <https://doi.org/10.1520/D0543-21>
- [6] ISO 22088-1:2006. *Plastics — Determination of resistance to environmental stress cracking (ESC) — Part 1: General guidance*. International Organization for Standardization.
- [7] Aminabhavi, T. M.; Naik, H. G. Sorption/desorption, diffusion, permeation and swelling of high density polyethylene geomembrane in the presence of hazardous organic liquids. *Journal of Hazardous Materials* 1999, 64, 251-262. [https://doi.org/10.1016/S0304-3894\(98\)00183-6](https://doi.org/10.1016/S0304-3894(98)00183-6)
- [8] ISO 11357-5:2025. *Plastics — Differential scanning calorimetry (DSC) — Part 5: Determination of characteristic reaction-curve temperatures and times, enthalpy of reaction and degree of conversion*. International Organization for Standardization.
- [9] ASTM E537-24. *Standard Test Method for Thermal Stability of Chemicals by Differential Scanning Calorimetry*. ASTM International. <https://doi.org/10.1520/E0537-24>
- [10] ASTM E698-23. *Standard Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method*. ASTM International. <https://doi.org/10.1520/E0698-23>
- [11] Endo, Y.; Kimura, R.; Imaeda, Y. Temperature Distribution in a Dry Container III. *The Journal of Japan Institute of Navigation* 1981, 65, 99-105. <https://doi.org/10.9749/jin.65.99>
- [12] Segurola, J. *Photopolymer Storage, Reuse and Open-Vat State: Evidence Boundaries and Qualification Requirements*. 3Dresyns Engineering Review ER-032, Version 1.1, 2026. Concept record: <https://doi.org/10.5281/zenodo.22048038>; version record: <https://doi.org/10.5281/zenodo.22286461>

### **Related Engineering Review boundaries**

ER-032 retains the open-vat and repeated-use state after package opening. ER-080 retains mechanism-led in-can stability chemistry. ER-081 retains in-can latency. ER-054 retains permeability of printed parts. ER-170 retains accelerated-life inference and the validity of acceleration factors. ER-176 retains reactive process safety and runaway/fire risk. ER-179 owns package construction, headspace, gas transport, light transmission, storage history and excursion disposition before release to use.

### **Competing interests**

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. This review does not claim that any 3Dresyns resin, package or storage condition is qualified for a particular use.

### **Copyright**

© 2026 Juan Segurola. All Rights Reserved. No part of this work may be reproduced, distributed or transmitted without the prior written permission of the copyright holder, except where permitted by applicable law.

### **Data availability**

No new experimental dataset was generated for this review.