D4.

Formulating Stable Latex Paints With Zinc Oxide

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The stability of architectural latex paints containing zinc oxide was examined in terms of the influence each formulation component had on the stability of the formulation. This study examines the effect of dispersant selection, titanium dioxide grade, extenders, and binder, as well as formulation parameters such as pH, initial viscosity, pigment volume content, and percent volume solids. While typical single component effects were observed, interaction effects between components were found to be equally important in determining the stability of the formulation.

INTRODUCTION

Zinc oxide offers the coatings formulator a method to enhance many of the performance aspects of a latex paint. In its own right, zinc oxide is an excellent mildewstat[1] and functions synergistically with isothiazolone microbiocides.[2] Zinc oxide also improves the film's weathering characteristic through both the absorption of ultraviolet radiation[3,4] and by decreasing the water sensitivity of the film through ionic complexation of carboxylate moieties in the paint.[5] Finally, the refractive index of zinc oxide is high[6] allowing the particle to contribute somewhat to hiding as well, assuming that the particle size is in a range that can effectively scatter light.[7] With this impressive list of formulating benefits, one would expect zinc oxide to be used as a matter of course. However, during shelf aging or in accelerated aging tests, some latex paint formulations will show a catastrophic viscosity increase that can be attributed to the zinc oxide. As a result, many formulators have chosen to forego the advantages of zinc oxide to reduce the risk of product loss.

Over the years, several mechanisms have been proposed for the viscosity instability. While zinc oxide is relatively insoluble in water,* its amphoteric nature and its complex chemistry allow it to be solubilized in significant quantities in the presence of acids and bases.[8] In the presence of ammonia, the most common neutralizing agent in latex paints, zinc can form a series of zinc ammine complexes which further promotes its solubilization.[9] As this pool of zinc cations develops, the latex is destabilized by both the double layer compression effect caused by this multivalent ion[10] and the neutralization of surface charge caused by the specific interaction of carboxylate stabilizing moieties with the zinc complex ions.[11] It is interesting to note that this mechanism is used by the rubber industry for the gelation of latex rubber foams.

Another mechanism has been proposed[12] that predicts the hetero-flocculation of titanium dioxide (TiO_2) (as well as other anionically charged particles, such as latex binder) based upon the isoelectric behavior of the pigments. This work points out that zinc oxide carries a positive electrostatic charge at pH's below 9.5 whereas other particles, such as TiO_2 would be negatively charged above its isoelectric point of 7.6 in water. Therefore, the isoelectric behavior of the zinc oxide sets the stage for an attractive coulombic interaction between the zinc oxide and the other particles. While this effect occurs in relatively pure water, one would expect significant modification of the isoelectric behavior through the adsorption of a polyelectrolyte dispersant thus reducing or eliminating this interaction.

Other work[13] has suggested that the formation of a complex between zinc oxide and a lower fraction of the latex may form, resulting in "conglomerates or gel-like formations with latices, which are not readily redispersible."

Presented at the 68th Annual Meeting of the Federation of Societies for Coatings Technology, in Washington, D.C., on Monday, October 29, 1990.
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*Approximately 0.005 g/l in pure water at 25°C.

Table 1—Zinc Oxide Gloss Formulation

Materials	Lb	Gal
Propylene glycol	60.0	6.98
Dispersant (35% solids)	7.9	0.87
Water	5.1	0.62
Defoamer	1.0	0.13
TiO_2	250.0	7.30
Zinc oxide	25.0	0.54

Grind the above materials in a high speed mill (Cowles, 3800 to 4500 fpm for 20 to 25 min) and letdown at a slower speed as follows:

Water	30.0	3.60
Acrylic latex binder (46%)	546.7	62.38
Texanol	25.7	3.16
Propylene glycol	38.0	4.42
Microbiocide	2.0	0.23
Defoamer	1.0	0.13
Water/Low Mw HEC (2.5%)	74.2	9.64
Total	1071.2	100.00

Formulation Constants	
PVC, %	22.5
VS, %	34.8
WS, %	49.0
pH	9.0
Initial viscosity, KU	72 to 76

While most of these mechanisms seen plausible, none of them have offered a general formulation solution to the problem. Since no one mechanism can offer a general panacea to the problem, it becomes important to understand the effect of every formulation parameter on the paint's stability. While conventional wisdom has it that dispersant selection controls the overall stability of the zinc oxide formulation, it is demonstrated that many other factors, including binder selection, volume solids, initial viscosity, adjuvant dispersants, and surfactants, are equally important.

