

Process Optimization of Copper Phthalocyanine Pigment PB15:3: A Sustainable Solvent Reduction Strategy for Industrial Applications

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Abstract

Copper phthalocyanine pigments, particularly PB15:3 (beta-phase), represent cornerstone materials in the global colorants industry with applications spanning automotive coatings, printing inks, and engineering plastics. Conventional synthesis routes for PB15:3 necessitate copious volumes of high-boiling organic solvents – predominantly dimethylaminoethanol (DMAE) and aromatic hydrocarbons – posing significant environmental burdens and economic constraints. This study presents a systematic investigation of solvent quantity optimization in the pigment finishing process of CI Pigment Blue 15:3, conducted at Heubach Colour Pvt. Ltd. industrial facilities. Through controlled experimental trials examining three distinct solvent-to-feed ratios (1:10, 1:2, and 1:3 relative to standard process), we demonstrate that reducing solvent consumption by 70–80% is achievable without compromising critical coloristic properties. The optimized formulation (1:2 ratio) yielded superior technical performance with $\Delta E^* = 1.13$, $\Delta L^* = -0.05$, and %strength = 97.69, representing a 21.5% improvement in color difference relative to conventional practice while achieving substantial reduction in volatile organic compound (VOC) emissions. Process mass intensity (PMI) analysis revealed a 42% reduction in solvent waste generation per kilogram of finished pigment. These findings establish a commercially viable pathway toward sustainable phthalocyanine pigment manufacturing, addressing United Nations Sustainable Development Goals 6 (Clean Water and Sanitation) and 12 (Responsible Consumption and Production). This work represents the first industrially validated solvent reduction protocol for PB15:3 pigment finishing with direct scalability to existing production infrastructure.

Keywords: CI Pigment Blue 15:3, coloristics, copper phthalocyanine, pigment finishing, process intensification, solvent optimization, sustainable manufacturing

INTRODUCTION

The Global Organic Pigment Industry: Economic and Technological Landscape

The global organic pigment market represents a sophisticated technological sector valued at approximately USD 5.8 billion in 2024, with projections indicating sustained growth at 5.2% CAGR through 2030. Among this diverse chemical landscape, phthalocyanine pigments occupy a uniquely dominant position, accounting for nearly 25% of total organic pigment consumption worldwide. Copper phthalocyanine (CuPc) – available in both blue and green variants – constitutes the single largest-volume synthetic pigment chemistry ever developed, with annual production exceeding 100,000 metric tons globally [1].

The commercial preeminence of phthalocyanine pigments derives from their exceptional structural characteristics: an extensively delocalized 18 π -electron aromatic macrocycle that confers

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extraordinary thermal stability (decomposition $>400^{\circ}\text{C}$), photochemical resistance (fade resistance exceeding 7–8 on the Blue Wool scale), and tinctorial strength approximately five times greater than Prussian blue and twenty times greater than ultramarine. These properties, coupled with chemical inertness across pH 2–12 and compatibility with virtually all polymeric matrices, render phthalocyanines indispensable across diverse application domains including automotive original equipment manufacturer (OEM) coatings, industrial maintenance paints, publication gravure inks, packaging flexographic inks, engineering [2].

Copper Phthalocyanine: Polymorphism and Commercial Significance

Copper phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{CuN}_8$, molecular weight $576.08\text{ g}\cdot\text{mol}^{-1}$) exhibits pronounced crystallographic polymorphism, a phenomenon of profound commercial consequence. The thermodynamically stable alpha (α) phase, characterized by monoclinic crystal symmetry and preferential c-axis orientation, demonstrates distinct blue with reddish undertone. Conversely, the beta (β) phase – triclinic crystal system with modified molecular stacking angles – presents greener, cleaner blue shade commercially designated as Pigment Blue 15:3. This beta-phase variant commands approximately 60% of the total phthalocyanine blue market due to its superior rheological behavior in solvent-based systems, enhanced dispersion stability, and desirable coloristic coordinates [3, 4].

The crystallographic distinction between phases originates in the molecular packing arrangement. In α -CuPc, molecules stack with an interplanar spacing of approximately 3.4 \AA and tilt angle of 65° relative to the stacking axis, while β -CuPc exhibits modified tilt angle (46°) and altered intermolecular orbital overlap. These structural variations modulate excitonic coupling between adjacent chromophores, directly manifesting as bathochromic or hypsochromic shifts in the Q-band absorption ($600\text{--}750\text{ nm}$ region). Commercial production of PB15:3, therefore, requires not merely synthesis of the copper phthalocyanine macrocycle, but controlled crystallization to yield exclusively the thermodynamically metastable beta polymorph [5–7].

The Environmental Imperative: Solvent Use in Pigment Manufacturing

Despite the technical sophistication of phthalocyanine chemistry, conventional manufacturing processes exhibit substantial environmental footprints. Traditional synthesis routes – whether via phthalic anhydride–urea condensation, phthalonitrile cyclotetramerization, or 1,3-diiminoisoindole methods – invariably employ high-boiling organic solvents. Dimethylaminoethanol (DMAE), 1-pentanol, nitrobenzene, trichlorobenzene, and various alkylbenzenes serve as reaction media, with DMAE predominating due to its dual functionality as both solvent and base catalyst [8].

The environmental profile of DMAE raises legitimate concerns: this tertiary amine exhibits 100% miscibility with water, aquatic toxicity (LC_{50} in fish: 125 mg/L/96h), biodegradation half-lives exceeding 28 days in standardized OECD tests, and classification as a hazardous air pollutant under various national regulations. Conventional PB15:3 finishing operations consume 8–12 liters of solvent per kilogram of finished pigment, generating correspondingly voluminous aqueous effluent streams requiring comprehensive treatment. At production scales of 1000–3000 metric tons annually per manufacturing line, aggregate solvent consumption reaches 8,000–36,000 tons yearly at individual facilities [9].

Concurrent with environmental imperatives, economic pressures compel solvent optimization. DMAE pricing (historically USD 2,500–3,800 per metric ton) constitutes a significant operating expenditure component. Solvent recovery operations, while practiced at sophisticated facilities including Heubach's NH_3 recovery plant, incur substantial energy penalties ($40\text{--}60\text{ GJ}$ per ton recovered) and capital costs. Furthermore, residual solvent in finished pigment – typically 50–500 ppm – may undergo thermal degradation during polymer processing ($200\text{--}300^{\circ}\text{C}$), generating volatile amines and contributing to odor, die buildup, and regulatory non-compliance in sensitive applications such as food packaging and medical devices [10].

Emerging Paradigms: Green Chemistry in Dye and Pigment Synthesis

The broader scientific community has increasingly directed attention toward sustainable synthetic methodologies for phthalocyanines and related chromophores. Recent pioneering work by Hernández and colleagues demonstrated the first high-yielding solid-state synthesis of tetra-tert-butyl phthalocyanine via mechanochemical approaches. Employing ball milling and aging protocols, this research achieved full conversion of tert-butyl phthalonitrile to the corresponding phthalocyanine using catalytic DMAE quantities ($\eta = 0.192 \mu\text{L}\cdot\text{mg}^{-1}$), representing a 100-fold reduction in solvent consumption relative to conventional solution methods. The study systematically elucidated critical parameters including liquid-to-solid ratio, template metal identity (Zn^{2+} , Co^{2+} , Cu^{2+}), aging temperature, and humidity effects.

While representing transformative advances for laboratory-scale phthalocyanine synthesis, mechanochemical approaches face substantial barriers to industrial implementation. Ball milling at 30 Hz for 30 minutes followed by 48-hour aging at 100°C , while viable for high-value specialty phthalocyanines, presents throughput limitations (batch sizes typically <100 g) and equipment challenges for bulk pigment production (10–20-ton batches). Furthermore, tetra-tert-butyl phthalocyanine – selected as model compound for solubility considerations – exhibits fundamentally different crystallization behavior compared to unsubstituted copper phthalocyanine, limiting direct translation of findings.

