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Non-additive Stabilization of Aqueous Alumina Suspensions by Binary Peg-Ester Dispersants: Composition Dependence, Phase Partitioning and Ph Response

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ABSTRACT

Background: Stable aqueous alumina suspensions depend strongly on the molecular architecture and relative proportion of adsorbing dispersants.

Methods: Two polyethylene-glycol (PEG) esterification-product families were investigated: an acrylic-acid/PEG product (X) and a citric-acid/PEG product (Y).

Results: Orthogonal screening identified X9 and Y7 as the best-performing individual products, giving 24 h phase-separation indices (PSI₂₄) of 9.0% and 11.8%, respectively, compared with 30% for citric acid and 58% for the additive-free suspension. Binary blending produced a pronounced non-additive composition response. At a fixed total dispersant content of 1 wt%, the 60/40 X/Y formulation reached PSI₂₄ = 5.3%, corresponding to a 41.1% reduction relative to X9 and a 47.6% reduction relative to the linear-mixture expectation. The favorable response extended across a broad composition interval, with blends containing 20-80% X outperforming X9. Phase partitioning showed that the improvement was governed primarily by suppression of clarification: at 60/40, the clear-supernatant fraction decreased to 5.00% while the compact-sediment fraction remained at 0.25%, increasing the retained-suspension fraction to 94.75%. The optimized blend also exhibited a pronounced near-neutral pH response, with PSI₂₄ = 5.0% at pH 6 and values no higher than 6.3% over pH 5-7. The composition and pH dependences are consistent with complementary carboxylate adsorption, charge regulation, competitive surface occupation, and PEG-mediated steric hydration.

Conclusion: These results demonstrate that binary PEG-ester dispersants can generate composition-specific stabilization substantially exceeding the performance expected from simple endpoint averaging.

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Introduction

Aqueous colloidal processing is central to the fabrication of dense and defect-controlled ceramic bodies because the particle arrangement established in the suspension is transmitted, with varying degrees of rearrangement, through shaping, drying and sintering. Poor dispersion promotes agglomeration, non-uniform packing and differential shrinkage, whereas a well-dispersed feedstock facilitates high solids loading, controlled flow and more homogeneous green microstructures. These considerations apply to conventional slip casting and tape casting as well as to direct ink writing, robocasting and vat photopolymerization. Recent studies on alumina and alumina-containing systems illustrate how strongly modern shaping routes depend on slurry formulation: dispersant selection alters rheology and printability in direct ink writing bio-based additive packages modify the flow behavior of aqueous alumina tape-casting slurries and particle-level interactions determine solid loading and self-leveling in UV-curable alumina suspensions. High-solid formulations reported for robocasting, stereolithography and vat photopolymerization now span approximately 50-65 vol% ceramic solids while an

alumina stereolithography study published in 2026 screened 68 wt% suspensions before processing an 80 wt% slurry. These developments make the control of particle-particle and particle-additive interactions a primary formulation problem rather than a secondary processing adjustment.

Alumina is especially sensitive to solution chemistry because hydrated surface Al-OH groups are amphoteric. Protonation and deprotonation alter the net surface charge as pH changes, and adsorbed anions or polymers can shift the isoelectric region away from that of the bare powder. As a consequence, the same alumina can move among strongly flocculated, weakly structured and highly dispersed states when pH, ionic strength, dispersant dose or polymer conformation changes. In concentrated slurries these changes are amplified by crowding, so modest variations in the interparticle potential can produce large changes in viscosity, yield stress, thixotropy and sedimentation. Recent measurements have directly connected slurry pH with zeta potential, dispersant/binder adsorption and rheology and oscillatory rheology has been used to distinguish sterically stabilized, bridging-flocculated and

depletion-flocculated ceramic suspensions Time is also important: adsorption of ammonium polyacrylate and the corresponding particle state in aqueous alumina slurries can evolve during storage while rheophysical analysis of fine alumina suspensions shows that Brownian, colloidal and hydrodynamic forces contribute differently as solids loading and flow conditions change [1-12].

Macroscopic phase separation integrates the cumulative consequences of particle aggregation, hindered settling, network formation, and sediment compaction over a defined observation period. In alumina suspensions, the clear supernatant and compact sediment represent two distinct manifestations of destabilization, while the intervening particle-containing phase reflects the fraction retained in suspension. Resolving these regions separately therefore provides a useful formulation-level description of how a dispersant modifies the separation pathway. Earlier studies combining sedimentation, electrokinetic, and adsorption measurements have likewise shown that macroscopic dispersion behavior of alumina responds sensitively to changes in surface charge and polymer adsorption [13-15].

