High-Performance Pigment Dispersant Additives Improve Pigment Wetting and Dispersion in Waterborne Coatings

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A new family of high performance pigment dispersant additives has been developed to improve pigment wetting and dispersion in waterborne coatings. These unique additives are highly effective for a wide range of organic and inorganic pigments in both resin free and resinous pigment grinds, where they provide increased pigment loading, improved color development, and enhanced stability. Additional advantages of these new additives versus traditional and other high-performance dispersants include low foam; effective pigment stabilization; outstanding pigment wetting; high color development; and environmental benefits as they are HAPs- and alkylphenol ethoxylate (APE)-free. These new additives are applicable to automotive, architectural, industrial, and wood coatings.

INTRODUCTION AND BACKGROUND

The process for dispersing pigments has been described as consisting of three stages: (1) wetting of the pigment by the continuous phase; (2) mechanical milling to break up particle aggregates and agglomerates; and (3) long-term stabilization of the dispersed particles to prevent coagulation (flocculation).[1] For waterborne coatings and inks, the dispersion process presents a number of challenges. For example, the high surface tension (γ_{LV}; subscripts refer to liquid-vapor) of water and the interfacial tension (γ_{SL}; subscripts refer to solid-liquid) between the continuous water phase and the pigment must be reduced to adequately wet the pigment particles as shown schematically in *Figure* 1.

Wetting of the pigment particles is necessary to displace adsorbed air from their surfaces and to facilitate particle separation, so that, in step 2, the pigment agglomerates can be more readily reduced to the desired primary particles or much smaller agglomerations. The condition for wetting (or spreading) of the aqueous phase onto the solid pigment particle is

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Figure 1—Representation of step 1 (pigment wetting) in the pigment dispersion process. Surfactants facilitate the wetting of the pigments by the continuous water phase.

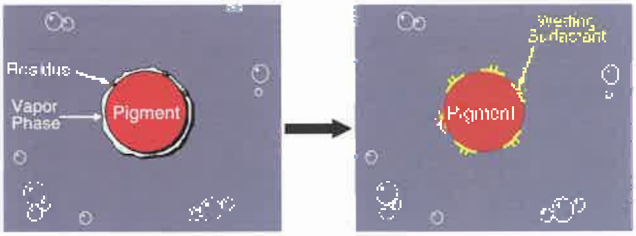
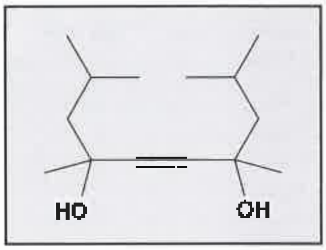


Figure 2—Molecular structure of the acetylenic diol surfactant TMDD (2,4,7,9-tetramethyl-5-decyne-4,7-diol).



given by the spreading coefficient, S, which is defined as:

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$$

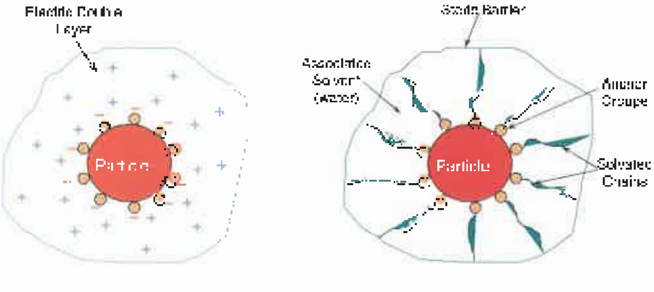
Spreading will occur if $S > 0$. Therefore, for the pigment to be wet out, γ_{SL} and γ_{LV} must be reduced such that their sum is less than the surface energy (γ_{SV}) of the pigment.[2]