Table 2—Zinc Oxide Flat Formulation A

Materials	Weight Ratio	Parts per Hundred (volume solids)
Water	125.0	15.00
Dispersant (40%)	7.1	0.67
Wetting agent	2.5	0.28
Defoamer	1.0	0.13
Propylene glycol	34.0	3.95
Low Mw HEC 250 MR (100%)	3.0	0.26
Ethylene glycol premix	25.0	2.69
TiO_2	225.0	6.54
Zinc oxide	25.0	0.54
Alumina silicate extender	147.3	6.76
Calcium carbonate	50.0	2.33
Attapugite clay	5.0	0.25

Grind the above materials in a high speed mill (Cowles, 3800 to 4500 fpm for 20 to 25 min) and letdown at a slower speed as follows:

Acrylic latex binder	305.9	34.17
Defoamer	3.0	0.39
Texanol	9.3	1.17
Microbiocide	2.0	0.24
Ammonium hydroxide (28%)	2.0	0.27
Water/Low Mw HEC MHR (2.5%)	202.4	24.36
Total	1176.9	100.00

Formulation Constants	
PVC, %	45.4
VS, %	36.2
WS, %	54.2
pH	9.2 to 9.6
Initial viscosity, KU	90 to 95

METHODS

To evaluate the effect of compositional variation on the stability of the paint, three base formulations, given in *Tables* 1, 2, and 3, were used. These formulations were selected based upon their marginal stabilities and the degree to which formulating parameters could affect that stability. All materials were commercial products and were used as supplied. All paints were prepared from the same lot of each raw material.

The stability of these paints was evaluated by accelerated aging methods. A great deal of conflict exists regarding accelerated stability testing and the conditions used. Most use the viscosity change after storage at elevated temperatures as an indicator of long-term stability. Typical conditions for this type of testing regime are 60°C for 10 days. Since the primary concern is the length of time that the paint's viscosity will remain stable during shipping and storage, it would seem reasonable to run the accelerated testing until the paint demonstrates this failure and compare the times required to induce this failure. Since this protocol would be impractical for laboratory testing, we have opted to extend this regime to 28 days. During this period, the paints were evaluated daily. The stability of paints exhibiting a catastrophic rise in viscosity in less than 28 days was recorded in terms of the number of days to failure. Those which remained fluid throughout the 28-day testing regime but showed an in-

Table 3—Flat Formulation B

Materials	Lb	Gal
Water	200.0	24.00
Defoamer	1.0	0.13
Ethylene glycol	27.9	3.00
HEC	2.0	0.17
KTPP	1.5	0.07
Wetting agent	2.5	0.28
TiO_2	250.0	7.60
ZnO	50.0	1.07
Alumino silicate extender	150.0	6.48

Grind the above materials in a high speed mill (Cowles, 3800 to 4200 fpm) then add the following at a slower speed as follows:

Acrylic latex binder (60.5%)	363.6	40.55
Defoamer	1.0	0.13
Texanol	11.0	1.39
Microbiocide	1.5	0.17
Water/HEC Medium Mw (2.5%)	115.9	13.91
Total	1188.4	100.00

Formulation Constants	
PVC, %	39.1
VS, %	38.7
WS, %	56.5
Initial KU	80
pH	9.3 to 9.5

Table 4—Initial Evaluation of Formulation Stability with and without Zinc Oxide

Dispersant Type	Flat Formulation A w/o ZnO Heat Aged	Flat Formulation A w/o ZnO Roller	Flat Formulation A with ZnO Heat Aged	Flat Formulation A with ZnO Roller	Gloss Formulations w/o ZnO Heat Aged	Gloss Formulations w/o ZnO Roller	Gloss Formulations with ZnO Heat Aged	Gloss Formulations with ZnO Roller
High Mw poly acid, Na+ salt	P	P	P	F(27)	P	P	P	P
Hydrophobic copolymer, Na+ salt	P	P	P	P	P	P	F(3)	F(3)