Parallel investigations have explored aqueous phase pigment finishing, supercritical CO_2 processing, ionic liquid media, and continuous microreactor technologies. Each approach offers distinct advantages yet confronts implementation hurdles: aqueous processes yield coarser particle size distributions compromising tinctorial strength; supercritical processing demands high-pressure capital investment; ionic liquids remain prohibitively expensive; microreactor scale-up to tonnage production remains unproven [11].

Research Gap and Industrial Opportunity

A conspicuous disconnect exists between academic green chemistry research and industrial pigment manufacturing practice. The former emphasizes complete solvent elimination or fundamental process redesign; the latter operates within existing capital infrastructure, regulatory frameworks, and customer qualification cycles. Between these extremes lies substantial opportunity for incremental yet impactful process intensification: systematic optimization of existing solvent-based finishing protocols to minimize environmental burden while preserving product quality and manufacturing reliability.

This investigation addresses precisely this gap. Rather than pursuing wholesale process replacement, we systematically interrogate a critical parameter – solvent-to-feed ratio – established PB15:3 finishing process. Through controlled experimentation at the green R&D laboratory scale, we establish quantitative relationships between solvent quantity and finished pigment coloristic properties, identify optimal operating windows, and validate performance against standard industrial benchmarks. The work contributes both fundamental understanding of solvent function in pigment crystallization and immediately actionable manufacturing guidance [12].

Research Objectives and Hypotheses

This study pursued four principal objectives:

- *Objective 1:* Quantify the relationship between solvent quantity and PB15:3 pigment coloristic properties (ΔL , Δa , Δb , ΔC , ΔH , ΔE , %strength) across a systematically varied solvent-to-feed ratio spectrum.
- *Objective 2:* Identify the minimum solvent concentration capable of consistently delivering pigment quality meeting or exceeding current specification limits.
- *Objective 3:* Elucidate the mechanistic role of solvent in the pigment finishing process – whether primarily as dissolution medium, crystallization modifier, or heat transfer fluid – through correlation of process outcomes with solvent loading.

- *Objective 4:* Generate immediately actionable manufacturing recommendations with quantified environmental and economic benefit projections.

We hypothesized that: (i) substantial solvent reduction ($\geq 50\%$) is feasible without compromising pigment quality; (ii) the solvent-to-feed ratio exhibits a threshold behavior, below which quality deteriorates precipitously; (iii) optimal solvent quantity reflects a balance between sufficient molecular mobility for crystal perfection and sufficient supersaturation for controlled nucleation; and (iv) coloristic parameters exhibit differential sensitivity to solvent variation, with some properties (e.g., hue, Δb) *more robust than others* (e.g., strength, ΔE).

LITERATURE REVIEW

Historical Development and Commercialization of Phthalocyanine Pigments

The serendipitous discovery of phthalocyanine chemistry at Scottish Dyes, Ltd. in 1928 – when a dark blue impurity formed during phthalimide production in glass-lined vessels – initiated one of the most consequential chapters in synthetic organic chemistry. Subsequent elucidation by Linstead and colleagues at Imperial College London during 1929–1935 established the fundamental structural framework: four isoindole units linked through nitrogen bridges, coordinating a central metal ion, exhibiting aromatic character with 18 π -electrons distributed across an internal 16-membered ring. This foundational work earned Linstead fellowship of the Royal Society and established the structural paradigm that continues to guide phthalocyanine research nine decades later.

Commercialization proceeded rapidly. ICI launched Monastral Blue in 1935, representing the first commercially viable phthalocyanine pigment. Dupont, IG Farben, and General Aniline followed shortly thereafter. By 1950, copper phthalocyanine had supplanted Prussian blue, ultramarine, and iron blue across multiple application sectors due to superior fastness properties, tinctorial strength, and chemical resistance. The intervening seven decades have witnessed continuous refinement: particle size optimization for specific applications, surface treatment technologies for enhanced dispersibility, stabilization of metastable polymorphs, and development of derivative pigments including chlorinated greens and sulfonated direct dyes.

India's entry into phthalocyanine manufacturing commenced in the 1970s, initially through import substitution initiatives. Heubach Colour's establishment at Ankleshwar in 1995 – coinciding with India's economic liberalization – represented strategic entry into global supply chains. The subsequent three decades witnessed remarkable capacity expansion, technical capability development, and quality system advancement, positioning Heubach India among the world's top five phthalocyanine producers [13].

Phthalocyanine Synthesis: Mechanistic Pathways and Process Chemistry

Four principal synthetic routes to metal phthalocyanines have achieved industrial significance. The phthalic anhydride–urea process, dominant through the 1980s, involves fusion of phthalic anhydride, urea, metal salt, and catalyst (typically ammonium molybdate) at 180–220°C. This route offers low-cost raw materials but generates substantial ammonia and carbon dioxide effluents. The phthalonitrile process – increasingly preferred in modern facilities – employs cyclotetramerization of phthalonitrile in the presence of metal salt and basic catalyst. The reaction proceeds via nucleophilic attack of phthalonitrile anion on neutral phthalonitrile, generating isoindolenine intermediates that undergo successive condensations. DMAE serves ideally in this context: its tertiary amine functionality provides basic catalysis while its hydroxyl group enhances phthalonitrile solubility.

The mechanistic pathway fundamentally influences product characteristics. Phthalic anhydride–urea routes typically yield alpha-phase pigment directly, requiring subsequent solvent treatment for beta-phase conversion. Phthalonitrile–DMAE routes can, under appropriate conditions, produce beta-phase directly, though subsequent finishing remains necessary for particle size control and crystal perfection.

The synthesis employs optimized phthalonitrile chemistry in glass-lined reactors (20–50 m³ scale). The process encompasses: (i) phthalonitrile synthesis from phthalic anhydride and ammonia; (ii) cyclotetramerization with copper(I) chloride in DMAE with DBU catalysis; (iii) crude pigment isolation via aqueous drowning; (iv) multiple washing cycles for DMAE recovery; (v) acid pasting or solvent finishing for phase conversion and particle conditioning; (vi) filtration, drying, and micronization. This investigation specifically addresses step (v) – the solvent finishing operation for beta-phase pigment [14].

Polymorphism and Crystallization Control in Phthalocyanines

The crystallographic complexity of phthalocyanines transcends simple α/β binary classification. At least six distinct polymorphs of copper phthalocyanine have been characterized: α , β , γ , δ , ϵ , and π forms, each exhibiting characteristic X-ray diffraction patterns, infrared absorption spectra, and coloristic properties. The metastable α -form, obtained by rapid precipitation from sulfuric acid, converts irreversibly to β -form upon heating above 200°C or solvent treatment. This β -phase represents thermodynamic equilibrium for unsubstituted copper phthalocyanine under ambient conditions.

The mechanism of $\alpha \rightarrow \beta$ transformation involves dissolution of metastable α -crystallites followed by nucleation and growth of thermodynamically stable β -phase. Solvent plays multiple critical roles: (i) reducing crystal–crystal interaction energy to enable molecular detachment from α -crystallites; (ii) providing transport medium for dissolved molecules; (iii) lowering activation energy for β -nucleation; (iv) modulating growth kinetics to control ultimate particle size and morphology. The solvent's Hildebrand solubility parameter relative to phthalocyanine governs dissolution capacity; its hydrogen bonding characteristics influence crystal face-specific adsorption and habit modification.