As *Figure* 1 shows, in order to reduce the surface and interfacial tensions, a pigment wetting surfactant is required. The wetting surface adsorbs onto the pigment surface, reduces the interfacial tension, and "conditions" the surface for further adsorption of dispersion-stabilizing molecules. Commonly, the wetting surfactants are alkylphenol ethoxylates (APEs) or modified versions thereof. However, APEs have been implicated as endocrine disruptors, and there is a growing trend to replace these surfactants in coatings. In addition, the APE-based surfactants usually increase the foaminess of waterborne coatings and can also negatively impact the coatings' water resistance. Thus, the use of these surfactants necessitates the need to add strong defoamers to curtail the development and subsequent build up of unwanted foam. Defoamers, however, often produce negative consequences such as surface defects (e.g., craters) and poor flow and leveling (e.g., orange peel), so it is obviously desirable to use surfactants that minimize foam.[3]

A stated above, the primary role of the surfactant is to reduce the γ_{LV} and the γ_{SL}, so that the aqueous phase can more effectively wet out the pigment particles. Lower surface and interfacial tensions provide for a more efficient milling process by reducing the time (and energy) to reach the desired particle size distribution and, thus, maintaining a lower milling temperature. Since the milling process occurs under dynamic conditions, surfactants that confer low dynamic γ_{LV} and γ_{SL} should further enhance the efficiency of the milling process. The Gemini-type[4-6] acetylenic diol surfactant TMDD (*Figure* 2) and its low molecular weight ethoxylates are examples of surfactants that impart low dynamic surface tensions in aqueous systems, whereas the APE surfactants mentioned before generally have significantly higher dynamic γ_{LV}.[7] Also, the appropriate surfactant can help to reduce the viscosity of the mill base, so that a higher pigment loading can be used for better equipment-utilization rates.

After the pigment agglomerates are broken apart and the particles are dispersed in the aqueous phase during the milling process, the particles must be stabilized to prevent flocculation. As illustrated in *Figure* 3, stabilization is usually accomplished through electrostatic (charge) repulsion and/or steric barriers. As described by the classic DLVO theory and its modifications, electrostatic stabilization is accomplished not through the actual charge on the particle but rather through the associated electric double layer.[8] Steric barriers arise through the interaction in the aqueous phase of hydrophilic segments of molecules that are adsorbed onto the particle surfaces. In either case, the stabilization barrier is due to adsorbed molecules on the particle surfaces. The simplest cases are ionic or nonionic surfactants that contain one hydrophobic group and one hydrophilic group; examples of these surfactants are ethoxylates of alkylphenols and various alcohols and neutralized alkyl sulfonates. In the more complex cases, the adsorbed molecules are polymeric and contain multiple stabilizing (hydrophilic) and anchoring

Figure 3—Schematic representation of the mechanisms of dispersion stabilization. The sizes of the stabilization shells are exaggerated for illustration purposes.



Charge Stabilization

Steric Stabilization

Table 1—Properties of New Pigment Dispersants Evaluated

Product Code	Actives (% wt)	Pour Point (°C)	Viscosity (cP)		Clarity/Color	VOC (% wt)	
			10°C	25°C		U.S.[a]	EU[b]
Z-1200	45	< −25	800	300	Clear/light amber	< 25	< 17
Z-1400	40	< −25	1850	650	Clear/light amber	< 20	< 20
Z-1600	50	-18	450	200	Clear/reddish amber	< 25	< 14
Z-2100	100	3	350	150	Slight haze/straw-light amber	< 1.5	0.0
Z-2300	95	0	1400	450	Clear/straw	< 1.5	0.0

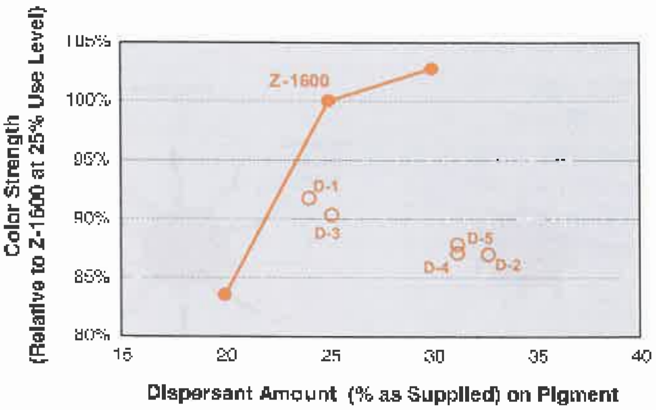
(a) EPA Method 24.
(b) European Directive 1999/13/EC.
Refer to Appendix 1 for material identification and suppliers.