P = Pass.
F(x) = Fail (days to failure).
Note: Samples subject to accelerated aging conditions for 28 days (see text).

crease in Stormer viscosity of more than 10 Krebs Units (KU) were recorded as 28 days to failure. Those that exhibited viscosity change of less than 10 KU were considered to pass. Using this protocol, the relative stability of the paints can be assessed based upon the days to failure.

A similar protocol was used for another accelerated testing method, mechanical agitation. In this test, 250 g of the formulated paint was placed into ½ pint paint cans. These cans were then subjected to agitation for 28 days on a roller mill revolving at ca. 130 rpm and evaluated as previously mentioned.

Paints were considered to be stable only if they passed both testing protocols.

Even with this more rigorous protocol, the evaluation of accelerated testing data must be interpreted cautiously. In a study correlating the accelerated stability testing of nearly 300 paints to shelf stability of these paints for one year at ambient conditions, we found only 78% correlation. Of that 22% which did not correlate, 13% were found to pass accelerated testing but failed one-year shelf stability. Therefore, one must be exceedingly cautious.

RESULTS AND DISCUSSION

Verify Formulation Instability

Before proceeding with an evaluation of the factors controlling zinc oxide stability, it is imperative to verify that the stability problem with the formulation is indeed caused by the presence of zinc oxide. To verify this, both flat formulation A and the gloss formulation were prepared with and without zinc oxide. For both formulations, TiO_2 was substituted for the zinc oxide removed on an equal volume basis. The data in *Table* 4 demonstrate that the viscosity instability that was observed was linked to the presence of zinc oxide in the formulation and not a result of other instability. This table also demonstrates another important observation echoed throughout this study. The correct selection of a 'zinc oxide stable' component, in this case a dispersant, is specific to the given formulation. Neither dispersant used provided stability in both formulation types.

pH Effect

Based upon the possible failure mechanisms previously presented, the pH of the continuous phase should have a remarkable effect on the formulation stability both through its influence on the charge on the dispersed particles and through the influence over the zinc ion species present. At a pH in excess of 9.7, the zinc oxide, as well as the other dispersed phases, would carry a negative charge, thus eliminating any attractive coulombic interactions. Likewise, at high pH, zinc ion is present as the zincate anion (ZnO_2^{-2}) which is less destabilizing than the zinc cation complexes present at lower pH. To demonstrate these effects, the pH of the gloss formulation was raised to pH = 12 using 50% NaOH solution at the end of the letdown. From the data in *Table* 5, it was observed that this formulation remained stable at high pH. However, as zinc oxide solubilizes, the pH of the paint drops as the base is consumed. While academically interesting,

Table 5—pH Effect on Heat Age Stability of Gloss Formulation (Paints Adjusted with NaOH)

Initial pH	1 day pH	1 day Stability	10 days pH	10 days Stability	28 days pH	28 days Stability
pH = 9	9	F	F	F	F	F
pH = 12	12	P	9.8	P	9.3	F(25)

P = Pass.
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

Table 6—Dispersant Effect on Zinc Oxide Stability

Dispersant Type	Flat Formulation Roller	Flat Formulation Heat Age	Gloss Formulation Roller	Gloss Formulation Heat Age
Hydrophilic copolymer NH_4+ salt	P	F(10)	F(4)	P
Hydrophobic copolymer Na+ salt	P	P	F(5)	F(1)
Hydrophobic copolymer NH_4+ salt	P	F(28)	F(3)	F(3)
High Mw acid homopolymer Na+ salt	P	F(27)	P	P
Low Mw acid homopolymer Na+ salt	P	F(17)	P	P

P = Pass.
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

Table 7—Effect of Potassium Tripolyphosphate (KTPP) on the Stability of Flat Formulation A