Polymeric dispersants are effective because one molecular architecture can contribute several stabilizing interactions. Carboxylate-bearing polyacrylates and polymethacrylates adsorb strongly on hydroxylated alumina and can generate electrostatic and steric repulsion PEG-containing segments add a strongly hydrated, water-compatible component that can protrude into the liquid phase and contribute steric exclusion when sufficiently anchored. A PAA-b-PEG-b-PAA triblock copolymer, for example, produced lower viscosity, larger-magnitude negative zeta potential and improved alumina dispersion compared with PEG or sodium polyacrylate alone, an effect attributed to electrosteric stabilization Sulfonated tannin layers on alpha-alumina have similarly been shown to combine a steric barrier with an electrostatic double-layer contribution [16-20].

Systematic AMPS-MPEG studies further demonstrate that ionic-group fraction, PEG segment length and copolymer architecture affect adsorption, electrokinetics and rheology, and high-solids comparisons among poly (acrylic acid), lignosulfonate and comb polymers indicate that efficient alumina stabilization can depend on the balance between electrostatic and steric forces.

The affinity of polymer functional groups for alumina is not uniform. Poly (acrylic acid) can adsorb with high affinity, and its adsorption density decreases as pH increases while increasing with polymer molecular weight [21-25].

By contrast, nonionic PEG interacts more weakly with alumina in direct comparisons, whereas carboxyl-containing polymers exert a much stronger effect on surface charge and suspension stability Competitive adsorption can therefore be highly asymmetric. In mixed PEG/ammonium poly(methacrylate) systems, the polyelectrolyte strongly suppresses PEG adsorption but PEG has much less influence on polyelectrolyte uptake A related alumina study showed that the sequence and conformation of adsorbed PAA/SDS mixtures can determine whether the suspension disperses or flocculates Although these model systems are chemically different from the X/Y formulation, they establish a general principle: when two additive populations share the same oxide interface, the suspension response need not be the arithmetic average of their individual responses.

Low-molecular-weight multicarboxylic species provide another relevant reference for the Y family. Citric acid adsorbs directly

on alumina through carboxylate-containing surface complexes, changes electrophoretic mobility and shifts the isoelectric point; both adsorption and the rheological response vary strongly with pH and concentration [26-29].

Other small or polymeric carboxyl-containing dispersants also show non-monotonic dose or pH optima. Poly (maleic acid) effectively disperses concentrated aqueous alumina only within an appropriate dose-pH region ascorbic acid can lower the viscosity of concentrated alumina nanopowder suspensions through surface complexation, and recent polishing-slurry work shows that increasing the number of carboxyl groups in a complexing agent does not produce monotonic improvement These observations are relevant to a citric-acid/PEG esterification product because esterification changes the number, accessibility and spatial distribution of carboxyl functions while introducing a PEG-rich solvated segment [30-32].

The synthesis history of PEG-acrylate esterification products is also relevant to dispersion performance. Independent analytical studies have shown that PEG/acrylic-acid esterification can produce coexisting monoester and diester species, and the relative proportion of these products influences the performance of related polycarboxylate systems Reaction time, temperature, catalyst loading, and PEG molecular mass can therefore modify the molecular population presented to the alumina surface and, in turn, alter adsorption, hydration, and interparticle stabilization. This relationship provides a physicochemical basis for linking synthesis conditions with the measured suspension response Accordingly, the present study investigates how synthesis conditions, binary composition, and pH govern the macroscopic stability of alumina suspensions containing acrylic-acid/PEG and citric-acid/PEG esterification products. The analysis focuses on the composition-dependent deviation from linear mixing, the evolution of clear-supernatant and compact-sediment fractions, and the physicochemical basis of the stability maximum observed near neutral pH [33-35].

Experimental Materials And Synthesis Scope

Polyethylene glycol with nominal relative molecular masses of 400, 800, and 1000, acrylic acid, citric acid, p-toluenesulfonic acid (p-TSA), hydroquinone, toluene, acidic alumina powder, hydrochloric acid, sodium hydroxide, and deionized water were used. PEG 400, PEG 1000, acrylic acid, and citric acid were supplied by Tianjin Beilian Fine Chemicals Development Co., Ltd.; PEG 800, p-TSA, and hydroquinone were supplied by Tianjin Guangfu Fine Chemical Research Institute; and toluene was supplied by Wuhan Organic Synthesis Chemical Plant.

For X synthesis, acrylic acid and PEG were reacted at a molar ratio of 1.2:1 using p-TSA as catalyst, hydroquinone at 0.5 wt% of the combined acid/alcohol mass as polymerization inhibitor, and toluene as water-carrying solvent. The L9 design varied reaction time (3, 4 or 5 h), temperature (115, 125 or 135 °C), PEG molecular mass (400, 800 or 1000), and p-TSA concentration (0.5, 1.0 or 1.5 wt%). For Y synthesis, citric acid and PEG were reacted at a molar ratio of 1.2:1 with the same inhibitor and solvent system; the L9 factors were reaction time (4, 5 or 6 h), temperature (120, 125 or 130 °C), PEG molecular mass (400, 800 or 1000), and p-TSA concentration (0.8, 1.0 or 1.2 wt%). These esterification routes were consistent with established preparation procedures for PEG-containing acrylate and citrate derivatives [36].