segments which are arranged in various configurations (e.g., block or comb structures). A common example of such a molecule is an amine-neutralized copolymer of poly(acrylic acid). The polymeric molecules may include both ionic and nonionic hydrophilic groups. The multiple anchoring groups afford strong adsorption of these molecules onto the surfaces of the particles. The so-called polymeric dispersants with numerous anchoring and stabilizing groups provide excellent long-term stabilization to dispersed pigment particles.

The wetting and dispersing additives may be introduced into the formulation as separate components. However, it may be advantageous (e.g., compatibility, raw material minimization, etc.) to utilize products that are formulated to provide both wetting and stabilization. In this article, the benefits of a new series of high-performance pigment dispersants that provide optimal wetting and long-term dispersion stability are described. The effectiveness of these dispersant products has been tested with organic and inorganic pigments in resin-free grinds and in final paint formulations. The advantages of this pigment dispersant technology include:

- Effectiveness on a wide variety of pigments
- Lower dispersant demand levels
- Better cost in use
- Superior color development/reduced color-pigment concentration in paint
- Enhanced pigment wetting/lower viscosity grinds or higher pigment loadings in grind for higher equipment utilization rates
- Increased pigment (extender) loading in paint
- Improved long-term stability of dispersion and paint

Figure 4—Color strength comparison of the Z-1600 dispersant relative to commercial dispersants with a yellow organic pigment. 30% pigment dispersion, 1:20 TiO_2 blush, Pigment Yellow 83 (diarylide dimethoxy chloranilide).



EXPERIMENTAL

The properties of the new pigment dispersants evaluated in this study are provided in *Table* 1.

Pigment dispersions (grinds) were prepared by one of three methods: ball mill, vertical pearl mill, or high-speed dispersion (inorganic pigments only) with a Cowles-type blade. The viscosities of the pigment grinds were evaluated using Brookfield Digital Viscometers with LV and RV spindle series. For the inorganic pigments, the spindle speed was fixed at 20 rpm. The viscosities of the paint formulations were measured using a digital Stormer viscometer. To prepare the resin-free pigment dispersions, defoamers were typically added at 0.1% by weight of the total dispersion formulation.

Color development was determined in either blushes or tint bases. The blushes contained 1:50 to 1:20 pigment solids with a commercial TiO_2 slurry and 10% styrene-acrylic resin. The tint bases were 2–5% in various decorative and industrial maintenance waterborne tint-bases. A MiniScan spectrophotometer (HunterLab) was used to obtain the CIELab color space values. (See publication CIE 15:2004, *Colorimetry*.)

All coating formulations were prepared and applied using standard techniques. To determine stability, the coating formulations were aged for one week at 50°C. Films were applied by either draw-down onto sealed

Figure 5—Color strength comparison of the Z-2300 dispersant and commercial dispersants with organic red pigment. 40% pigment dispersion, 1:20 TiO_2 blush, Pigment Red 254 (diketo-pyrrolo-pyrrole).

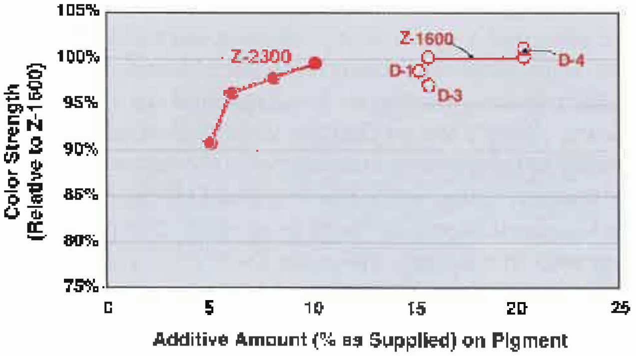


Figure 6—Color strength comparison of the Z-2100 dispersant and commercial dispersants with carbon black. 36% actives on pigment, 25% dispersion (2.5% in tint base), Pigment Black 7.

