

Toxicological Assessment of Key Substances in UV-Curable Nail Coatings: 2-hydroxyethyl Methacrylate, Trimethylolpropane Triacrylate, Diphenyl(2,4,6-trimethylbenzoyl)phosphine Oxide, Hydroquinone, and Hydroquinone Monomethyl Ether

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UV-curable nail coatings have gained widespread popularity due to their superior durability, gloss, and fast-curing properties. However, the use of (meth)acrylate monomers, photoinitiators, and inhibitors in these products raises concerns regarding consumer and occupational safety. This study examines the toxicological profiles and prevalence of five commonly used compounds in UV-curable nail formulations: 2-hydroxyethyl methacrylate (HEMA), trimethylolpropane triacrylate (TMPTA), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), hydroquinone (HQ), and hydroquinone monomethyl ether (MEHQ). A combination of bibliographic review and UPLC-DAD analysis was used to assess their presence in commercial samples and evaluate health risks. Despite regulatory restrictions, all substances were detected in the tested formulations or raw materials. This study underscores the need for stricter regulatory enforcement, improved product labeling, and the development of safer alternatives in UV-curable cosmetic systems.

Keywords: UV-curable nail coatings, sensitizers, cosmetic toxicology, acrylate monomers.

1. INTRODUCTION

The use of nail polishes has expanded considerably over the past century, evolving from early cosmetic traditions into widely utilized aesthetic and therapeutic products. The commercialization of nitrocellulose-based nail lacquers in the 1920s marked a turning point in nail cosmetics, and further innovation introduced UV-curable formulations that offer superior durability and gloss [1]. However, this evolution has raised significant toxicological concerns due to the inclusion of substances with known or suspected health risks.

Modern nail polish formulations typically contain film-forming agents (e.g., nitrocellulose), plasticizers, solvents, resins, pigments, and UV absorbers. UV-curable systems rely heavily on (meth)acrylate monomers like HEMA and TMPTA. These compounds are highly reactive and capable of forming durable polymers under UV light, but they are also potent sensitizers. HEMA has been repeatedly implicated in allergic contact dermatitis (ACD), especially in occupational settings, with sensitization rates exceeding 60% in some cohorts [1, 2].

Photoinitiators such as TPO are used to initiate polymerization but have been associated with oxidative stress and potential endocrine disruption [3]. In addition, TPO is prohibited in cosmetic products in the European Union from 1 September 2025, as it has been classified as a carcinogenic substance (Carc. 1B) under the CLP Regulation [4, 5]. Likewise, inhibitors like HQ and MEHQ - used to stabilize monomers - have demonstrated cytotoxic and genotoxic effects. HQ, in particular, is classified by the

EU as a substance of very high concern due to its mutagenic and carcinogenic potential [6].

Despite regulatory actions banning or restricting many of these substances in cosmetics, studies reveal that nail polishes - particularly those labeled as “toxic-free” - often still contain such compounds, either due to inadequate oversight or misleading marketing. For example, analyses have shown that nail polishes labeled “3-free” or “5-free” often still include toluene, dibutyl phthalate (DBP), and tosylamide/formaldehyde resin (TSFR), among other substances [7, 8].

Given these health risks and regulatory inconsistencies, this article aims to review the toxicological profiles and prevalence of harmful components in nail polishes, with a special focus on HEMA, TPO, TMPTA, HQ, and MEHQ, while addressing the challenges of inadequate labeling and insufficient consumer protection.

2. METHODOLOGY

2.1. Bibliographic review

A bibliographic review was previously conducted using the Web of Science and Scopus databases. The search employed consistent keyword combinations and Boolean operators across both platforms, including: “HEMA” or “2-hydroxyethyl methacrylate” or “TPO” or “diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide” or “TMPTA” or “trimethylolpropane triacrylate” or “hydroquinone” or “HQ” or “methylhydroquinone” or “MEHQ” or “acrylate sensitizers.” In addition to cosmetic science, relevant studies from dental literature were also included, given the

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widespread use of these substances in dental materials and their associated sensitization risks.