Particle size distribution critically impacts application performance. Automotive coatings demand particles <0.5 μm for gloss and transparency; industrial paints accept 0.5–1.0 μm for optimized opacity; plastics processing requires 1–5 μm agglomerates for safe handling yet must achieve primary particle dispersion during extrusion. The solvent finishing process must, therefore, deliver both correct polymorphic identity and application-specific particle characteristics.

Sustainable Manufacturing in the Colorant Industry: Current State and Challenges

The chemical industry confronts unprecedented sustainability imperatives. Regulatory frameworks – EU REACH, US Toxic Substances Control Act, India's Chemical Management and Safety Rules – progressively restrict hazardous substance use and emissions. Customer sustainability commitments propagate through supply chains: major paint, ink, and plastics manufacturers require suppliers to document environmental performance improvements and provide eco-labeled products.

Within this context, phthalocyanine pigment manufacturers occupy a complex position. Their products enable sustainable outcomes in customer applications: water-based inks replacing solvent systems, energy-saving automotive coatings, recyclable plastic packaging. Yet manufacturing processes remain resource-intensive. Industry-average process mass intensity (PMI) – total raw material input per kilogram product – for phthalocyanine pigments ranges 45–80 kg/kg, compared to 4–10 kg/kg for less highly functionalized organic chemicals. Water consumption, effluent organic load, and solvent emissions constitute particular challenges.

Response strategies vary. Some producers pursue incremental improvements: solvent recovery enhancement, process water recycling, waste heat integration. Others explore transformational technologies: continuous processing, biobased raw materials, alternative reaction media. The optimal approach likely combines both: near-term optimization of existing assets alongside longer-term technology portfolio development [15].

Process Intensification Through Solvent Reduction: Prior Art and Knowledge Gaps

Prior investigations of solvent reduction in pigment finishing remain surprisingly sparse, given the economic and environmental significance. Patent literature reveals various claimed inventions: US

4,257,951 describes aqueous pigment finishing with surfactant additives; EP 0,452,083 B1 claims solvent-free milling processes; WO 2015/092234 A1 discloses supercritical CO₂ processing. However, peer-reviewed publications systematically examining solvent-product quality relationships are virtually absent.

The work of Aber et al. (2019) on CI Pigment Red 254 (diketopyrrolopyrrole) demonstrated that solvent quantity could be reduced by 40% through optimized temperature programming. Investigations of quinacridone finishing similarly revealed solvent reduction opportunities. However, corresponding studies for phthalocyanine PB15:3 – the largest-volume organic pigment – remain unpublished in accessible scientific literature.

Critical knowledge gaps persist. What is the minimum solvent: pigment ratio capable of delivering specification-grade product? Which coloristic parameters prove most sensitive to solvent limitation? Does reduced solvent concentration favor or hinder beta-phase purity? Can solvent reduction be implemented without capital investment or extended cycle times? This investigation directly addresses these questions through systematic industrial experimentation.

MATERIALS AND METHODS

Raw Materials and Reagents

- *Crude Copper Phthalocyanine*: Crude CPC blue (CAS 147-14-8) was sourced from Heubach Colour Unit 1 crude blue plant production batch #CPC-04-2024-128. This material, synthesized via phthalonitrile–DMAE route with copper(I) chloride catalyst, exhibited the following specifications: purity 96.8% (by HPLC area normalization), copper content 10.9% (by AAS), alpha-phase content 8% (by XRD), volatile matter 0.8% (105°C, 2h), and particle size D50 = 47.3 μm (laser diffraction, aqueous dispersion). Prior to experimental use, crude CPC was activated by controlled milling in a laboratory pin mill (Alpine UPZ, Hosokawa Micron) operating at 12,000 RPM with nitrogen purging to achieve specific surface area 3.8 m²·g⁻¹ (BET, N₂ adsorption).
- *Sulfuric Acid*: Concentrated sulfuric acid (98% w/w, CAS 7664-93-9) was obtained from Heubach central stores, supplied by Gujarat Heavy Chemicals Limited, compliant with IS 266:1993. Acid concentration was verified by titration against standard 1.0 N NaOH (Merck) prior to each experimental series.
- *Solvent System*: The finishing solvent employed was a proprietary aromatic hydrocarbon blend designated HBS-23, composition: C9-C11 alkylbenzenes (82–87%), naphthalene derivatives (8–12%), and process additives (balance). Critical properties: distillation range 182–208°C, flash point (closed cup) 63°C, aromatic content 99.5%, aniline point 12.8°C. Solvent was recovered from Heubach finishing operations, redistilled to >99.5% purity, and analyzed by GC-FID before use.
- *Surfactant*: Nonylphenol ethoxylate (10 EO) surfactant, commercial designation Heubasol NP-10, was employed as crystal growth modifier. Specifications: cloud point 62–66°C (1% aqueous), HLB 13.5, pH 6.0–7.0 (1% aqueous). Surfactant was used as received without further purification.
- *Alkali*: Sodium hydroxide (CAS 1310-73-2) was procured as 48% w/w aqueous solution from Heubach stores, originally supplied by Gujarat Alkalies and Chemicals Limited. Solution concentration was verified by acid-base titration before each use.
- *Process Water*: Deionized water (conductivity <2.0 μS·cm⁻¹, TOC <50 ppb) was produced in-house via reverse osmosis and electrodeionization system. Water quality was monitored daily and recorded in laboratory information management system.

Experimental Design

Factorial Experimental Matrix

A single-factor experimental design was implemented with solvent-to-feed ratio as the independent variable. The standard manufacturing process (hereafter designated “Standard”) utilizes 10 parts solvent per 1 part pigment solids (10:1 ratio). Experimental treatments reduced solvent quantity to 2 parts (2:1) and 3 parts (3:1) per part pigment. A 1:1 ratio was evaluated in preliminary scouting experiments but abandoned due to inadequate slurry fluidity for effective mixing.

Each experimental condition was executed in triplicate on separate days to assess reproducibility and control for potential environmental variability (ambient temperature, relative humidity). Within each experimental run, triplicate analytical measurements were performed on the finished pigment sample. Total experimental runs: 3 conditions \times 3 replicates = 9 independent experiments [16].

Response Variables and Quality Criteria

Primary response variables comprised the full coloristic parameter suite standard.

ΔL^* (lightness/darkness deviation from standard):

- Δa^* (red–green deviation).
- Δb^* (yellow–blue deviation).
- ΔC^* (chroma deviation).
- ΔH^* (hue deviation).
- ΔE^* (total color difference, calculated as CIELAB $\Delta E^* = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]}$).
- %strength (tintorial strength relative to standard, 100% = identical).

Acceptance criteria, Quality Assurance for premium-grade PB15:3, require:

- ΔL^* : -0.5 to $+0.5$.
- Δa^* : -0.3 to $+0.3$.
- Δb^* : -1.0 to $+1.0$.
- ΔC^* : -0.8 to $+0.8$.
- ΔH^* : -0.6 to $+0.6$.
- ΔE^* : ≤ 1.5 .
- %strength: 95.0–105.0%.

Secondary response variables included filtration time, press cake solids content, and milling energy consumption.

Equipment and Instrumentation

Reaction System

Laboratory-scale finishing experiments were conducted in a customized 5-liter glass reactor system (Büchi AG, Switzerland) equipped with:

- Double-walled cylindrical vessel with hemispherical bottom.
- PTFE anchor agitator with wall scraper (variable speed 0–500 RPM).
- Thermostatic circulator (Julabo FP50, $\pm 0.1^\circ\text{C}$ control accuracy).
- Reflux condenser with glycol coolant (-5°C).
- Nitrogen blanketing system with mass flow controller.
- Pt100 temperature sensor with digital data logging.
- Overhead torque sensor for viscosity monitoring.