Dispersant	w/o KTPP		With KTPP	
	Heat Age	Roller	Heat Age	Roller
Hydrophilic copolymer NH_4+ salt	F(10)	F(10)	F(10)	F
Hydrophobic copolymer NH_4+ salt	F(28)	P	P	P
High Mw acid homopolymer Na+ salt	F(27)	P	P	P
Low Mw acid homopolymer Na+ salt	F(17)	P	F(28)	P

KTPP added to millbase at 1.5 lbs/100 gal.
P = Pass.
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

this method of stabilizing a paint offers no practical solace to the paint formulator. First, the permanent base NaOH was used for the pH adjustment, since a rather large amount of ammonium hydroxide would have been required to reach a pH of 12. Furthermore, if ammonia had been used, the increased level would have further promoted the solubilization of the zinc oxide through the formation of zinc ammine complexes. Even more importantly though, it would be impossible to maintain stability over time, since the zinc oxide solubilization process will cause the pH to drift downward.

Dispersant Effect on Stability

Clearly, the industry recognizes pigment dispersants to be the primary controlling factor for zinc oxide stability. This belief is so strong that raw materials suppliers classify dispersants based upon their 'zinc oxide stability.' While it is true that they do play an important role in stability, no one dispersant can be considered to be zinc oxide stable in all formulations. None of the dispersants shown in *Table* 6 conveyed stability to both formulations. While the Na+ salt acid homopolymers convey greater stability overall than the ammonium salt copolymers, no generalization would be rigorously correct.

Adjuvant Dispersants and Surfactants

The use of adjuvant dispersants, such as potassium tripolyphosphate (KTPP) or aminomethylpropanol (AMP), and surfactants have long been touted for their ability to improve zinc oxide stability. Indeed, the adjuvants can act as dispersants in their own right, and all of these additives can improve the dispersion stability. In addition, KTPP can complex with zinc cations reducing their adverse impact on stability.

To demonstrate this effect, KTPP was added to the millbase of flat formulation A at 1.5 lb/100 gal of paint. As shown in *Table* 7, a stability improvement with those dispersants that were producing a marginally stable formulation without KTPP can be observed. Those formulations which exhibited poor stability without KTPP were not improved sufficiently to pass this testing protocol.

In *Table* 8, the use of surfactants and adjuvants is demonstrated with similar results. In only one of the three cases, the formulation dispersed with hydrophilic copolymer, was the addition of a surfactant sufficient to convey good stability to the paint. In both of the other cases, significant stability improvements were observed with the addition of both surfactant and adjuvant, but their effect was still insufficient for these formulations.

Effect of TiO_2 Type

Remarkably, the choice of TiO_2 grade can have a profound effect on the formulation stability. In *Table* 9, the stabilities of three classes of TiO_2 were compared; these included grades with alumina, alumina/silica, and alumina/organic surface treatments. While each pigment demonstrated good stability with at least one dispersant type, none were stable with all of the dispersants. It was also remarkable that the rather typical combination of the copolymer dispersants with the alumina coated gloss grade pigment was the least stable. However, the sodium salt copolymer dispersant was stable with both of the other pigments.

Effect of Extender Selection

With an appreciation for the effect of the TiO_2 grade on zinc oxide stability, we would predict that the surface characteristics of other dispersed phases may also exert an important influence on stability. To examine this question, small portions of each of several different extenders were added to separate portions of the gloss formulation. Two china clays, a silica and a calcium carbonate extender were added at a loading of 0.7 gal/100 gal. This selection of extenders covered a wide range of particle sizes, oil absorption, and pH behavior. At this low level, almost no effect on stability was observed (*Table* 10).