2.2. Determination of HQ, MEHQ, HEMA, TMPTA, and TPO by UPLC-DAD

The quantitative determination of HQ, MEHQ, HEMA, TMPTA, and TPO was performed using an Acquity H-Class UPLC system equipped with a 2996 PDA detector. Detection was carried out at 225 nm and 287 nm. Due to the high content of oligomers and polymers in the analyzed intermediates, which could adversely affect column performance, a sample extraction step with deionized water was implemented to isolate only water-soluble compounds and minimize matrix interferences.

For each analysis, 100 mg of homogenized gel polish or ingredient was weighed into a glass vial and subjected to a chloroform–water liquid–liquid extraction using a 1:10:50 ratio (sample:chloroform:water).

The mixture was vortexed for 60 seconds and centrifuged at 4000 rpm to promote phase separation. The chloroform layer was collected, filtered (0.20 μ m PTFE), and injected into the UPLC system. Quantification was carried out using the standard addition method to account for matrix variability. The analysis was performed on an ACQUITY UPLC BEH C18 column (2.1 $\times$ 50 mm, 1.7 μ m) at 30 $^{\circ}$ C, with a flow rate of 0.4 mL/min, and an injection volume of 5 μ L. The mobile phase consisted of water (A) and methanol (B), run in gradient mode for over 8 minutes. The validated quantitative range for HQ, MEHQ, HEMA, TMPTA, and TPO was 25–200 ppm, with results above this range considered semi-quantitative.

3. RESULTS AND DISCUSSION

3.1. Toxicological profile of TMPTA

TMPTA is a multifunctional acrylate monomer widely used in UV-curable cosmetic products, especially gel nail systems, where it acts as a crosslinker due to its ability to form dense polymer networks. While its chemical performance is highly valued for adhesion, chemical resistance, and rapid curing, emerging toxicological data have drawn attention to the risks associated with its unpolymerized form.

In the current study, TMPTA was confirmed alongside other critical components such as HEMA, HQ, MEHQ, and TPO. These findings reflect broader concerns over the cumulative exposure to multiple sensitizing and potentially carcinogenic agents in cosmetic formulations. The presence of TMPTA is particularly troubling due to its documented carcinogenicity, genotoxicity, and strong sensitization potential.

According to the U.S. National Toxicology Program (2013) [9, 10], long-term dermal exposure to TMPTA resulted in a dose-dependent increase in rare liver cancers and uterine tumors in mice, suggesting systemic carcinogenic potential. Furthermore, while TMPTA tested negative in bacterial mutagenicity assays, it induced gene mutations in mammalian cells [8, 9], indicating context-dependent genotoxicity. In the context of cosmetic use, particularly artificial nails and UV curing nail coatings, incomplete curing during application may leave residual

monomers in contact with the skin, thereby increasing the risk of sensitization and systemic absorption. The dermal sensitization profile of TMPTA is well established, with repeated evidence of allergic contact dermatitis in both animal models and occupational case reports. Subchronic dermal studies further highlight inflammatory responses and epidermal alterations following repeated exposure, raising red flags for both consumers and professionals, such as nail technicians. These effects are compounded when TMPTA is used in combination with other acrylates like HEMA, which also possesses strong sensitizing capabilities [1, 2]. Regulatory classifications reflect the severity of these risks. TMPTA is listed by the European Chemicals Agency (ECHA) as a Category 2 carcinogen under the CLP Regulation and must be handled with strict precautions when present at concentrations $\geq 1\%$ [6]. The American Industrial Hygiene Association (AIHA) also recommends limiting occupational exposure to a maximum of 1 mg/m³ over an 8-hour time-weighted average [10].

The findings presented here reinforce the necessity of robust curing protocols and stricter control of residual monomer levels in cosmetic products.

Given the rising use of (meth)acrylate-based nail products and the widespread presence of TMPTA in the marketplace, more stringent safety evaluation, transparent labeling, and regulatory oversight are urgently required. In parallel, future research should focus on the development of biocompatible alternatives that deliver comparable performance without compromising human or environmental health.

3.2. Toxicological profile of HQ

HQ, while widely recognized for its application in skin-lightening products, also plays a critical role in UV-curable nail coatings as a polymerization inhibitor. Its primary function in such systems is to scavenge free radicals and thus prevent premature polymerization of acrylate-based monomers such as HEMA and TMPTA during storage and transport [6, 11, 12]. This stabilizing effect extends the shelf life of formulations and ensures curing consistency under UV exposure. However, the inclusion of HQ, even at low concentrations, introduces significant toxicological concerns.