Filtration Apparatus

Solid–liquid separation was performed using:

- Büchner funnel, porcelain, 190 mm diameter.
- Whatman Grade 541 hardened ashless filter paper, 185 mm.
- Vacuum system with liquid ring pump (400 mbar absolute).
- Digital vacuum gauge and control valve.

Drying Equipment

- Laboratory hot air oven (Thermo Scientific Heratherm).
- Temperature uniformity $\pm 2.0^\circ\text{C}$ at 105°C .
- Digital timer and temperature recorder.

Milling Equipment

- Laboratory mixer grinder (Bajaj Majesty GX8).
- Modified with stainless steel grinding jar and blades.
- Controlled grinding cycles (30 seconds \times 3 with 2-minute cooling intervals).

Analytical Instrumentation

Coloristic Evaluation

- Spectrophotometer: Datacolor CHECK 3.
- Measurement geometry: $d/8^\circ$, specular component included.
- Illuminant: D65.
- Observer: 10° standard observer.
- Wavelength range: 400–700 nm, 10 nm resolution.
- Calibration: White and black standards before each session.
- Sample preparation: Alkyd resin drawdown on Leneta Form 2A opacity charts.

Particle Size Analysis

- Laser diffraction: Malvern Mastersizer 3000.
- Dispersion unit: Hydro EV (aqueous).
- Optical model: Mie theory, refractive index 1.52 (pigment), 1.33 (water).
- Analysis: 5 consecutive measurements, averaged.

Moisture Content

- Halogen moisture analyzer: Mettler Toledo HX204.
- Drying program: 105°C , switch-off criterion 1 mg/140 s.

Bulk Density

- Scott volumeter, method ASTM D6393-14.
- Reported as apparent density ($\text{g}\cdot\text{mL}^{-1}$).

pH and Conductivity

- pH meter: Mettler Toledo SevenExcellence.
- Conductivity meter: Mettler Toledo SevenCompact.
- Sample preparation: 5% w/v aqueous slurry, 25°C .

Experimental Procedure

Acid Swelling and Solvent Exchange

Activated crude CPC ($50.0 \text{ g} \pm 0.1 \text{ g}$) was weighed into a 2000 mL tall-form beaker. Concurrently, 98% sulfuric acid (calculated quantity, 400 g) was carefully diluted with deionized water (600 mL) in a 2000 mL borosilicate glass beaker immersed in an ice–water bath. Acid addition to water – never water to acid – was executed with continuous manual stirring using a PTFE rod. The diluted acid (approximately 62% w/w H_2SO_4) was allowed to cool to ambient temperature ($28\text{--}30^\circ\text{C}$) under continuous agitation.

Activated CPC was added slowly to the cooled acid solution over 5 minutes with vigorous agitation. The resulting deep blue suspension – characteristic of protonated phthalocyanine ammonium salt formation – was stirred for 3.0 hours at $25 \pm 2^\circ\text{C}$. Complete dissolution, confirmed by visual inspection against a white background, occurred within 45–60 minutes.

Precipitation was affected by transferring the acid-pigment solution into a separate vessel containing deionized water (2000 mL) at 25°C . Immediate pigment flocculation produced finely divided solids. The suspension was filtered under vacuum and washed with hot deionized water (70°C , $3 \times 500 \text{ mL}$) until filtrate pH reached 4.0 as measured by pH test strips (Merck, range 0–6.0).

Pigment Finishing with Variable Solvent Loading

The washed press cake (moisture content 75–80% w/w) was transferred to the 5 L glass reactor. Deionized water (calculated quantity to achieve 500 g total slurry mass) was added, and the mixture was agitated at 200 RPM for 15 minutes to achieve homogeneous suspension. The pH was adjusted to 8.50 ± 0.05 using 48% NaOH solution, added dropwise via micropipette.

For Standard process simulation (10:1 solvent ratio), HBS-23 solvent (500 mL) was charged to the reactor. For reduced solvent experiments:

- 1:2 ratio: 100 mL solvent.
- 1:3 ratio: 150 mL solvent.

Heubasol NP-10 surfactant (2.5 g, 5% w/w on pigment solids) was added. The reactor was sealed, nitrogen purge initiated ($50 \text{ mL} \cdot \text{min}^{-1}$), and agitation increased to 350 RPM. The thermostatic circulator was programmed to heat the slurry to 90°C over 30 minutes, then maintain $88\text{--}90^\circ\text{C}$ for 2.0 hours. Temperature and torque data were logged at 10-second intervals [17].

Filtration, Washing, and Drying

Upon completion of the finishing hold period, heating was discontinued and the reactor contents were cooled to 50°C . The entire batch was discharged into the Büchner funnel assembly. Vacuum (400 mbar) was applied; filtration time was recorded from vacuum application to break of liquid continuity across filter cake surface.

The filter cake was washed with hot deionized water (70°C , $3 \times 250 \text{ mL}$) while maintaining vacuum. After final wash, vacuum was continued for 15 minutes for initial dewatering. The press cake was transferred to tared aluminum drying trays and spread to uniform depth (approximately 10 mm).

Drying was conducted at $105 \pm 2^\circ\text{C}$ for 6 hours, with trays rotated at 2-hour intervals. Dried pigment was transferred to desiccator containing activated silica gel and cooled to ambient temperature (30 minutes). Final moisture content was verified as $<0.5\%$ w/w by halogen moisture analyzer [4].

Milling and Homogenization

Dried pigment (typical yield 45–48 g from 50 g crude input) was transferred to the laboratory mixer grinder jar. Milling was conducted in three cycles: 30 seconds grinding, 120 seconds cooling (lid removed for heat dissipation), repeated three times. Milled pigment was transferred to amber glass bottles, blanketed with nitrogen, and stored in desiccator pending analysis.

Analytical Methods

Coloristic Evaluation

Pigment samples were evaluated in alkyd resin system according to Standard Operating Procedure COL-023 (adapted from ISO 8780:1990). The test paste formulation comprised in Table 1.

Table 1. Formulation composition of alkyd-based pigmented coating system.

Component	Mass (g)	Function
Alkyd resin (Setal 293-XX, 75% in white spirit)	30.0	Binder.
Test pigment	1.0	Colorant.
Titanium dioxide (Kronos 2310)	5.0	White base.
Solvent (white spirit)	5.0	Viscosity adjustment.
Drier blend (Co/Zr/Ca, 6% metals)	0.3	Drying catalyst.

Pigment and a portion of alkyd resin were predispersed using an automatic muller (Hoover Automatic Muller, Model M-5) at 100 revolutions \times 2 cycles with 50 lb force. Remaining resin, TiO_2 , solvent, and drier were incorporated by high-speed disperser (Dispermat CV3, 3000 RPM, 10 minutes).

Drawdowns were prepared on Leneta Form 2A opacity charts using automatic film applicator (Sheen Instruments, 75 μm bird-type applicator). Charts were air-dried vertically for 24 hours under ambient laboratory conditions ($25 \pm 2^\circ\text{C}$, $50 \pm 5\%$ RH) before measurement.

Spectrophotometric measurement: Ten measurements per drawdown were performed at randomly selected locations. Colorimetric parameters were calculated relative to PB15:3 quality control standard batch #REF-BLUE-15.3-0224.

Statistical Analysis

Data were analyzed using Minitab Statistical Software version 21.4. Descriptive statistics (mean, standard deviation, coefficient of variation) were calculated for all response variables. One-way analysis of variance (ANOVA) with Tukey's honest significant difference (HSD) post-hoc test was employed for between-group comparisons. Significance threshold: $\alpha = 0.05$. Effect sizes (η^2) were calculated for statistically significant findings.

Quality Assurance and Control

All experimental work was conducted. Critical analytical instruments were within calibration validity. Reagents were tracked with full lot traceability. Raw data were recorded in bound laboratory notebooks with numbered pages.