Table 8—Effect of Adjuvant Dispersants and Surfactant as Stabilizing Additives to Gloss Formulation

Dispersant	Additives	Roller Stability	Heat Age Stability
Hydrophobic copolymer... NH_4+ salt	None	F(3)	F(1)
	Surfactant	F(28)	F(3)
	Surfactant, AMP	P	F(6)
	Surfactant, AMP, KTPP	P	F(6)
Hydrophobic copolymer... Na+ salt	None	F(18)	F(1)
	Surfactant	P	F(5)
	Surfactant, AMP	P	F(10)
	Surfactant, AMP, KTPP	P	F(10)
Hydrophilic copolymer.... NH_4+ salt	None	F(4)	P
	Surfactant	P	P
	Surfactant, AMP	P	P
	Surfactant, AMP, KTPP	P	P

Additives were blended with millbase liquids prior to pigment addition at the following levels:

		Level
Surfactant	—Octyl phenol ethoxylate $(EO)_{9.5}$	2.5 lb/100 gal
AMP	—Amino-2-methyl propanol	3.2 lb/100 gal
KTPP	—Tripotassium phosphate	1.5 lb/100 gal

P = Pass.
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

Table 9—Effect of TiO_2 Type on the Stability of the Gloss Formulation

	TiO_2					
	Gloss Grade Alumina Surface Treatment		Gloss Grade Organic/ Alumina Surface Treatment		Gen Purpose Alumina/ Silica Surface Treatment	
Dispersant	Heat Age	Roller	Heat Age	Roller	Heat Age	Roller
Hydrophilic copolymer NH_4+ salt	P	F(4)	P	F(7)	P	F(4)
Hydrophobic copolymer Na+ salt	F(3)	F(18)	P	P	P	P
High Mw acid homopolymer Na+ salt	P	P	F(25)	P	F(25)	P
Low Mw acid homopolymer Na+ salt	P	P	F(14)	F(17)	F(14)	P

P = Pass.
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

Table 10—Effects of Extender/Dispersant Variations on Stability of the Gloss Formulation

	China Clay		Silica	$CaCO_3$
Extenders	A	B	C	D
pH of 10% Slurry	4.5	7.0	6-7	9.5
Particle size (μ)	0.2	0.4	2.4	2.0
Oil adsorption value	47	39	30	18
Dispersant	Heat Stability			
Hydrophilic copolymer NH_4+ salt	P	F(5)	P	P
Hydrophobic copolymer Na+ salt	F(3)	F(3)	F(3)	F(3)
Acid homopolymer Na+ salt	P	P	P	P
	Roller Stability			
Hydrophilic copolymer NH_4+ salt	F(3)	F(3)	F(3)	F(3)
Hydrophobic copolymer Na+ salt	F(3)	F(7)	F(10)	F(3)
Acid homopolymer Na+ salt	P	P	P	P

P = Pass.
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

Only one combination, the hydrophilic copolymer dispersant with china clay B, substantially affected stability performance. To be conclusive, the examination of this effect should include higher extender pigment volume contents.

Effect of Latex Binder Selection

The selection of the latex binder, normally chosen for other performance characteristics, has an important influence on the stability of the formulation. For this study, four latex binders with dramatically different stabilization systems were substituted into flat formulation-B. The results in *Table* 11 suggest that while binder selection influences the stability, no generalization about binder stabilization type could be drawn. None of the binders exhibited good stability with all of the formulation variants. Each binder, though, was found to have at least one stable dispersant variant.

Effect of Zinc Oxide Selection

Two large particle size, latex coating grade, French Process zinc oxides from two different suppliers were evaluated in the gloss formulation at a level equal to 25 lb/100 gal. Despite the obvious importance of zinc oxide's role in the failure of these paints, the data in *Table* 12 show remarkably few differences in stability between the zinc oxides. This does not suggest that all zinc oxide grades are equal in terms of latex stability. However, where the zinc oxides were very similar in terms of process, morphology, and particle size, substitution had a limited effect in this formulation.

Effect of Pigment Volume Content, Volume Solids, and Initial Viscosity

To examine the effect of these formulation parameters on zinc oxide stability, the flat formulation B was modified as follows. Pigment volume content was varied by holding the relative volume ratio of the pigments, except zinc oxide, constant while the total content was varied. The zinc oxide level was maintained at 50 lb/100 gal. Dispersant level was held constant relative to the total pigment level (0.7% weight solids of dispersant on pigment). Volume solids was adjusted by dilution with water and 2.5% HEC solution to maintain constant initial viscosity. Viscosity was varied by changing the water/thickener balance.