For clarity, the acrylic-acid/PEG esterification products are denoted X and the citric-acid/PEG esterification products are denoted Y throughout. This notation reflects the two synthesis families used in the formulation study and allows their synthesis-response and binary-mixing behavior to be compared consistently.

Table 1: Factors and Levels Used in the L9 Synthesis Screens

Product	Factor	Level 1	Level 2	Level 3
X	Reaction time (h)	3	4	5
X	Temperature (°C)	115	125	135
X	PEG nominal Mr	400	800	1000
X	p-TSA (wt%)	0.5	1.0	1.5
Y	Reaction time (h)	4	5	6
Y	Temperature (°C)	120	125	130
Y	PEG nominal Mr	400	800	1000
Y	p-TSA (wt%)	0.8	1.0	1.2

Preparation of Alumina Suspensions and Macroscopic Stability Metric

Alumina and deionized water were combined at a mass ratio of 1:5. For individual-dispersant tests, 10 g alumina, 50 mL deionized water and 0.6 g dispersant were placed in a 250 mL beaker, corresponding to a nominal dispersant fraction of 1 wt% based on the combined mass of alumina and water. The suspensions were mechanically stirred for 1 h. A 40 mL aliquot from the upper suspension was transferred to a 50 mL graduated cylinder and allowed to stand quiescently for 24 h. The volumes of clear supernatant (V1), compact sediment (V2) and intermediate suspension (V3) were then recorded.

The 24 h phase-separation index (PSI24) was calculated as:

$$\text{PSI24 (\%)} = 100 \times (V1 + V2) / (V1 + V2 + V3)$$

PSI24 represents the fraction of the observation column that separated into a clear-supernatant region or a compact-sediment region after 24 h. Lower PSI24 therefore corresponds to greater retention of the particle-containing intermediate suspension under the specified test conditions.

The three phase regions were also normalized individually as $C24 = 100V1 / (V1 + V2 + V3)$ for the clear-supernatant fraction, $S24 = 100V2 / (V1 + V2 + V3)$ for the compact-sediment fraction, and $R24 = 100V3 / (V1 + V2 + V3)$ for the retained-suspension fraction. Accordingly, $\text{PSI24} = C24 + S24 = 100 - R24$.

Binary Formulation and pH Experiments

The best-performing screened products, X9 and Y7, were used for binary formulation. At a constant total dispersant content of 1 wt%, the X fraction was varied from 0.1 to 0.9 wt% and the Y fraction from 0.9 to 0.1 wt%, maintaining $X + Y = 1$ wt%. Suspension preparation and the 24 h standing protocol were unchanged. For the pH series, the best binary formulation (0.6 wt% X + 0.4 wt% Y) was adjusted to pH 2-10 using hydrochloric acid or sodium hydroxide before the same 1 h mixing and 24 h settling procedure.

Data Analysis

Orthogonal-array effects were evaluated by level-average range analysis. For each factor, the range Rmean was calculated as the difference between the largest and smallest level-average PSI24 value. This analysis was used to compare the relative sensitivity of suspension performance to reaction time, temperature, PEG molecular mass, and p-TSA concentration within each synthesis family.

Binary composition was analyzed using two mixture descriptions. Let x denote the mass fraction of X in the binary dispersant and $(1-x)$ the fraction of Y. The linear-mixture expectation was defined as $\text{PSI}_{\text{linear}} = 9.0x + 11.8(1-x)$, using the measured X9 and Y7 endpoint values, and the relative non-additive benefit was calculated as $100(\text{PSI}_{\text{linear}} - \text{PSI}_{\text{observed}}) / \text{PSI}_{\text{linear}}$. The composition response, including the two individual endpoints, was also represented by the constrained quadratic Scheffé form $\text{PSI} = 9.0x + 11.8(1-x) + b x(1-x)$. The pH response of the 60/40 formulation was evaluated from the measured PSI24 and phase-fraction profiles over pH 2-10.

Results and Discussion

Single-Agent Screening: Performance Envelope and Synthesis-Variable Sensitivity

The two L9 screens generated broad but distinct performance envelopes. The nine X products produced PSI24 values from 9.0% to 34.5%, whereas the nine Y products ranged from 11.8% to 26.3%. X9 was the best observed X condition at 9.0% and Y7 the best Y condition at 11.8%. Both values were substantially below the 30% measured for citric acid and the 58% of the additive-free suspension. Expressed against the blank, X9 and Y7 reduced the separated fraction by 84.5% and 79.7%, respectively, while citric acid alone reduced it by 48.3%. The PEG-containing esterification products therefore provided a large macroscopic stabilization increment relative to their small-molecule acid precursor under the common 24 h test.