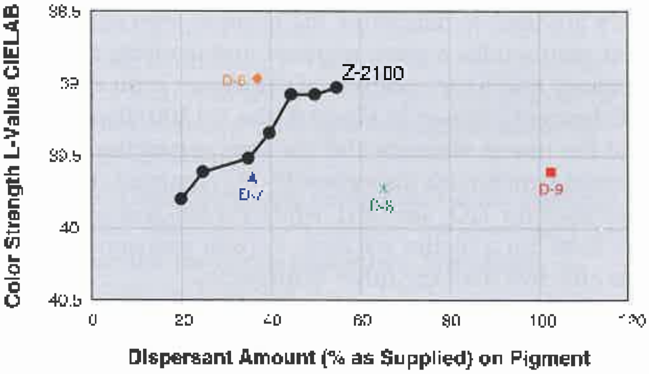


Figure 7—Dispersion stability comparison of the Z-2100 dispersant and commercial dispersants with carbon black. 36% actives on pigment, 25% dispersion (2.5% in tint base), Pigment Black 7. The dispersions were aged for 1 week at 50°C.

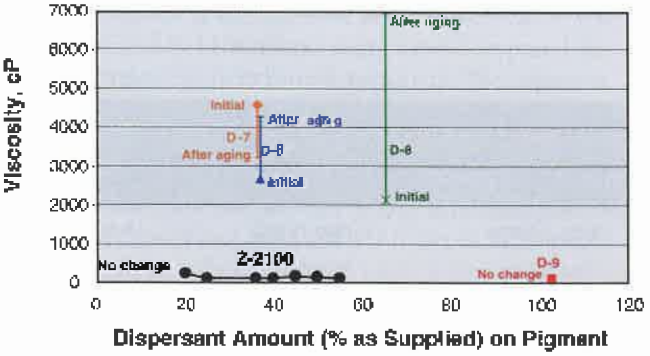


Figure 8—Dispersant demand curves for the new dispersants with TiO_2. 78% by weight pigment dispersion.

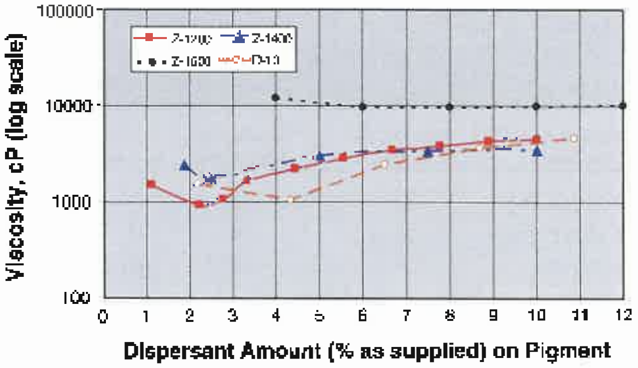


Figure 9—Dispersant demand curves for the new dispersants with red iron oxide pigment #1. 70% by weight pigment dispersion.

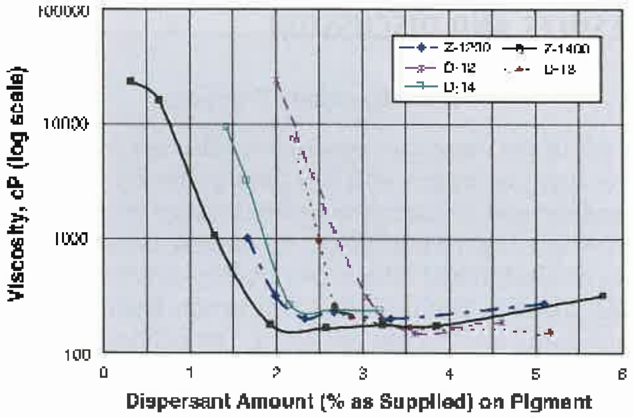


Figure 10—Dispersant demand curves for the new dispersants with red iron oxide pigment #2. 70% by weight pigment dispersion.