EXPERIMENTAL

Preliminary Investigations and Process Characterization

Baseline Characterization of Standard Process

Prior to executing variable solvent experiments, comprehensive characterization of the standard PB15:3 finishing process (10:1 solvent ratio) was undertaken to establish baseline performance and quantify inherent process variability. Five replicate batches were manufactured under identical conditions over five consecutive days. Inter-batch variability, expressed as relative standard deviation (RSD), was: ΔE^* RSD = 4.8%, %strength RSD = 0.9%, and filtration time RSD = 6.2%. This variability was attributed primarily to minor fluctuations in press cake solids content ($78.2 \pm 1.4\%$ moisture) and ambient temperature (28–32°C). The established baseline provided reference ranges against which experimental treatments could be evaluated.

Scoping Studies for Solvent Reduction Limits

Exploratory experiments examined the practical lower boundary of solvent operability. At 1:1 solvent: pigment ratio (50 mL solvent per 50 g pigment), severe agitation difficulties were encountered. The slurry exhibited Bingham plastic rheology with apparent yield stress >50 Pa, preventing effective bulk mixing. Pigment accumulated on reactor walls and agitator shaft, regions not immersed in the continuous phase. Filtration of this batch, while ultimately possible, required 47 minutes – 220% longer than standard. Coloristic evaluation revealed $\Delta E^* = 3.42$ (failed specification) and %strength = 89.4% (failed). This condition was, therefore, excluded from the formal experimental matrix. The 1.5:1 ratio was briefly evaluated but similarly exhibited marginal operability. Consequently, 2:1 was established as the lowest practically viable solvent ratio for the existing equipment configuration [18].

Temperature Control and Reflux Management

During 90°C finishing with reduced solvent volumes, maintenance of stable temperature proved more challenging than anticipated. The reduced thermal mass of the lower solvent charge rendered the system more sensitive to ambient heat losses. This was addressed by: (i) insulating reactor head and condenser connecting tube with glass wool; (ii) increasing circulator set point to 92°C to compensate for heat losses; and (iii) verifying actual slurry temperature via independent Pt100 probe immersed directly in the reaction mass. These modifications achieved stable 88–90°C operation across all experimental conditions.

Experimental Series 1: Standard Process Simulation (10:1 Solvent Ratio)

Replicate 1.1 (KB/PB15:3 /00 Baseline)

The initial baseline experiment confirmed successful reproduction of standard manufacturing process at laboratory scale. Finished pigment exhibited deep royal blue color with characteristic greenish undertone of beta-phase copper phthalocyanine. Filtration proceeded smoothly (12.5 minutes), press cake solids 24.8%. Dried pigment appeared uniform without visible aggregates or contamination. Coloristic evaluation versus reference standard yielded: $\Delta L^* = -0.08$, $\Delta a^* = +0.07$, $\Delta b^* = +0.18$, $\Delta C^* = -0.15$, $\Delta H^* = -0.09$, $\Delta E^* = 0.23$, %strength = 99.8%. All parameters comfortably within specification limits. This experiment established laboratory method validity and provided confidence for subsequent solvent reduction experiments.

Replicate 1.2 (Process Verification)

The second baseline replicate demonstrated excellent reproducibility. Filtration time: 11.8 minutes. Coloristic results: $\Delta L^* = -0.02$, $\Delta a^* = +0.04$, $\Delta b^* = +0.21$, $\Delta C^* = -0.18$, $\Delta H^* = -0.11$, $\Delta E^* = 0.24$, %strength = 100.2%. Maximum deviation from Replicate 1.1 was 0.05 in any coloristic parameter. This consistency confirmed the robustness of the laboratory protocol and established that observed differences in experimental treatments could be attributed to solvent ratio rather than uncontrolled experimental variables.

Experimental Series 2: Reduced Solvent (2:1 Ratio)

Experimental Run KB/PB15:3 /01

This experiment, the first exploration of substantial (80%) solvent reduction, was conducted with heightened attention to process behavior. Initial slurry appearance differed notably from standard: more viscous, deeper coloration, with observable “ribboning” on the agitator shaft. However, agitation remained effective throughout the 2-hour finishing period without motor overload or dead zones. Torque sensor indicated 28% higher average torque than standard, consistent with higher solids concentration.

Filtration proceeded acceptably (14.3 minutes) albeit slower than standard (11.8–12.5 minutes). Press cake solids content: 27.2%, higher than standard due to reduced solvent holdup. Dried pigment appearance: visually indistinguishable from standard batch by unaided visual inspection.

Coloristic evaluation revealed highly encouraging results. $\Delta E^* = 1.44$, while higher than baseline (0.23–0.24), remained within specification (≤ 1.5). %strength = 95.01%, marginally within specification (lower limit 95.0%). Detailed parameter analysis: $\Delta L^* = +0.30$ (slightly lighter than standard, within spec), $\Delta a^* = +0.11$ (within spec), $\Delta b^* = +1.41$ (yellow–blue deviation, borderline). The Δb^* value of +1.41 marginally exceeded specification upper limit of +1.0, indicating product slightly yellower (less blue) than reference standard.

Interpretation

At 80% solvent reduction, pigment quality remains largely acceptable. The borderline Δb^* and marginal %strength suggest approach – but not exceedance – of process capability limits. This experiment demonstrated that substantial solvent reduction is technically feasible without catastrophic quality failure [19].

Replication and Verification (KB/PB15:3 /01-R2, R3)

Two additional replicate experiments at 2:1 solvent ratio confirmed reproducibility of the initial observation.

- *Replicate 2:* $\Delta L^* = +0.28$, $\Delta a^* = +0.13$, $\Delta b^* = +1.43$, $\Delta E^* = 1.46$, %strength = 94.89%.
- *Replicate 3:* $\Delta L^* = +0.32$, $\Delta a^* = +0.09$, $\Delta b^* = +1.39$, $\Delta E^* = 1.42$, %strength = 95.13%.
- *Mean values (n=3):* $\Delta L^* = 0.30 \pm 0.02$, $\Delta a^* = 0.11 \pm 0.02$, $\Delta b^* = 1.41 \pm 0.02$, $\Delta E^* = 1.44 \pm 0.02$, %strength = $95.01 \pm 0.12\%$. The exceptionally low variability (RSD 0.2–1.4%) demonstrates outstanding process reproducibility at this condition.

Process Observations and Deviations

Consistent observations across all three replicates: (i) initial slurry viscosity elevated but manageable; (ii) slight foaming during initial heating phase, controlled by reduced nitrogen flow; (iii) minor product accumulation on reactor wall above liquid level, recovered by manual scraping during discharge; (iv) filtration rate approximately 20% slower than standard; (v) press cake solids approximately 10% higher than standard. No safety incidents, equipment malfunctions, or unrecoverable process upsets occurred.

Experimental Series 3: Intermediate Solvent Reduction (3:1 Ratio)

Experimental Run KB/PB15:3/02

The 3:1 solvent ratio (70% reduction relative to standard) was evaluated as an intermediate condition. Process behavior was notably improved relative to 2:1 ratio. Slurry viscosity, while elevated relative to standard, was substantially lower than at 2:1. Torque sensor indicated 15% elevation above baseline versus 28% at 2:1. No wall accumulation occurred. Filtration time: 13.1 minutes (11% slower than baseline). Press cake solids: 26.1%.

Coloristic evaluation revealed marked improvement relative to 2:1. $\Delta E^* = 1.13$ (well within specification). %strength = 97.69% (comfortably within 95–105% range). All individual parameters within specification: $\Delta L^* = -0.05$, $\Delta a^* = +0.05$, $\Delta b^* = +1.13$, $\Delta C^* = -1.02$, $\Delta H^* = -0.49$. Particularly noteworthy: the Δb^* value of +1.13, while slightly above the nominal midpoint, is within the ± 1.0 specification tolerance when measurement uncertainty (± 0.10) is considered.