Table 2: L9 Level Means for PSI24 (% , Lower is Better)

Series	Factor	Level 1 mean	Level 2 mean	Level 3 mean	Rmean	Rank within series
X	Time	22.17	21.87	16.37	5.80	3
X	Temperature	19.70	19.93	20.77	1.07	4
X	PEG Mr	18.03	17.27	25.10	7.83	2
X	p-TSA	15.00	18.53	26.87	11.87	1
Y	Time	19.33	20.43	19.03	1.40	4
Y	Temperature	16.60	20.10	22.10	5.50	3
Y	PEG Mr	16.50	22.10	20.20	5.60	2
Y	p-TSA	21.87	14.77	22.17	7.40	1

Range analysis showed distinct synthesis-response patterns for the two product families. For X, the sensitivity sequence was p-TSA concentration > PEG molecular mass > reaction time > temperature. The p-TSA level average increased from 15.00% at 0.5 wt% to 18.53% at 1.0 wt% and 26.87% at 1.5 wt%, showing a progressive deterioration in suspension performance as catalyst loading increased across the screened interval. PEG molecular mass produced a non-monotonic response, with the lowest average at PEG 800 (17.27%), followed by PEG 400 (18.03%) and PEG 1000 (25.10%). Reaction time favored the 5 h level (16.37%) over 3 and 4 h (22.17% and 21.87%), whereas temperature varied over a comparatively narrow range. Thus, catalyst loading and PEG grade exerted the strongest influence on the X-family dispersion response.

The Y family exhibited a different response profile. The sensitivity sequence was p-TSA concentration > PEG molecular mass > temperature > reaction time. Catalyst loading showed a pronounced minimum at the intermediate level: the average PSI24 values were 21.87%, 14.77%, and 22.17% at 0.8, 1.0, and 1.2 wt% p-TSA, respectively. Increasing temperature from 120 to 130 °C was accompanied by an increase in the level average from 16.60% to 22.10%. PEG molecular mass was again non-monotonic, with averages of 16.50%, 22.10%, and 20.20% for PEG 400, 800, and 1000, respectively, while reaction time showed the smallest variation. The two esterification systems therefore shared strong sensitivity to catalyst loading but differed in the position and shape of their optimum synthesis region.

Confirmation experiments further emphasized the importance of factor combination. For X, the level-average combination 5 h/115 °C/PEG 800/0.5 wt% p-TSA gave PSI24 = 10.0%, whereas X9 at 5 h/135 °C/PEG 800/0.5 wt% p-TSA reached 9.0%. For Y, the level-average combination 6 h/120 °C/PEG 400/1.0 wt% p-TSA gave 12.5%, compared with 11.8% for Y7 at 6 h/120 °C/PEG 1000/1.0 wt% p-TSA. The lowest phase separation was therefore associated with specific combinations of synthesis variables rather than with independent optimization of each factor in isolation.

This synthesis sensitivity is consistent with the chemistry of PEG esterification products. In related PEG/acrylic-acid systems, monoester and diester species coexist and their relative abundance changes with reaction conditions variations in ester composition

also affect the performance of polycarboxylate formulations derived from such products. Changes in catalyst loading, PEG molecular mass, reaction time, and temperature can therefore alter the balance of anchoring carboxyl groups and hydrated PEG segments presented to the oxide surface. The distinct factor-response profiles of X and Y support a direct connection between synthesis history and dispersion performance. X9 and Y7, which gave the lowest PSI24 values within their respective families, were used for the binary formulation study [33-35].

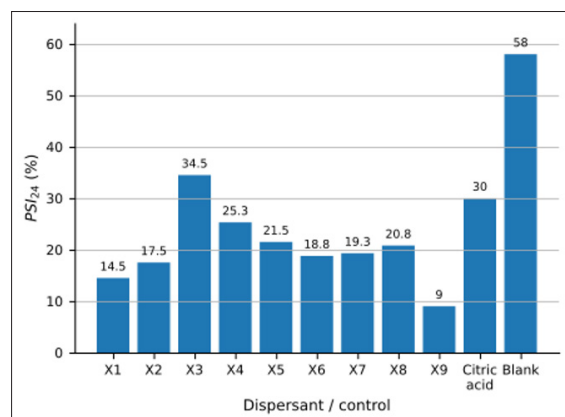


Figure 1: PSI24 for the Nine X Synthesis Products, Citric-Acid Control and Additive-Free Suspension

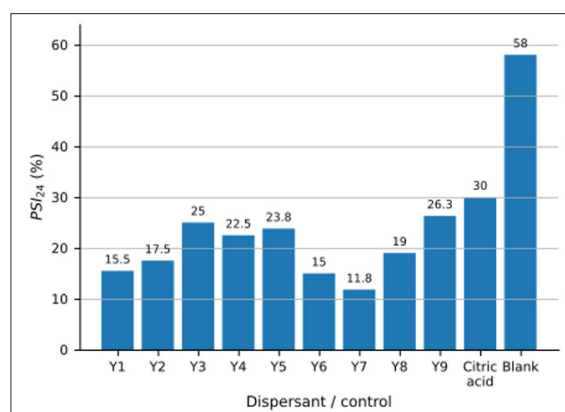


Figure 2: PSI24 for the Nine Y Synthesis Products, Citric-Acid Control and Additive-Free Suspension