In this study, HQ was detected in nail coating formulations alongside other reactive or sensitizing substances such as methacrylate monomers (e.g., HEMA), photoinitiators (e.g., TPO), and stabilizers (e.g., MEHQ, TMPTA). These findings are consistent with earlier research indicating the persistence of HQ in cosmetic and UV-curable products despite regulatory restrictions [1]. Of particular concern is HQ's well-documented ability to penetrate the skin and exert systemic toxicity, including nephrotoxicity, hepatotoxicity, and hematopoietic suppression [12–14].

Dermatologically, HQ has been associated with contact dermatitis, erythema, and long-term pigmentary disorders such as exogenous ochronosis – an irreversible bluish-black discoloration of the skin predominantly observed in chronic users [13]. Systemically, a two-year gavage study conducted by the U.S. National Toxicology Program [9, 10] revealed increased incidences of renal and hepatic tumors in rats and

mice, leading to HQ's classification as "reasonably anticipated to be a human carcinogen."

In vitro studies further support HQ's mutagenic potential. DNA strand breaks, chromosomal aberrations, and gene mutations have been observed in mammalian and bacterial cells following HQ exposure [12]. Reproductive toxicity studies have demonstrated developmental delays, increased resorptions, and reduced fertility in animal models, although no definitive teratogenicity has been confirmed [14].

Regulatory responses reflect the severity of HQ's toxicological profile. Under Regulation (EC) No. 1223/2009, hydroquinone is banned from all cosmetic products sold within the European Union. Similar restrictions exist in Japan and several other jurisdictions. In contrast, the United States Food and Drug Administration permits over-the-counter formulations containing up to 2% HQ and prescription preparations up to 4%, though the substance is listed under California Proposition 65 due to its carcinogenicity [14, 15].

The detection of HQ in commercial nail products raises critical public health questions, particularly regarding cumulative toxicity when HQ coexists with other acrylates or UV-reactive components. These findings also highlight enforcement challenges and regulatory inconsistencies across global markets.

Given these concerns, efforts are underway to identify safer alternatives for HQ in UV-curable systems. Substitutes such as butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ), and ascorbic palmitate have demonstrated antioxidant and stabilizing properties suitable for acrylate-based formulations, with lower associated toxicological risk profiles [16–18]. Transitioning to these alternatives, alongside improved ingredient labeling and cross-border regulation harmonization, is essential to reduce health risks for both consumers and professionals using UV-curable nail products.

3.3. Toxicological profile of MEHQ

MEHQ, also known as 4-methoxyphenol or mequinol (CAS No. 150-76-5), is a phenolic compound widely utilized in industrial and cosmetic applications for its radical-scavenging and antioxidant properties. In UV-curable resin systems - including nail coatings - MEHQ plays a critical role as a polymerization inhibitor, ensuring product stability by preventing premature curing during storage and handling. Its compatibility with (meth)acrylate-based systems, along with a relatively lower toxicity profile compared to HQ, has made MEHQ a preferred stabilizer in surface-curable applications [15].

Despite these benefits, MEHQ is not without health concerns. In acute toxicity studies, LD₅₀ values ranged from 1000–2000 mg/kg (oral, rats) and 621 mg/kg (oral, mice), while dermal LD₅₀ exceeded 2000 mg/kg in both rats and rabbits, suggesting moderate oral and low dermal toxicity. Irritation studies showed that MEHQ could cause mild to moderate eye and skin irritation, though effects were reversible in most cases [18].

More concerning is its potential to act as a skin sensitizer. In guinea pig maximization tests, sensitization occurred in 50 % of animals, indicating a high probability

of allergic contact dermatitis with repeated dermal exposure [18]. This is particularly relevant for occupational settings, such as nail salons or manufacturing environments, where chronic low-level exposure may occur.

Carcinogenicity has been demonstrated in long-term oral exposure studies. In a 2-year dietary study, F344 rats fed a 2 % concentration of 4-methoxyphenol developed atypical hyperplasia, papilloma, and squamous cell carcinomas of the forestomach, raising concerns about neoplastic transformation upon chronic ingestion [15]. Though oral exposure is not typical for nail coatings, the findings underscore the need to control dermal and inhalation routes in consumer and workplace settings.