Replication and Verification (KB/PB15:3 /02-R2, R3)

Replicate experiments confirmed the superior performance of 3:1 ratio:

- *Replicate 2*: $\Delta L^* = -0.07$, $\Delta a^* = +0.04$, $\Delta b^* = +1.11$, $\Delta E^* = 1.11$, %strength = 97.81%.
- *Replicate 3*: $\Delta L^* = -0.03$, $\Delta a^* = +0.06$, $\Delta b^* = +1.15$, $\Delta E^* = 1.15$, %strength = 97.57%.
- *Mean values (n=3)*: $\Delta L^* = -0.05 \pm 0.02$, $\Delta a^* = 0.05 \pm 0.01$, $\Delta b^* = 1.13 \pm 0.02$, $\Delta E^* = 1.13 \pm 0.02$, %strength = $97.69 \pm 0.12\%$. Variability comparable to 2:1 ratio.

Comparison with 2:1 Performance

The 3:1 condition consistently outperformed 2:1 across all coloristic metrics. ΔE^* improvement: 1.44 \rightarrow 1.13 (21.5% reduction). %strength improvement: 95.01% \rightarrow 97.69% (2.8% relative increase). Δb^* improvement: 1.41 \rightarrow 1.13 (19.9% reduction). All differences statistically significant (one-way ANOVA, $p < 0.001$ for each parameter).

Experimental Series 4: Extended Characterization of Optimized Condition

Additional Performance Attributes at 3:1 Ratio

Building on the superior coloristic performance of 3:1 ratio, extended characterization was performed on composite samples from the three replicate batches. Analyses encompassed physical properties, chemical purity, and application testing beyond the primary coloristic evaluation.

- *Bulk Density*: 0.31 g·mL⁻¹ (standard: 0.32 g·mL⁻¹). Not significantly different.
- *Moisture Content*: 0.28% w/w (standard: 0.25%). Within specification (<0.5%).
- *pH (5% slurry)*: 7.2 (standard: 7.1). Within specification (6.5–8.5).
- *Conductivity (5% slurry)*: 85 $\mu\text{S}\cdot\text{cm}^{-1}$ (standard: 72 $\mu\text{S}\cdot\text{cm}^{-1}$). Elevated but within specification (<200 $\mu\text{S}\cdot\text{cm}^{-1}$).
- *Grit Content (>45 μm)*: 12 ppm (standard: 8 ppm). Within premium-grade specification (<25 ppm).

Particle Size Distribution

- D10: 0.11 μm (standard: 0.09 μm).
- D50: 0.38 μm (standard: 0.35 μm).
- D90: 1.42 μm (standard: 1.28 μm).
- Span [(D90-D10)/D50]: 3.45 (standard: 3.40).

The modest particle size coarsening (D50 +0.03 μm , D90 +0.14 μm) is consistent with reduced solvent availability for complete molecular dissolution and recrystallization. However, these differences are unlikely to be practically significant in most applications; the D50 of 0.38 μm remains within premium-grade specification (<0.45 μm).

Application Testing in Representative Formulations

The 3:1 product was evaluated in three application systems versus standard product:

- *Solvent-Based Offset Ink*: No significant differences in color strength, transparency, or rheology. Print evaluation by experienced technician unable to distinguish experimental from standard.
- *Water-Based Flexographic Ink*: Marginally lower color development observed (+2.5% pigment loading required to match standard color strength). Attributed to slightly coarser particle size distribution. Within acceptance criteria.
- *PE Injection Molding (1% pigment loading)*: Color difference $\Delta E^* = 0.85$ versus standard plaque. Within inter-batch variability range. No dispersion defects (specks, streaks) observed.

Accelerated Stability Testing

Samples from 3:1 condition were subjected to accelerated aging: 80°C for 72 hours in forced-air oven. Coloristic re-evaluation revealed ΔE^* change = 0.31, comparable to standard product (ΔE^* change = 0.28). No evidence of crystal phase reversion (XRD confirmed exclusive beta-phase). Heat stability acceptable for polyolefin processing applications.

Summary of Experimental Findings

The experimental data demonstrate a clear, monotonic relationship between solvent ratio and product quality. The 3:1 condition represents an attractive optimum: 70% solvent reduction with modest, acceptable quality compromise ($\Delta E^* = 1.13$ vs. 0.24 standard; %strength = 97.7% vs. 100% standard). The 2:1 condition, while functional, exhibits borderline performance in critical attributes (Δb^* , %strength). The 3:1 condition is, therefore, recommended as the preferred formulation for scale-up consideration in Table 2.

Table 2. Comparative summary of experimental conditions.

Parameter	Standard process (10:1)	Experimental (2:1)	Experimental (3:1)
Solvent: Pigment Ratio	10:1	2:1	3:1
Solvent Reduction	Baseline	80%	70%
ΔL^*	-0.05 ± 0.03	$+0.30 \pm 0.02$	-0.05 ± 0.02
Δa^*	$+0.05 \pm 0.02$	$+0.11 \pm 0.02$	$+0.05 \pm 0.01$
Δb^*	$+0.20 \pm 0.03$	$+1.41 \pm 0.02$	$+1.13 \pm 0.02$
ΔC^*	-0.17 ± 0.02	-1.29 ± 0.03	-1.02 ± 0.02
ΔH^*	-0.10 ± 0.02	-0.57 ± 0.02	-0.49 ± 0.02
ΔE^*	0.24 ± 0.01	1.44 ± 0.02	1.13 ± 0.02
% Strength	100.0 ± 0.3	95.01 ± 0.12	97.69 ± 0.12
Filtration Time (min)	12.2 ± 0.5	14.3 ± 0.4	13.1 ± 0.3
Press Cake Solids (%)	25.0 ± 0.5	27.2 ± 0.3	26.1 ± 0.3
D50 (μm)	0.35 ± 0.02	0.41 ± 0.02	0.38 ± 0.02

Note: *All values: mean \pm standard deviation (n = 3)*.

RESULTS AND DISCUSSION

Solvent Ratio Effects on Coloristic Performance

Total Color Difference (ΔE^*) Response Surface

The relationship between solvent ratio and ΔE^* exhibits a non-linear, approximately exponential decay pattern. Reducing solvent from 10:1 to 3:1 (70% reduction) increases ΔE^* from 0.24 to 1.13 – an absolute increase of 0.89 ΔE^* units. Further reduction from 3:1 to 2:1 (additional 10% reduction on

absolute scale) increases ΔE^* from 1.13 to 1.44 – an additional 0.31 ΔE^* units. The marginal deterioration accelerates as solvent is progressively removed.

This functional form suggests that solvent serves multiple roles with different concentration dependencies. At high solvent ratios ($\geq 5:1$), solvent is present in substantial excess relative to stoichiometric requirements for dissolution and crystal growth. Under these conditions, solvent reduction yields minimal quality impact. As solvent approaches a critical threshold (approximately 3:1 in this system), one or more solvent functions become limiting, and quality deterioration accelerates. Identification of this threshold is a principal contribution of this work.

The practical implication is unambiguous: 3:1 represents the optimal operating point. At this ratio, quality remains within commercial specifications for premium-grade pigment while achieving 70% solvent reduction. Operating at 2:1 would yield additional 10% solvent reduction but at the cost of unacceptable quality compromise for premium applications. For lower-tier applications with less stringent coloristic requirements, 2:1 might be considered, but this investigation recommends 3:1 as the primary target.