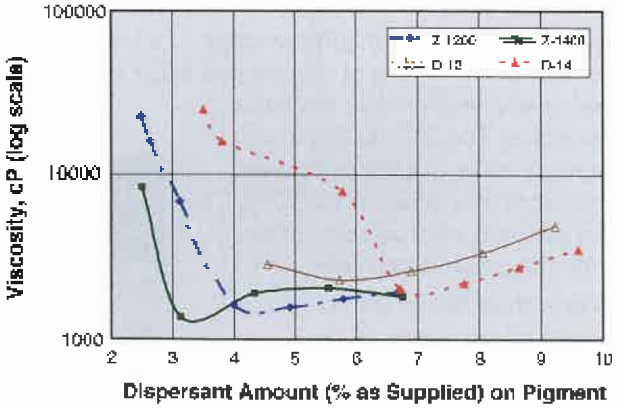


Table 2—Results of the Heat-Aging Stability Testing of the TiO_2 Pigmented Formulations Prepared with the Dispersants

Material Name (Use Level)	Viscosity, KU Initial	Viscosity, KU After Aging	Initial 60° Gloss
D-11 (10.5%)	54	54	78
Z-1200 (2.5%)	54	55	79
D-10 (4%)	55	54	Not determined

Leneta charts or sprayed (conventional suction-fed) onto cold-rolled steel panels to a wet film thickness of about 152 μm (6 mils). Gloss was measured using hand-held gloss meters (either HunterLab or BYK-Gardner). Covered spot tests (one-hour exposure) with various reagents were performed on the paints to determine their resistance properties.

RESULTS AND DISCUSSION

New Dispersant Products

All of the dispersant products studied are relatively low viscosity liquids with low pour points for excellent handling and storage. Activity levels range from 40% to 100% by weight as delivered. All of these products are free of alkylphenol ethoxylates (APEs) and contain no HAP solvents. The surfactant-type products are Z-2100 (nonionic) and Z-2300 (anionic). The polymeric products are Z-1200 (nonionic and anionic), Z-1400 (nonionic and anionic), and Z-1600 (nonionic). All of the products are formulated for pigment wetting and dispersion stabilizing.

Organic Pigments and Carbon Black[9]

The color strength of a pigment yellow 83 dispersion prepared with the Z-1600 dispersant was measured in a TiO_2 blush. As shown in *Figure* 4, the Z-1600 dispersant provided excellent color strength at a lower use level compared to that of dispersions made with a number of commercially available dispersants. The Z-1600 dispersant was more efficient (5% to 8% less dispersant) and effective (10–20% color strength improvement) than the commercial dispersants.

For carbon black, the color strength performance of the Z-2100 dispersant is shown in *Figure* 6. The color strength obtained with the Z-2100 dispersant was superior to that seen for three out of four commercial dispersants that were claimed to be effective for dispersing carbon black. Only the D-6 dispersant showed better color strength. As shown in *Figure* 7, the Z-2100 dispersant provided a much lower viscosity dispersion which, at an equivalent dispersant level, could translate into a higher pigment loading in the dispersion. In aging studies, *Figure* 7 shows that the Z-2100 dispersant provided good dispersion stability with no change in viscosity upon aging, while the D-6 and D-8 products increased significantly in viscosity, and the D-7 product decreased in viscosity. Although the D-9 product showed no change in viscosity upon aging, the use level required was significantly higher and the dispersion quality was poor.