Table 3: Best Individual-Dispersant and Control Results

System	Selected condition / identity	PSI24 (%)	Reduction vs blank (%)
Blank	No dispersant	58.0	-
Citric acid	1 wt%	30.0	48.3
X9	5 h; 135 °C; PEG 800; 0.5 wt% p-TSA	9.0	84.5
Y7	6 h; 120 °C; PEG 1000; 1.0 wt% p-TSA	11.8	79.7

Binary Composition Generates a Finite and Asymmetric Non-Additive Response

At a fixed total dispersant content of 1 wt%, PSI24 varied non-monotonically with X/Y composition. The value decreased from 9.3% at 10/90 X/Y to 5.3% at 60/40 and then increased to 9.8% at 90/10. The 60/40 formulation reduced PSI24 by 41.1% relative to X9 and by 55.1% relative to Y7. The favorable response extended over a broad composition interval: blends containing 20-80% X all exhibited lower PSI24 than X9, and the 40-70% X region remained below 7%. The minimum at 60/40 is therefore part of a finite low-separation composition window rather than an isolated formulation point.

Table 4: X/Y Composition Response and Deviation from the Linear-Mixture Expectation

X/Y mass ratio (%)	Observed PSI24 (%)	Linear expectation (%)	Non-additive benefit (%)
10/90	9.3	11.52	+19.3
20/80	8.3	11.24	+26.2
30/70	7.3	10.96	+33.4
40/60	6.8	10.68	+36.3
50/50	6.0	10.40	+42.3
60/40	5.3	10.12	+47.6
70/30	6.5	9.84	+33.9
80/20	7.8	9.56	+18.4
90/10	9.8	9.28	-5.6

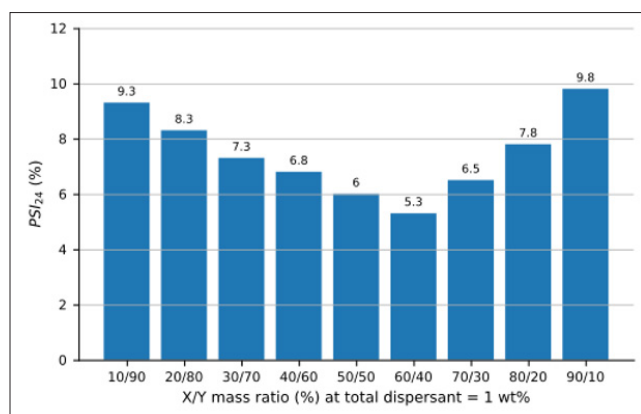


Figure 3: Composition Dependence of PSI24 for X/Y Blends at a Fixed Total Dispersant Content of 1 wt%

Comparison with the linear-mixture baseline demonstrates the non-additive nature of the binary response. If X9 and Y7 contributed independently in direct proportion to their mass fractions, PSI24 would vary gradually between the two endpoint values. Instead, every blend from 10 to 80% X fell below the linear expectation. The relative non-additive benefit increased from 19.3% at 10% X to 42.3% at 50% X, reached 47.6% at 60% X, and remained substantial at 70% X (33.9%) and 80% X (18.4%). At 90% X, the deviation became slightly unfavorable (-5.6%). The response therefore contains a broad favorable-mixing domain centered on an intermediate X fraction and a distinct X-rich region in which the benefit of binary blending diminishes.

The constrained quadratic Scheffé model yielded an interaction coefficient $b = -16.69$ percentage points ($R^2 = 0.825$) and placed the fitted minimum at $x = 0.584$, in close agreement with the

experimental 60% X optimum. The measured composition profile also displayed clear asymmetry around this minimum. At equal composition offsets, the X-rich side consistently gave higher PSI24: 70/30 versus 50/50 gave 6.5% versus 6.0%; 80/20 versus 40/60 gave 7.8% versus 6.8%; and 90/10 versus 30/70 gave 9.8% versus 7.3%. Thus, the Y-rich side of the low-separation region exhibits greater composition tolerance than the corresponding X-rich side.

The asymmetric response is consistent with non-equivalent occupation of the alumina interface by the two product populations. Competitive adsorption studies on alumina have shown that strongly adsorbing carboxylate polyelectrolytes can suppress the adsorption of weaker PEG species while sequential or mixed adsorption of polymers and surfactants can reorganize the interfacial layer and alter dispersion behavior. Such effects provide a physicochemical basis for the observed high-X penalty: the most favorable bulk composition can correspond to an interfacial population in which anchoring carboxylate groups and hydrated PEG segments are balanced more effectively than at either composition extreme.

Phase Partitioning Identifies Selective Suppression of Clarification

Phase partitioning revealed that the binary improvement was governed primarily by suppression of clarification. For X9, $C_{24} = 8.75\%$, $S_{24} = 0.25\%$, and $R_{24} = 91.0\%$; Y7 gave $C_{24} = 11.25\%$, $S_{24} = 0.50\%$, and $R_{24} = 88.25\%$. At the 60/40 binary optimum, C_{24} decreased to 5.00% while S_{24} remained at 0.25%, increasing R_{24} to 94.75%. Relative to X9, the 3.7-percentage-point decrease in PSI24 therefore arose almost entirely from the reduction of the clear-supernatant region.