Table 13 shows that these formulation parameters did not have any significant effect on the more stable polyacid dispersant variation of this formulation. However, some trends did emerge for the marginally stable formulation variant dispersed with the copolymer dispersant. As volume solids of the formulation were increased, the stability of the formulation decreased. If the failure mechanism involves the flocculation and/or coagulation

Table 11—Effect of Binder Selection on the Stability of Flat Formulation B

	Stability with Hydrophobic Copolymer Disp, NH_4+ salt		Stability High Mw Polyacid Disp, Na+ salt		Stability with Hydrophilic Copolymer Disp, NH_4+ salt	
Acrylic Binder Type	Heat Age	Roller	Heat Age	Roller	Heat Age	Roller
A	P	F	P	P	P	F
B	P	P	P	P	F	F
C	P	P	P	P	P	F
D	P	P	F	P	P	P

Both binder and dispersant substituted at an equal weight solids basis.
A—Small particle, non-ionically stabilized architectural vehicle.
B—Large particle, HEC stabilized architectural vehicle.
C—Small particle, anionically stabilized architectural vehicle.
D—Small particle, highly stabilized anionic maintenance vehicle.
P = Pass.
F = Fail.
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

Table 12—Effect of Zinc Oxide Type on the Stability of the Gloss Formulation vs Dispersant and TiO_2 Selection

	Gloss Grade Alumina Surface Treatment		Gloss Grade Alumina/Organic Surface Treatment		Gen Purpose Grade Alumina/Silica Surface Treatment	
	ZnO-A	ZnO-B	ZnO-A	ZnO-B	ZnO-A	ZnO-B
Heat Stability						
Hydrophilic copolymer, NH_4 + salt	P	P	P	P	P	P
Hydrophobic copolymer, Na + salt	F(3)	F(3)	P	F(10)	P	P
High Mw acid homopolymer Na + salt	P	P	F(27)	F(10)	F(25)	F(26)
Low Mw homopolymer, Na + salt	P	P	F(14)	F(6)	F(14)	F(25)
Roller Stability						
Hydrophilic copolymer, NH_4 + salt	F(4)	F(3)	F(7)	F(3)	F(4)	F(7)
Hydrophobic copolymer, Na + salt	F(18)	F(3)	P	P	P	P
High Mw acid homopolymer Na + salt	P	P	P	F(19)	P	P
Low Mw homopolymer, Na + salt	P	P	F(17)	F(19)	P	P

Zinc oxide substituted at 25 lb/100 gal.
P = Pass
F(x) = Fail (days to failure).
Note: Samples subjected to accelerated aging conditions for 28 days (see text).

of the dispersed phases, the likelihood of failure would increase with increasing volume solids due to the reduction of interparticle distance and the increase of collisional frequency at higher solids concentration. The data also suggest that for this formulation, increased pigment volume content and decreased initial viscosity improve stability; however, the reason for these effects are less clear.

Interaction Effects on Formulation Stability

Thus far, we have been able to make very few clear generalizations about the formulation effects important to the stability of a zinc oxide paint. The source of this complexity could be two-fold. First, the chemistry of the zinc oxide failure mechanism is exceedingly complicated. Second, very few of the formulation stability responses previously shown could be interpreted in terms of a single factor effect. That is to say, many variables act in concert to affect the stability of the paint. Several will be examined.

For example, in *Table* 6, the effect of dispersant selection was also a factor of the formulation type. None of the dispersants selected were stable in both formulations. On the other side, several were unstable in both. When a dispersant is said to be zinc oxide stable, this does not suggest that it will render any zinc oxide containing formulation stable. It does suggest, though, that the dispersant has a tendency to produce stable formulations when other factors are controlled.

While the previously mentioned example is obvious and simplistic, it does illustrate a point. Other more interesting and more complicated interaction effects were also observed. For example, in *Table* 9, the interaction effects between the dispersant and the TiO_2 became quite apparent. The stability of any given dispersant was highly dependent on the TiO_2 grade selected. Similarly, a binder/dispersant interaction effect became apparent in *Table* 11. It does not take much of an excursion beyond the data presented to assume that the interactions go well beyond these binary pairs.