Inorganic Pigments: TiO_2

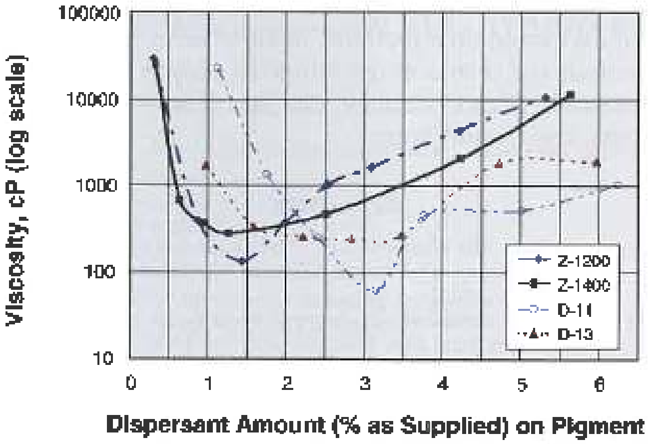
Dispersant efficiency of the new dispersants was evaluated by preparing dispersant-demand curves. The dispersant-demand curves are plots of dispersion viscosity versus amount of dispersant for a pigment at a set amount (loading) of pigment in the dispersion. They are used to determine the optimal level of dispersant required for a given pigment and loading; a lower viscosity and lower amount of dispersant indicate more efficiency. As shown in *Figure* 8, the Z-1200 dispersant had the lowest viscosity and use level versus the commercial benchmark dispersant D-10 (common dispersant used for TiO_2 slurries), while Z-1400 had a low use level but a higher viscosity. Z-1600 was significantly less effective than the other dispersants.

Because of its low use level and low dispersion viscosity, the Z-1200 dispersant was further evaluated in a low-VOC (< 100 g/L) coating based on a urethane-acrylic hybrid resin. The coating formulation is provided in *Appendix* 2. The original formula used 10.5% dispersant (D-11) per weight of pigment. Based on the dispersant demand curves in *Figure* 8, the amount of Z-1200 dispersant was set to 2.5% of the pigment weight. Also, the commercial dispersant D-10 was evaluated at a 4% level. All of the grinds had viscosities of 1500±50 cP at a pigment loading of 79%. Coatings were sprayed onto steel panels and drawn down onto sealed Leneta

Table 3—Results of the Chemical Spot Testing of the TiO_2 Pigmented Formulations Prepared with the Dispersants

Reagent	D-11 (10.5%)	Z-1200 (2.5%)	D-10 (4%)
Water	No effect	No effect	No effect
10% wt NH_4OH	Moderate swelling	No effect	Blisters
Ethanol/water (50:50)	Moderate swelling	Very slight swelling	Blisters
Clorox	No effect	No effect	Slight swelling

Figure 11—Dispersant demand curves for the new dispersants with red iron oxide pigment #3. 70% by weight pigment dispersion.



charts. The results of the heat-aging stability testing (50°C for one week) of the coatings are provided in *Table* 2. Even at one quarter of the original-formula use level, the Z-1200 dispersant gave excellent formulation stability. No pigment settling was observed with the aged samples containing Z-1200 or D-11, while some settling was seen with the D-10 sample. Initial gloss of the Z-1200-containing coating was as good as that of the original formulation.

Chemical spot tests were performed on the coatings to determine whether the changes to the dispersant had an effect on the resistance properties. The results reported in *Table* 3 show that the Z-1200-based coating had improved NH_4OH and ethanol/water resistance compared to the original coating with the D-11 dispersant, while the coating with the D-10 dispersant showed poorer overall resistance. These results illustrate that the choice of dispersant can affect coating performance.[10-11]

Inorganic Pigments: Iron Oxides

Dispersant demand curves were developed for a number of iron oxide pigments. *Figures* 9 through 11 show the data for three red iron oxide pigments, where the Z-1200 and Z-1400 dispersants were compared to several commercial benchmark products. The pigment dispersions studied were at a relatively high pigment loading of 70% by weight. The Z-1400 dispersant provided the best combination of low use level and low minimum-viscosity for two out of the three red iron oxides. In the case of red iron oxide #3, the Z-1200 performed the best, although the Z-1400 was also effective. In several instances, the commercial benchmarks had lower minimum viscosities, but their use level at minimum viscosity was higher. Generally, the Z-1400 dispersant provided the best overall performance.