Differential Sensitivity of Coloristic Parameters

Individual coloristic parameters exhibit markedly different sensitivity to solvent reduction:

- *Low Sensitivity Parameters:* ΔL^* and Δa^* remained within specification across all tested conditions. Lightness/darkness (ΔL^*) actually improved from +0.30 at 2:1 to -0.05 at 3:1, essentially matching standard. Red/green balance (Δa^*) remained near zero throughout. These parameters are evidently robust to solvent variation, suggesting they are primarily determined by crude pigment quality and polymorphic identity rather than finishing conditions.
- *Moderate Sensitivity Parameters:* ΔH^* (hue deviation) increased from -0.10 (standard) to -0.57 (2:1) and -0.49 (3:1). While all values remain within specification, the shift is directionally consistent and statistically significant. This hue shift toward slightly greener shade likely reflects subtle alterations in crystal habit or particle morphology.
- *High Sensitivity Parameters:* Δb^* (yellow–blue balance) and %strength proved most sensitive to solvent reduction. Δb^* increased from +0.20 (standard) to +1.41 (2:1) and +1.13 (3:1). The +1.13 value at 3:1, while within specification, represents substantial shift relative to standard. %strength decreased from 100% to 95.0% at 2:1 – barely acceptable – and 97.7% at 3:1 – comfortably within specification.

The Mechanistic Interpretation

Δb^* sensitivity likely relates to particle size effects. Finer particles (higher surface area) scatter more short-wavelength (blue) light, appearing more blue (lower Δb). *Coarser particles scatter less blue light, appearing relatively yellower (higher Δb).* The modest particle size coarsening observed at reduced solvent ratios (D50: 0.35 \rightarrow 0.41 \rightarrow 0.38 μm) correlates directly with Δb^* progression. This relationship is well-established in pigment optics and consistent with our observations.

%strength sensitivity similarly correlates with particle size. Tinctorial strength in organic pigments is maximized at specific particle size ranges (typically 0.05–0.2 μm for transparent applications, 0.3–0.6 μm for opacity). Departure from optimum – in either direction – reduces effective color yield per gram of pigment. Our observed strength reduction at reduced solvent ratios (100% \rightarrow 95.0% \rightarrow 97.7%) is quantitatively consistent with the measured particle size shifts.

Comparison with Mechanochemical Approaches

The solid-state phthalocyanine synthesis reported by Hernández et al. achieved 99% conversion using catalytic DMAE ($\eta = 0.192 \mu\text{L} \cdot \text{mg}^{-1}$) at 100°C with 48-hour aging. This represents substantially greater solvent reduction ($\geq 99\%$) than achieved in our work (70–80%). However, critical distinctions warrant emphasis. The mechanochemical approach targeted tetra-tert-butyl phthalocyanine, a highly substituted

derivative with markedly different solubility and crystallization behavior than unsubstituted copper phthalocyanine. Additionally, the ball-milling/aging sequence, while elegant, required 48 hours at 100°C – longer than conventional solvent processes (2–6 hours). Finally, translation of mechanochemistry to 10-ton industrial batch scales presents formidable engineering challenges.

The process modifications require only revised operating procedures and operator training. This represents a complementary strategy to academic green chemistry initiatives: pragmatic, incremental improvement that delivers real-world environmental benefit today rather than potential benefit at uncertain future date.

Process Intensification and Operational Implications

Throughput and Productivity Impacts

Solvent reduction directly increases reactor volumetric productivity. At constant batch size (50 kg pigment equivalent), reducing solvent from 500 L to 150 L (3:1) reduces total batch volume by 64%. This translates to:

- 2.8-fold increase in reactor throughput capacity ($\text{kg pigment} \cdot \text{L}^{-1} \cdot \text{batch}^{-1}$).
- 64% reduction in solvent inventory requirement.
- 58% reduction in wastewater generation from solvent recovery operations.

For Blue 1 plant, with annual PB15:3 production capacity of approximately 2400 metric tons, Free substantial reactor capacity for additional production:

- Reduce annual solvent consumption by approximately 350,000 liters.
- Reduce effluent treatment plant organic load by approximately 180 tons COD equivalent.
- Reduce natural gas consumption for solvent recovery by approximately 4.2 million MJ annually.

These projections, while approximate pending full-scale validation, indicate substantial economic and environmental benefits.

Filtration and Dewatering Trade-offs

Reduced solvent ratio increased filtration time (12.2 → 13.1 minutes at 3:1; 12.2 → 14.3 minutes at 2:1). This penalty is expected: higher slurry solids concentration increases filter cake thickness and hydraulic resistance. However, the magnitude is modest (7–17% increase) and partially offset by higher press cake solids (25.0% → 26.1% → 27.2%). Higher press cake solids reduce drying energy requirements and drying time. Net energy impact (filtration + drying) is approximately neutral at 3:1 ratio.

Process Robustness and Operating Window

The 3:1 condition demonstrated excellent reproducibility (ΔE^* RSD = 1.8%, n=3). Process robustness – insensitivity to minor uncontrolled variations – appears adequate for routine manufacturing. However, the proximity to threshold behavior warrants caution. Should raw material quality fluctuate (e.g., crude pigment purity, particle size) or process control deviate (e.g., temperature, pH), the 3:1 condition may prove less forgiving than the highly over-solvated standard process. Comprehensive process capability studies during scale-up are recommended to establish appropriate control limits.

Mechanistic Interpretation: Solvent Functions in Pigment Finishing

Dissolution and Recrystallization

The conventional understanding posits that pigment finishing proceeds via dissolution of crude pigment in the solvent phase followed by recrystallization of the desired polymorph. This mechanism requires sufficient solvent to achieve meaningful pigment solubility. Our results suggest this dissolution–recrystallization pathway may not be the dominant mechanism at reduced solvent ratios.

Copper phthalocyanine exhibits limited solubility (<0.1% w/w) in aromatic hydrocarbon solvents at 90°C. At 10:1 solvent ratio, maximum dissolved pigment concentration is approximately 0.5 g·L⁻¹ – insignificant relative to total pigment loading (100 g·L⁻¹). Complete dissolution–recrystallization would require far longer times than the 2-hour finishing period.

We propose an alternative mechanism: solvent-enhanced solid-state transformation. At finishing temperature (90°C, approaching the $\alpha \rightarrow \beta$ transition temperature of approximately 200°C but far below), the metastable α -phase crystallites possess sufficient thermal energy for solid-state polymorphic conversion. However, conversion kinetics are slow without solvent assistance. Solvent adsorbed on crystal surfaces reduces interfacial energy, increases molecular mobility at crystal surfaces, and lowers activation energy for nucleation of β -phase. This mechanism operates at solvent concentrations far below those required for bulk dissolution.

This interpretation explains our experimental observations: (i) substantial solvent reduction is possible because only surface-adsorbed solvent (not bulk dissolution) is required; (ii) a threshold exists below which insufficient surface coverage slows conversion kinetics; (iii) particle size coarsening occurs because some dissolution–reprecipitation contributes at higher solvent concentrations, which is suppressed at lower concentrations.

Heat Transfer and Fluid Dynamics

An additional solvent function – often overlooked – is heat transfer medium. The finishing process requires maintaining 88–90°C for 2 hours. At reduced solvent ratios, slurry heat capacity per unit volume decreases, and thermal gradients between reactor wall and bulk fluid increase. Our observations of modest temperature control challenges at 2:1 ratio support this interpretation. The 3:1 condition provided adequate thermal mass for stable temperature control.

Rheological Mediation

Solvent reduces slurry viscosity, enabling effective mixing. Our torque measurements confirmed elevated apparent viscosity at reduced solvent ratios. At 2:1 ratio, viscosity approached the upper practical limit for the laboratory reactor. At 3:1 ratio, viscosity was acceptable. Plant-scale reactors with different agitation systems may exhibit different viscosity tolerance; this must be evaluated during scale-up.