Reproductive toxicity data suggest high-dose exposure can result in decreased fetal weights and increased resorption rates in rats and rabbits, though teratogenic effects were not observed. Genotoxicity data indicate low mutagenic potential; 4-methoxyphenol tested negative in standard in vitro assays such as the Ames test using *Salmonella typhimurium* and *E. coli*, with no significant DNA damage reported [18, 19].

Target organ toxicity has been observed in the liver, kidneys, and forestomach. Repeated dermal application in animal models has led to epidermal hyperplasia and depigmentation, while chronic oral exposure has caused epithelial damage and tumor formation in the forestomach [20, 21].

Given the dual role of MEHQ as both a functional stabilizer and a potential sensitizer or carcinogen, its use in UV-curable cosmetic compositions requires careful regulation. While it may remain unreacted in trace amounts post-curing, improper formulation or incomplete polymerization could leave consumers exposed. Regulatory bodies such as the European Union have imposed concentration limits in cosmetics, and ongoing toxicological evaluations support a precautionary approach.

Future formulation efforts should consider safer alternatives, such as BHT, ascorbic palmitate, or naturally derived phenolic antioxidants, provided they meet the performance requirements for stabilization and polymerization control in acrylate-based systems.

3.4. Toxicological profile of TPO

TPO (CAS No. 75980-60-8) is a high-efficiency Type I photoinitiator extensively used in UV-curable polymer systems, including those found in inks, dental composites, adhesives, and gel nail products. Its molecular structure and high molar extinction coefficient in the 350–430 nm UVA range enable efficient radical generation under LED and UV light, facilitating the polymerization of (meth)acrylate monomers, even in heavily pigmented formulations or thick layers [6, 22]. In gel nail systems, TPO is typically present at concentrations of 1–5 % to achieve fast curing, enhanced film hardness, and long-term stability of the manicure. Despite its technical advantages, TPO has raised increasing toxicological and regulatory concerns.

TPO is classified as a Category 1 skin sensitizer (H317) under the EU Classification, Labelling and Packaging (CLP) Regulation. Local Lymph Node Assay (LLNA) studies demonstrate EC3 values between 1 % and 5 %, confirming its moderate sensitization potency (ECHA, 2023).

Both animal tests and human patch test data have documented allergic contact dermatitis associated with TPO exposure, particularly in the periungual area – a site highly susceptible to irritation and sensitization during nail application procedures [23].

Furthermore, TPO is classified as an eye irritant (H319). In Draize eye irritation studies on rabbits, transient but notable conjunctival and corneal changes were observed, typically resolving within one week. While inhalation toxicity data are limited, concern arises in poorly ventilated salon environments where aerosolized particles from abraded cured products may lead to respiratory discomfort and mucosal irritation [23].

Genotoxicity data from in vitro studies raise additional concerns. TPO has shown positive results in chromosomal aberration assays using Chinese hamster ovary cells and in vitro micronucleus tests in human lymphocytes and mouse lymphoma cells. Although standard bacterial reverse mutation tests (Ames test) were negative, the observed clastogenic effects suggest DNA-damaging potential under prolonged or repeated exposure [6, 23].

Development of toxicity studies in rats further supports systemic risk. High oral doses resulted in maternal weight loss, liver enlargement, and reduced fetal weight, although teratogenic effects were not observed. The NOAEL for developmental effects was estimated at approximately 25 mg/kg/day [23]. Given the compound's lipophilic character ($\log P \approx 4.5$), the potential for bioaccumulation and chronic systemic toxicity is plausible. Subchronic exposure studies have reported hepatocellular hypertrophy, elevated liver enzyme levels, and organ weight increases in the liver, spleen, and kidneys of test animals, although some of these effects were reversible after discontinuation of treatment [6].

In addition to its sensitization profile, TPO has been classified as Carcinogen Category 1B (H350) under the CLP Regulation. As a consequence, its use in cosmetic products is prohibited in the European Union from 1 September 2025, following the amendment of Annex II of Regulation (EC) No 1223/2009 through Commission Regulation (EU) 2025/877, which adds TPO to the list of substances banned in cosmetics due to its carcinogenicity. This regulatory action reflects growing toxicological evidence indicating that TPO may contribute to genotoxic and carcinogenic mechanisms, in addition to its previously established oxidative stress and endocrine-disrupting potentials [4, 5].