Figure 12—Dispersant demand curves for the new dispersants with yellow iron oxide pigment #1. 70% by weight pigment dispersion.

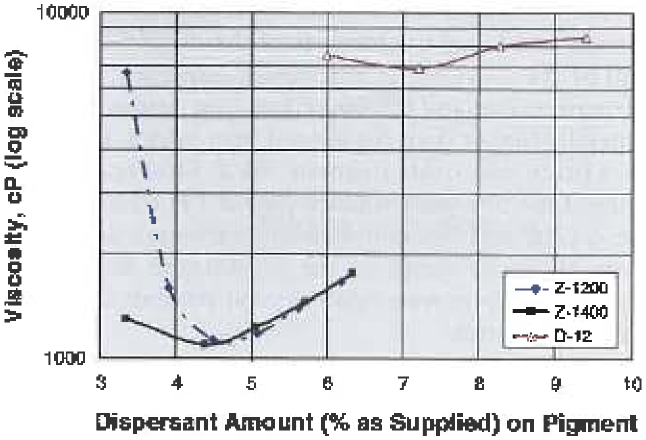


Figure 13—Dispersant demand curves for the new dispersants with yellow iron oxide pigment #2. 70% by weight pigment dispersion.

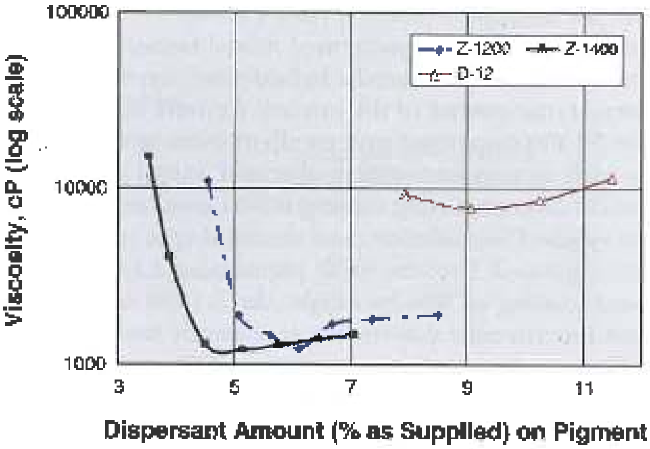
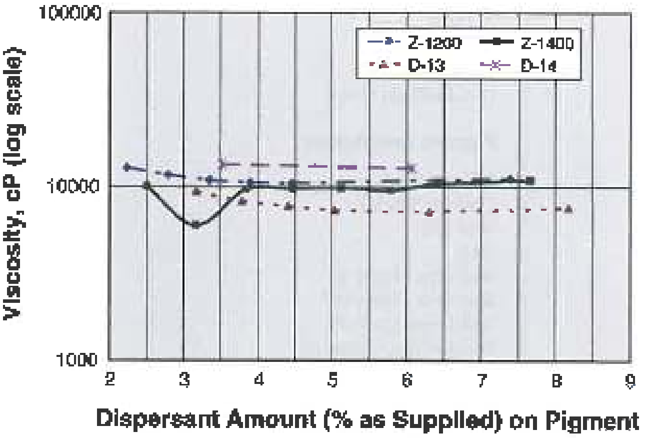


Figure 14—Dispersant demand curves for the new dispersants with black iron oxide pigment. 70% by weight pigment dispersion.



Figures 12 and 13 show the dispersant demand curves for two yellow iron oxides. In both examples, the Z-1400 dispersant showed lower minimum viscosities and lower use levels than the Z-1200 dispersant or the commercial benchmark dispersant (D-12). Dispersant demand for the yellow iron oxides was generally higher than for the red iron oxides. Likewise, for a black iron oxide pigment, the Z-1400 again showed the best performance (*Figure* 14) relative to the Z-1200 and two commercial benchmark dispersants. However, except for the Z-1400 case, the black iron oxide curves were relatively flat without distinct viscosity minima.