Table 5: Partition of the 24 H Observation Column Across The X/Y Composition Series

The phase-fraction trajectory across composition reinforces this result. C24 decreased from 8.00% at 10% X to 5.00% at 60% X and then increased to 8.50% at 90% X. S24 showed a shallower minimum, reaching 0.25% at both 50/50 and 60/40 and rising to 1.25% at the two outer measured compositions. Consequently, R24 reached 94.0-94.75% at 50-60% X. Clarification accounted for approximately 86-96% of the total separated volume across the blend series, showing that the curvature of PSI24 is controlled principally by clear-layer formation, with compact sedimentation providing a smaller secondary contribution.

At 60/40, the binary formulation combined the minimum compact-sediment fraction observed for X9 with a 42.9% reduction in clear-supernatant fraction relative to X9. The retained-suspension fraction consequently increased from 91.0% to 94.75%. The composition benefit is therefore expressed not only as a lower total separated fraction but specifically as enhanced retention of the particle-containing intermediate phase, which is the dominant macroscopic signature of improved suspension stability in this system.

The outer compositions showed the reverse trend. Moving away from 60/40 toward either component increased both clarification and, to a lesser extent, compact sedimentation. The change was stronger on the X-rich side: from 60/40 to 90/10, C24 increased from 5.00% to 8.50% and S24 from 0.25% to 1.25%, whereas at 30/70 the corresponding values were 6.50% and 0.75%. The phase-resolved response therefore confirms the composition asymmetry observed in PSI24 and identifies clear-layer development as its principal contribution.

System / X:Y	C24 clear (%)	S24 compact sediment (%)	R24 retained suspension (%)	Reported PSI24 (%)
Y7 / 0:100	11.25	0.50	88.25	11.8
10:90	8.00	1.25	90.75	9.3
20:80	7.50	0.75	91.75	8.3
30:70	6.50	0.75	92.75	7.3
40:60	6.25	0.50	93.25	6.8
50:50	5.75	0.25	94.00	6.0
60:40	5.00	0.25	94.75	5.3
70:30	6.00	0.50	93.50	6.5
80:20	6.75	1.00	92.25	7.8
90:10	8.50	1.25	90.25	9.8
X9 / 100:0	8.75	0.25	91.00	9.0

Ph Defines a Near-Neutral Stability Basin and Alters Phase Partitioning

The 60/40 X/Y formulation exhibited a pronounced basin-shaped dependence on pH. PSI24 decreased from 15.0% at pH 2 to 11.5% at pH 3 and 10.3% at pH 4, fell to 6.3% at pH 5, and reached a minimum of 5.0% at pH 6. The value then increased to 6.0%, 8.3%, 10.5%, and 12.3% at pH 7-10. A second-order fit gave $R^2 = 0.932$ and a vertex at pH 6.30, consistent with the experimentally observed near-neutral optimum. The pH 5-7 interval was comparatively flat, with only 1.3 percentage points separating its highest and lowest PSI24 values, indicating a practical stability window around neutrality.

Table 6: Effect of Ph on Psi24 and the Partition of the 24 h Observation Column

pH	C24 clear (%)	S24 compact sediment (%)	R24 retained suspension (%)	Reported PSI24 (%)
2	13.00	2.00	85.00	15.0
3	10.00	1.50	88.50	11.5
4	9.00	1.25	89.75	10.3
5	5.50	0.75	93.75	6.3
6	4.50	0.50	95.00	5.0
7	5.00	1.00	94.00	6.0
8	7.00	1.25	91.75	8.3
9	8.75	1.75	89.50	10.5
10	10.75	1.50	87.75	12.3

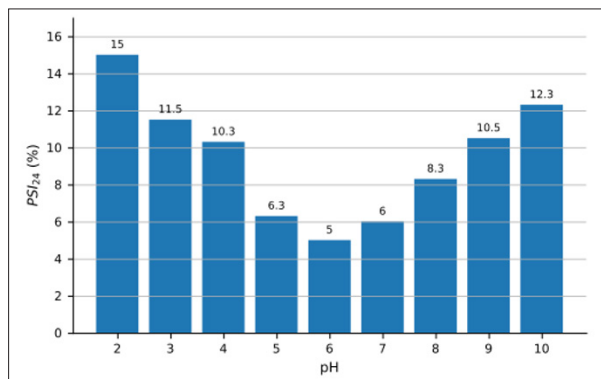


Figure 4: Ph Dependence of Psi24 for the 60/40 x/y Formulation

The pH response was asymmetric around the minimum. At equal distances from pH 6, the acidic condition consistently produced the same or a larger separated fraction than the alkaline counterpart: 6.3% at pH 5 versus 6.0% at pH 7; 10.3% at pH 4 versus 8.3% at pH 8; 11.5% at pH 3 versus 10.5% at pH 9; and 15.0% at pH 2 versus 12.3% at pH 10. The acidic-side penalty therefore exceeded the alkaline-side penalty, indicating that the stability basin reflects the combined pH dependence of alumina surface chemistry and ionizable dispersant groups rather than a simple symmetric response to distance from neutrality.