Table 13—Effect of Pigment Volume Content, Volume Solids, and Initial Viscosity on the Stability of the Flat Formulation B

			Roller Stability	
PVC	% Solids by Volume	Equil. Visc (KU)	High Mw Polyacid Dispersant, Na + salt	Hydrophobic Copolymer Dispersant, Na + salt
19	38.5	80	P	F
29	38.5	80	P	F
39	38.5	80	P	F
49	38.5	80	P	P
39	18.5	80	P	P
39	28.5	80	P	F
39	38.5	80	P	F
39	38.5	60	P	P
39	38.5	70	P	P
39	38.5	80	P	F
39	38.5	90	P	F

Viscosity was adjusted by varying the 2.5% HEC/water balance.
Volume solids adjusted by dilution with water and correction of viscosity with thickener.
Pigment volume content varied by all pigments and extenders in equal proportion.
P = Pass.
F = Fail.
Pass/Fail evaluated at 28 days.

CONCLUSIONS

The intent of this paper was not to point out the number of factors which can lead to stability failure but to point out the number of formulation tools available to obtain stability. Dispersant selection is not the only controllable

parameter. Selection of TiO_2 grade, binder, volume solids, initial viscosity, pigment volume content, pH, choice of neutralizing base, the use of adjuvant dispersants and surfactants, and the selection of zinc oxide grade can all be used to optimize stability.

The results of this study suggest certain imperatives for the paint manufacturer. First and foremost, any zinc oxide formulation should be carefully designed and rigorously tested. The effect of each variable should be tested to determine its effect on stability. Once the formulation has been defined, the raw materials should be controlled very carefully. Substitution should be approached cautiously, and only if absolutely required. The TiO_2 grade should have the appropriate surface treatment for satisfactory durability and stability. Finally, the nature of the zinc oxide should be consistent from batch to batch.

References

(1) (a) Salvin, S.B., *Ind. & Chem.*, *36*, 336-40 (1944); (b) Zinc Institute, Inc., "Zinc Oxide Stability in Exterior Latex Paints," JOURNAL OF COATINGS TECHNOLOGY, *52*, No. 668, 79 (1980).
(2) "Zinc Oxide; Properties & Applications," International Lead Zinc Research Organization, Inc., New York, 1976, p 78.
(3) *Ibid*, p 11.
(4) Zinc Chemicals, Zinc Institute, Inc., New York, 1983, pp 40, 44.
(5) LeSota, S., Lewandowski, E.W., and Schaller, E.J., "Hydrophobically Modified Alkali-Soluble Emulsions as Thickeners for Exterior Latex Paints," JOURNAL OF COATINGS TECHNOLOGY, *61*, No. 777, 135 (1989).
(6) Bond, W., *J. Appl. Phys.*, *36* (5), 1674-7 (1964).
(7) Stutz, G., *Ind. & Eng. Chem.*, *19*, (1), 52 (1927).
(8) Blok, L. and DeBruyn, P.J., *Colloid Interface Sci.*, *32*, 518-38, (1970).
(9) Brown, H.W., "Zinc Oxide Rediscovered," New Jersey Zinc Co. (1957).
(10) Becher, P., "Colloid Stability," JOURNAL OF PAINT TECHNOLOGY, *41*, No. 536, 523 (1969).
(11) (a) Cassange, P., Revue Generale du Caoutchov, *28*, 39-42 (1951); (b) *Ibid*, pp 105-7.
(12) (a) Princen, L.H., "Pigment Interactions in Aqueous Media," *Official* DIGEST, *37*, No. 486, 766 (1965); (b) Princen, L.H., "Effects of Electrolytes on the Interaction Between Zinc Oxide and Titanium Dioxide," *Official* DIGEST, *36*, No. 473, 648 (1964); (c) Princen, L.H., *J. Colloid Sci.*, *19* (9), 786-97 (1964).
(13) (a) Kronstein, J. and Zipf, M.E., *Mod. Paint Coat.*, *75*, 180-5 (1985); (b) Kronstein, M., *Mod. Paint Coat.*, *73*, 24-8 (1983).