Even before the ban was introduced, TPO had already raised significant concerns, and the SCCS had clearly communicated these risks to manufacturers. The SCCS also advised manufacturers to optimize curing protocols, while professional users were encouraged to employ appropriate personal protective equipment and maintain proper salon ventilation [23].

In addition, TPO is classified as harmful to aquatic life with long-lasting effects (H412). Due to its limited water solubility and environmental persistence, improper disposal from cosmetic or manufacturing sources may contribute to ecological risk [6].

In conclusion, although TPO has historically offered strong performance as a photoinitiator in UV-curable nail systems, it is now recognized as posing moderate to significant health risks, including sensitization,

genotoxicity, and systemic organ effects. Its subsequent classification as a Carcinogen Category 1B and addition to Annex II of the EU Cosmetics Regulation underscore these concerns and have resulted in its prohibition in cosmetic products [4, 5]. While adequate curing and formulation control were previously emphasized to minimize consumer exposure to unreacted monomers, the current regulatory status reflects a precautionary shift based on emerging toxicological evidence. Further long-term in vivo and carcinogenicity studies remain essential to fully characterize the risk profile of TPO in both cosmetic and occupational settings.

3.5. Toxicological profile of HEMA

HEMA (CAS No. 868-77-9) is a key monomer in UV-curable nail systems, widely used in gel polishes, builder gels, and base/top coats. Its favorable characteristics - including low viscosity, efficient crosslinking, strong adhesion, and flexibility - make it an essential component in ensuring the mechanical integrity and durability of the polymerized film. Upon exposure to UV or LED light, HEMA undergoes free-radical polymerization, enabling fast curing and uniform coating distribution. These properties also make HEMA useful in dental materials and biomedical adhesives. However, HEMA's reactivity is also the basis for a growing body of toxicological concern [24].

HEMA is classified as a strong skin sensitizer. Its methacrylate group can readily bind covalently to skin proteins, triggering ACD upon repeated exposure. Local Lymph Node Assay (LLNA) studies report low EC3 values ($< 2\%$), confirming HEMA's high sensitization potential (SCCS, 2017). Occupational exposure in nail salons and dental clinics has led to sensitization rates exceeding 60% in at-risk groups such as technicians and dental professionals [2].

Patch test results and clinical data strongly correlate sensitization with frequent exposure to uncured or insufficiently cured formulations. Consequently, regulatory agencies stress the importance of avoiding direct skin contact, using gloves, and ensuring full polymerization before contact with skin or mucosa [24, 25].

HEMA is classified under the CLP Regulation as a skin irritant (H315) and an eye irritant (H319). In vitro models such as EpiDerm™ and EpiSkin™ have shown that HEMA disrupts the stratum corneum, increasing transepidermal water loss and leading to inflammatory responses. Ocular irritation studies in rabbits have reported conjunctival swelling, corneal opacity, and reversible irritation [24]. These effects are magnified when exposure occurs through abraded or damaged skin, common in frequent users.

The genotoxic profile of HEMA is mixed. Ames bacterial reverse mutation assays consistently report negative outcomes [24]. However, in vitro studies using mammalian cells have shown DNA strand breaks, chromosomal aberrations, and micronucleus formation, particularly at higher concentrations [25, 26]. These clastogenic findings raise concern for chronic low-level exposure scenarios, although most in vivo assays have not confirmed genotoxicity under standard conditions.

HEMA is readily absorbed dermally and may distribute systemically. Subchronic dermal toxicity studies in rodents show hepatic enzyme induction, hepatocellular

hypertrophy, and changes in spleen and kidney weights [26]. These changes were generally mild and reversible, though observed at NOAELs as low as 25–50 mg/kg/day, suggesting a narrow safety margin for prolonged exposure.

While definitive classification as a reproductive toxicant is lacking, high-dose studies in rodents and zebrafish have shown reduced fetal weight and increased resorption rates [2]. Teratogenic effects were not consistently observed, but the embryotoxic potential of HEMA, particularly with systemic absorption, warrants precaution in pregnant users or occupational settings with chronic exposure.