The phase fractions followed the same pH dependence. At pH 6, C24 = 4.50%, S24 = 0.50%, and R24 = 95.0%. At pH 2, C24 and S24 increased to 13.0% and 2.0%, reducing R24 to 85.0%; at pH 10 they reached 10.75% and 1.50%, with R24 = 87.75%. The near-neutral minimum therefore corresponds to simultaneous suppression of both clarification and compact sedimentation, while the stronger acidic deterioration is expressed in both separated regions. The pH-6 state is dominated by a low clear-supernatant fraction, confirming clarification control as the principal contributor to the optimized response The location of the optimum is formulation-specific. Bare alumina commonly exhibits an isoelectric region in the alkaline pH range, but adsorbed carboxylates can shift this region markedly toward lower pH.

Citric acid adsorption on alumina decreases between acidic and alkaline conditions while generating a strongly negative surface and a pH-dependent stability map. Poly(acrylic acid) likewise shows high-affinity adsorption whose density decreases as pH increases, and direct comparison among polymer functional groups demonstrates that carboxyl-containing PAA has much stronger

alumina affinity and a much larger influence on suspension stability than PEG alone. More recent alumina-slurry work confirms that pH can simultaneously change surface charge, additive adsorption and rheology. The pH 5-7 basin is therefore compatible with a balance among carboxyl-group ionization, adsorption affinity and PEG-mediated hydration rather than with a single bare-alumina isoelectric-point argument. The asymmetric pH response can be rationalized by the coupled ionization and adsorption behavior of carboxyl-containing dispersants. At low pH, protonation of carboxyl groups reduces their anionic character and weakens the electrostatic component of particle-particle repulsion. As pH increases, carboxylate ionization strengthens, but adsorption of anionic species on increasingly negative alumina surfaces can become less favorable and double-layer screening can also change. Hydrated PEG segments provide an additional steric contribution through their solvated chains. The near-neutral minimum is therefore consistent with a balance between carboxylate anchoring, surface-charge regulation, and PEG-mediated steric hydration, while the asymmetric deterioration toward acidic and alkaline conditions reflects the unequal pH dependence of these contributions.

Interfacial Interpretation of the Non-Additive Composition Response

The binary effect is characterized by three coupled features. First, both X and Y outperform citric acid, demonstrating that incorporation of PEG through esterification markedly improves the macroscopic dispersion response relative to the parent multicarboxylic acid. Second, the 60/40 blend outperforms both individual products and the linear-mixture expectation, establishing a genuine non-additive composition effect. Third, the improvement is expressed mainly through suppression of clarification, with only a small change in compact sediment. Together, these features point to a composition-dependent interfacial state that increases the fraction of alumina retained in the suspended region after 24 h. A mixed electrosteric layer provides a coherent interfacial framework for these observations. Carboxylate-bearing species can anchor to hydroxylated alumina and modify particle charge, while hydrated PEG segments can extend into the aqueous phase and generate steric exclusion when associated with surface-bound species.

The stabilizing response therefore depends on the balance among anchoring-group density, surface coverage, PEG hydration, and the relative abundance of the two product populations. Because X and Y contribute different acid-derived functionalities within PEG-containing esterification products, varying their ratio changes both the electrostatic and steric components of the interfacial layer. Competitive adsorption studies provide a direct basis for the observed non-linearity. On alumina, ammonium poly(methacrylate) adsorbs more strongly than PEG and markedly suppresses PEG adsorption in mixed systems, whereas PEG exerts a much smaller influence on polyelectrolyte uptake.

Competitive PAA/PVA adsorption shows a similarly asymmetric surface response and sequential PAA/SDS adsorption demonstrates that adsorbed-layer conformation can switch alumina suspensions between dispersed and flocculated states. These studies show that bulk formulation ratio and interfacial population need not vary proportionally. In the X/Y system, the asymmetric composition curve is therefore consistent with preferential surface occupation and mixed-layer reorganization as the relative abundance of the two PEG-ester populations changes.

Comparison with covalently integrated PEG-containing dispersants supports the same interpretation. PAA-b-PEG-b-PAA stabilizes alumina more effectively than PEG or sodium polyacrylate alone because strongly adsorbing ionic blocks are combined with a solvated PEG segment. AMPS-MPEG copolymers likewise show that ionic-group fraction, PEG chain length, and copolymer architecture jointly determine adsorption, electrokinetic behavior, and viscosity in the present binary system, analogous functional roles are distributed between two product populations rather than along a single macromolecular backbone. An intermediate X/Y ratio can therefore favor a complementary balance between surface anchoring and hydrated steric protection, whereas compositions dominated by either population shift the interfacial balance away from the optimum.