Environmental and Economic Assessment

Process Mass Intensity (PMI) Analysis

PMI – total mass input per mass product – is a widely accepted metric for process environmental performance. For standard PB15:3 finishing in Table 3.

Table 3. Material Input and process mass intensity (PMI) for pigment production.

Input	Mass per kg pigment (kg)
Crude CPC	1.05
Sulfuric acid	8.00
Solvent (HBS-23)	8.50
Surfactant	0.05
Sodium hydroxide	0.30
Water	35.0
Total Input	52.9
Product	1.00
PMI	52.9 kg·kg ⁻¹

At 3:1 solvent ratio, solvent input reduces from 8.50 kg to 2.55 kg per kg pigment. Water input reduces proportionally (washing water optimization). Revised PMI in Table 4:

Table 4. Optimized material input and process mass intensity (PMI) for pigment production.

Input	Mass per kg pigment (kg)
Crude CPC	1.05
Sulfuric acid	8.00
Solvent (HBS-23)	2.55
Surfactant	0.05
Sodium hydroxide	0.30
Water	21.0
Total Input	33.0
Product	1.00
PMI	33.0 kg·kg ⁻¹

PMI reduction: 52.9 → 33.0 (37.6% improvement). This substantial reduction places PB15:3 finishing in a more favorable sustainability position.

VOC Emissions and Carbon Footprint

Solvent reduction directly reduces VOC emissions. Assuming 98% solvent recovery efficiency standard process emits 0.17 kg VOC per kg pigment (8.50 kg × 2% loss). At 3:1 ratio, emissions reduce to 0.05 kg VOC per kg pigment – 71% reduction.

Carbon footprint reduction derives primarily from reduced natural gas consumption for solvent recovery distillation. Preliminary calculation: solvent recovery requires approximately 12 MJ·kg⁻¹ recovered solvent (steam generation, pumping, condensation). Annual solvent reduction of 350,000 liters (approximately 315,000 kg) avoids 3.78 million MJ natural gas consumption, equivalent to approximately 215 metric tons CO₂ emissions avoided annually at this single facility.

Economic Value Creation

At current HBS-23 solvent pricing (₹145/L ≈ \$1.74/L), annual solvent purchase cost reduction: 350,000 L × ₹145 = ₹50.75 million (≈\$610,000). Reduced effluent treatment cost adds additional savings: approximately ₹8.2 million (≈\$98,000) annually. Total direct cost savings: approximately ₹59 million (≈\$708,000) per year for Blue 1 plant alone.

These savings are achieved with zero capital investment. The only implementation costs are process development (sunk), revised documentation, operator training, and scale-up validation trials. Payback period: immediate upon implementation.

Limitations and Future Research Directions

Experimental Limitations

This investigation, while systematic and reproducible, possesses inherent limitations. Laboratory scale (50 g pigment) differs substantially from manufacturing scale (500–2000 kg pigment). Scale-up effects on heat transfer, mixing intensity, and filtration behavior cannot be fully predicted from laboratory data. Pilot-scale confirmation (minimum 100 kg batch size) is essential prior to full-scale implementation.

The experimental design examined only one factor (solvent ratio) while holding other parameters constant. Interactions between solvent ratio and other process variables (temperature, time, surfactant concentration, pH) were not explored. Factorial experimental designs in subsequent investigations may identify synergistic combinations enabling further optimization.

Generalizability to Other Pigment Systems

PB15:3, while commercially important, represents one member of the phthalocyanine family. PB15:1 (alpha-phase, red-shade blue), PB15:2 (alpha-phase, stabilized), PB15:4 (beta-phase, anti-

flocculating), and PB15:6 (epsilon-phase) utilize similar finishing processes but with modified conditions. Solvent reduction opportunities in these variants may differ. PG7 and PG36 (phthalocyanine greens) employ fundamentally different manufacturing processes (direct chlorination/bromination of CPC) and were not examined. Extension of this work to other pigment chemistries requires separate investigation.

Long-Term Stability and Customer Qualification

Customer acceptance of solvent-reduced pigment requires more extensive validation than conducted in this study. Individual customers maintain approved product specifications and may require formal re-qualification programs involving extended field trials. Some applications – particularly automotive OEM coatings and food contact materials – have extended approval cycles (12–24 months). Implementation timeline must accommodate these requirements.

CONCLUSION

This investigation established a systematic framework for solvent optimization in industrial PB15:3 pigment finishing, yielding both fundamental mechanistic insights and immediately actionable manufacturing guidance. The principal findings and their implications are summarized below.

Principal Scientific Contributions

This work provides the first published quantitative relationship between solvent loading and finished pigment quality attributes for copper phthalocyanine PB15:3. The relationship exhibits threshold behavior: substantial solvent reduction (70%) is achievable with modest, commercially acceptable quality compromise, while further reduction (80%) leads to borderline performance. This threshold occurs at approximately 3:1 solvent: pigment ratio under the investigated conditions.

The differential sensitivity of coloristic parameters was elucidated: ΔL^* and Δa^* are robust to solvent variation; ΔH^* exhibits moderate sensitivity; Δb^* and %strength are highly sensitive, with deterioration correlating to modest particle size coarsening. This differential sensitivity enables targeted optimization – sacrificing less-critical attributes to preserve essential performance.

Mechanistic interpretation suggests that solvent functions primarily through surface adsorption and crystal boundary wetting rather than bulk dissolution. This understanding challenges conventional assumptions and opens opportunities for further solvent reduction through surface-active additives or process intensification.

Practical Manufacturing Recommendations

Based on the experimental evidence, we recommend:

- Immediate implementation of 3:1 solvent ratio for PB15:3 finishing condition delivers:
 - $\Delta E^* \leq 1.2$, %strength $\geq 97.5\%$.
 - 70% reduction in solvent consumption.
 - 37.6% reduction in process mass intensity.
 - Annual cost savings estimated at ₹59 million ($\approx \$708,000$).

Retention of 2:1 ratio as contingency option for non-premium applications or periods of solvent supply constraint, with appropriate customer communication regarding modified coloristic specifications.

- Initiation of formal scale-up protocol comprising:
 - 100 kg pilot batch validation (Blue 1 plant).
 - Extended process capability study (minimum 20 batches).
 - Customer qualification samples distribution.
 - Revised standard operating procedure development.
 - Operator training program.

Broader Implications for Sustainable Chemical Manufacturing

This investigation demonstrates that substantial sustainability improvements can be achieved through systematic process optimization within existing manufacturing infrastructure. The tendency within both academic research and corporate R&D to pursue transformational technology breakthroughs, while valuable, should not obscure the significant cumulative benefit of incremental process intensification across multiple unit operations and product lines.

The methodology employed – systematic parameter variation, comprehensive response characterization, mechanistic interpretation, and economic/environmental assessment – provides a template applicable to numerous other pigment finishing processes. Extension to PB15:1, PB15:4, and selected azo pigment chemistries is already underway.

Final Remarks

The chemical industry stands at an inflection point. Stakeholder expectations regarding environmental performance escalate continuously; regulatory requirements tighten inexorably; customer sustainability commitments propagate through supply chains with increasing rigor. Simultaneously, economic pressures demand continuous productivity improvement. These forces, often portrayed as conflicting, can be reconciled through technically grounded, systematically executed process optimization.

This work contributes to that reconciliation. It demonstrates – with concrete experimental evidence, rigorous analytical characterization, and commercially relevant quality assessment – that substantial environmental footprint reduction and substantial cost reduction can be achieved simultaneously. No trade-off; no compromise; no regulatory exemption required. Just competent chemical engineering applied to an important industrial process.

The path to sustainable chemical manufacturing is not a single giant leap but many incremental steps. This investigation represents one such step. We commend it to the scientific community and to our industry colleagues as both practical contribution and methodological example.

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