SUMMARY AND CONCLUSIONS

For organic pigments, the Z-1600 dispersant showed improved color strength at lower dispersant levels. The Z-2100 dispersant showed good color strength and dispersion stability for a carbon black pigment. Using a model formulation for a urethane-acrylic hybrid resin and the dispersant-demand curves for the Z-1200 dispersant with TiO_2, a pigmented model formulation based on a urethane-acrylic hybrid resin was studied. Even at one quarter of the original-formula use level, the Z-1200 dispersant gave excellent oven-aging stability with no pigment settling observed. Initial gloss of the Z-1200-containing coating was as good as that of the original formulation, and chemical spot resistance was improved. For iron oxide pigments at a high pigment loading of 70% by weight, the Z-1400 dispersant gave low viscosity dispersions at relatively low use levels.

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APPENDIX 1—LIST OF RAW MATERIALS AND SUPPLIERS

Dispersant Designation	**Name**	**Supplier**
Z-1200	ZetaSperse™ 1200	Air Products and Chemicals, Inc.
Z-1400	ZetaSperse 1400	Air Products and Chemicals, Inc.
Z-1600	ZetaSperse 1600	Air Products and Chemicals, Inc.
Z-2100	ZetaSperse 2100	Air Products and Chemicals, Inc.
Z-2300	ZetaSperse 2300	Air Products and Chemicals, Inc.
D-1 through D-14	Commercial benchmarks	various suppliers

Pigment Designation	**Name**	**Supplier**
Yellow 83	Irgalite® Yellow B3R	Ciba Specialty Chemicals
Carbon Black 7	Special Black 4	Degussa
Red 254	Hostaperm® Red D3G 70	Clariant
TiO_2	Ti-Pure® R 706	DuPont
Red Iron Oxide #1	Kroma Red® RO 4097	Elementis Pigments
Red Iron Oxide #2	Copperas Red® R2199	Elementis Pigments
Red Iron Oxide #3	Bayferrox® 110M	LANXESS
Yellow Iron Oxide #1	YZ-1688	Elementis Pigments
Yellow Iron Oxide #2	YLO-2288D	Elementis Pigments
Black Iron Oxide	Bayferrox® 318M	LANXESS

APPENDIX 2—LOW VOC HYBRID RESIN FORMULATION

Material	Amount, % wt	Supplier
Resin-Free Grind: Combine the following under mild agitation and mix until dissolved:		
Deionized Water	3.38	
Dispersant (D-11)	2.84	Commercial benchmark
Defoamer (Surfynol® DF-75)	0.07	Air Products and Chemicals, Inc.
Continue agitation while adding the pigment below.		
TiO_2 Pigment (Ti-Pure® R-706)	27.06	DuPont
Increase the speed to high and disperse to Hegman > 7. Do not exceed 140°F.		
Reduce the speed and add the following with medium agitation until blended:		
Deionized Water	0.85	
Total Grind	34.20	
Blend: Add the following into a separate, clean container under mild agitation until blended:		
Hybrid Dispersion (Hybridur® 870)	61.74	Air Products and Chemicals, Inc.
Pre-blend the following items before adding to the hybrid dispersion with strong agitation:		
Solvent (TPnB)	2.33	
Coalescing Surfactant (EnviroGem® AD01)	1.69	Air Products and Chemicals, Inc.
Defoamer (Surfynol DF-75)	0.03	Air Products and Chemicals, Inc.
Wetting Surfactant (BYK®-346)	0.01	BYK-Chemie
Final Blend: Slowly add the grind to the blend and mix with mild agitation until homogeneous:		
Resin-free grind	34.20	
Blend of hybrid resin, additives, and solvent	65.80	
Total Formulation	100.00	