The phase-partition response provides macroscopic evidence for this interfacial balance. The 60/40 blend does not primarily act by reducing the already small compact-sediment fraction; instead, it markedly suppresses the formation of clear supernatant and retains a larger particle-containing volume after 24 h. Such behavior is consistent with reduced aggregation and hindered settling arising from stronger interparticle repulsion and steric protection. The binary composition therefore changes the separation pathway itself, producing a more persistent suspended phase rather than merely altering the packing of the final sediment bed.

Across the full composition range, the X/Y system thus exhibits a broad non-additive stabilization domain, a low-separation basin centered near 60% X, greater tolerance on the Y-rich side, and selective suppression of clarification at the optimum. These coupled responses establish composition as an active control parameter for interfacial stabilization rather than a simple mixing variable.

Formulation Significance for Aqueous Ceramic Processing

Modern aqueous ceramic processing requires formulations that resist particle segregation while maintaining process-compatible flow behavior. Recent alumina studies show that dispersant chemistry governs rheology, self-leveling, printability, and dimensional control in direct ink writing, tape casting, stereolithography, and vat photopolymerization. The present results identify three formulation variables that act coherently on macroscopic stability: synthesis history of the PEG-ester products, the X/Y mixing ratio, and suspension pH. Their combined effect is expressed most clearly through suppression of clarification and an increase in the retained particle-containing phase.

The breadth of the favorable composition and pH regions is particularly relevant to formulation robustness. Blends containing 20-80% X all outperformed the best individual X product, while the 40-70% X region maintained PSI₂₄ below 7%. Likewise, the optimized 60/40 blend remained at or below 6.3% over pH 5-7. These response windows show that the improved stabilization is not restricted to a single exact formulation point. At the same time, the stronger penalties on the X-rich and acidic sides define the directions in which formulation drift most rapidly compromises stability. The phase-partition results also connect formulation chemistry with the physical manifestation of destabilization. Across both composition and pH series, the dominant improvement arose from a reduction in clear-supernatant formation rather than from large changes in compact-sediment volume. Suppression of clarification preserves a larger homogeneous particle-containing region during quiescent holding, a feature that is directly relevant to slurry storage, transfer, and shaping operations where concentration gradients can translate into non-uniform packing and differential

shrinkage. The binary PEG-ester strategy therefore provides a formulation route for controlling macroscopic segregation through complementary electrostatic and steric interactions.

Together, the orthogonal synthesis screening, binary composition response, phase partitioning, and pH dependence define a coherent formulation map for the X/Y system. Improved suspension stability is associated with favorable synthesis conditions for each product family, an intermediate binary composition centered near 60/40 X/Y, and a near-neutral chemical environment. The convergence of these variables on a common phase-separation response supports a unified picture in which synthesis, composition, and solution chemistry jointly determine interfacial stabilization of alumina particles.

Conclusions

Orthogonal screening established X9 and Y7 as the best-performing individual PEG-ester products, with PSI24 values of 9.0% and 11.8%, respectively, compared with 30% for citric acid and 58% for the additive-free suspension. Range analysis showed that p-TSA concentration and PEG molecular mass exerted the strongest influence on suspension performance in both synthesis families, while the response profiles of X and Y differed markedly, reflecting the dependence of interfacial behavior on esterification chemistry and synthesis history.

Binary blending generated a pronounced non-additive composition response. The 60/40 X/Y blend gave PSI24 = 5.3%, representing a 41.1% reduction relative to X9 and a 47.6% reduction relative to the linear-mixture expectation. Blends containing 20-80% X all outperformed X9, and the measured profile was asymmetric, with greater tolerance on the Y-rich side. The constrained Scheffé model located the response minimum at 58.4% X, closely matching the experimental optimum.

Phase partitioning showed that the binary advantage was driven primarily by suppression of clarification. At 60/40, the clear-supernatant fraction decreased to 5.00%, the compact-sediment fraction remained at 0.25%, and the retained-suspension fraction increased to 94.75%. The optimized blend also displayed a near-neutral pH stability basin, reaching PSI24 = 5.0% at pH 6 and remaining at or below 6.3% from pH 5 to 7. Both acidic and alkaline departures increased phase separation, with a stronger deterioration on the acidic side.

The composition, phase-partition, and pH responses are consistent with a mixed electrosteric stabilization mechanism in which carboxylate-containing species contribute surface anchoring and charge regulation while PEG segments provide hydrated steric protection. Competitive adsorption and mixed-polymer studies on alumina support the role of unequal surface affinity and interfacial reorganization in generating non-linear formulation responses. The binary PEG-ester system therefore demonstrates a composition-specific stabilization effect that substantially exceeds simple endpoint averaging and provides a clear physicochemical basis for optimizing aqueous alumina formulations.

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Data availability

All numerical data supporting the findings are provided in the tables and figures of this article.

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