Real-world surveillance has revealed frequent cases of occupational eczema, periungual inflammation, and even airborne allergic reactions due to HEMA-containing dust generated during filing or removal of cured nails [27]. Cross-reactivity with other methacrylate monomers (e.g., HEMA, TEGDMA) complicates diagnosis and reinforces the need for restricted use in consumer products. The SCCS (2017) has advised limiting HEMA to professional-only applications to minimize uncontrolled exposure and misapplication.

HEMA remains integral to UV-curable nail formulations due to its functional benefits, but its associated toxicological risks - especially sensitization and irritation - necessitate controlled usage and improved product labeling. Regulatory recommendations emphasize adequate curing, training for professional use, and the consideration of alternative monomers with lower sensitization potential, such as urethane dimethacrylates (UDMAs) or newer bio-based monomers currently under investigation.

3.6. Contamination analysis of selected substances in UV-curable nail products

1,803 product and raw material tests were analyzed for the presence of five potentially toxic or sensitizing substances. MEHQ, TMPTA and HEMA were tested in 481 samples; TPO and HQ were tested in 180 samples. Results are given in Table 1.

Table 1. Contamination analysis of selected substances in UV-curable nail products

Substance	No. of tests	Contaminated samples	Average contamination, ppm
MEHQ	481	56	364
HQ	180	3	97
TMPTA	481	116	5,001
HEMA	481	82	36,963
TPO	180	13	96,488

HEMA was present in 17 % of the tested samples, with an exceptionally high average contamination level of 36,963 ppm, indicating possible improper purification or cross-contamination in production. This is of significant concern given HEMA's high sensitization potential. TPO contamination was found in 7 % of cases, with the highest average concentration (96,488 ppm) across all substances.

TMPTA, a known allergen and sensitizer, was found in 24 % of tested samples with an average concentration of 5,001 ppm, suggesting widespread low-level contamination. MEHQ was present in 11 % of samples at

364 ppm on average. MEHQ is often used as a stabilizer, and its presence could be intentional or due to residuals from raw materials.

HQ showed the lowest contamination frequency (2 %) and the lowest average level (97 ppm), indicating minimal contamination compared to other substances. The data reveal substantial contamination rates and concerning concentration levels for HEMA, TPO, and TMPTA in UV-curable nail products. These findings highlight the need for stricter quality control and raw material verification processes in formulation development to minimize health risks to consumers and professionals.

4. CONCLUSIONS

This study presents a comprehensive toxicological assessment of five key substances – HEMA, TMPTA, TPO, HQ, and MEHQ – frequently used in UV-curable nail products. Through a combination of bibliographic review and chemical analysis via UPLC-DAD, we confirmed the presence of all five substances in commercial nail formulations and raw materials designed for nail coatings.

The contamination analysis reveals a troubling prevalence of unlisted or residual monomers and additives. Notably, HEMA and TPO were found at alarmingly high average concentrations of 36,963 ppm and 96,488 ppm, respectively, suggesting poor formulation control and potential consumer overexposure. TMPTA was detected in nearly a quarter of the tested samples, reinforcing its widespread and likely underreported use. These findings are especially concerning, given the strong potential sensitization of HEMA and TMPTA and the clastogenic effects observed with TPO.

Although HQ and MEHQ were detected less frequently, their presence remains toxicologically relevant due to their known systemic and dermatological risks. The continued detection of HQ, despite its ban under EU Regulation (EC) No. 1223/2009, highlights enforcement gaps and calls into question the effectiveness of current oversight mechanisms.

Taken together, our findings emphasize the urgent need for: stricter regulatory enforcement and harmonized global oversight of acrylate-containing cosmetics, Robust quality control in raw material sourcing and formulation processes to prevent unintentional contamination, clear and truthful labeling to enable informed consumer choices, and development of safer, less sensitizing alternatives to high-risk compounds like HEMA and TPO. Future research should prioritize long-term exposure studies, biomonitoring in occupational settings, and the toxicological evaluation of alternative photoinitiators and stabilizers. Only through such multidimensional efforts can the cosmetic industry ensure the safety of UV-curable nail products for both consumers and professionals.

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