SURFACTANTS FOR PARTICLE DISPERSION, LATEX EMULSION AND FILM ADHESION

Analysis by Randy Lee for Graham Magnetics, Graham, TX, 1993-1995, Re-Printed and formatted in 1997

The company's primary product utilized solvent-based, Fe_2O_3 particle dispersions for flexible magnetic film coatings. Some of the solvents employed for the manufacture of these products included tetrahydrofuran (THF), toluene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK). Due (in part) to the requirement for rapid flash-off during the coating process, these products were originally formulated as 'polyurethane lacquers'. This assignment was based on the directive to develop a low VOC product with equivalent or improved properties when compared to the solvent-based counterpart. In efforts to research and develop an acceptable water-reducible resin system capable of dispersing highly interacting (flocculating) magnetic particle/pigments and one that provided superior adhesional and elastomeric properties, an extensive laboratory project was initiated to evaluate the effects of various surfactants and related developmental products available on the market and their interactions with one or more potential resin candidates.

At the onset, it was expected that the final system would be a highly synergistic one, consisting of two or more different surfactants and at least two base resin components. During the experiments, a specially tailored binary resin base was developed which appeared to provide very promising benefits for the proposed system and consisted of one of Toyobo's Vylon series of functionalized polyurethanes along with one of Witco's water-reducible polyurethane dispersions. A number of develomental resins and polymers were evaluated from various sources (solvent-based, aqueous dispersions, hybrids, copolymers), as well as standard solvent-based and water disperable crosslinkers and curing agents. However, none of these will not be covered in this discussion (see project report "Innovative Polymers & Hybrids For Elastomeric Resin Binder Systems"). Using the proper surfactants, these two resins comprized the basic resin/binder vehicle since they were found to be quite compatible with each other and exhibited complimentary physical properties in the solvent system which was experimentally determined to consist of about 45% water and 55% THF (w/w). With the primary resin base and related solvent system now identified in the discussion, this report will focus exclusively on the research efforts and surfactant technologies explored during laboratory experiments, formulation trials and characterizations undertaken to define the appropriate surfactant make-up required for success of the proposed resin/solvent system.

In this report, a brief overview is given for the primary surfactant types investigated along with a few basic definitions (academic but relevant), and then the particular surfactant types which provided the most promising benefits and were eventually down-selected are examined in greater detail. Over 300 agents and additives were evaluated (a near complete list is given at the end of the report). It is not the intent of this disussion to present a comprehensive review of surfactant science, nor to cover technologies associated with every type of material investigated. Rather, the focus will be on the particular surfactant types that were of significant interest for the proposed resin/solvent system.

Background:

There are thousands of surface active materials available on the market today, and new ones are being developed continuously. Perhaps the most common ones are used in household/industrial cleaners, soaps & detergents, anti-microbial and personal care products. Others permit the efficiency and feasibility of paint dispersions, latex emulsions, foams, pharmaceutical formulations, crude oil recovery, etc… These agents can consist of monomers (small or medium sized molecules), polymers (of varying sizes) and complex material bases or mixtures containing an 'active' portion within an inactive adduct phase or base. While certain surfactants are used in 100% solvent-based organic systems, the majority of surface active agents constitutes the very entities that are responsible for the successful formulation and application of many aqueous dispersions, emulsions, water-reducible systems and water compatable products. In the ladder cases, each molecule contains a region that is hydrophobic in nature (organic/oil soluble or water insoluble) and a group or region that is hydrophillic (water soluble). When dissolved into aqueous systems at concentrations ranging from 0.001% to 5%, these molecules quickly migrate to substrate surfaces and/or dispersed particle interfaces and orient themselves so that the hydrophillic group remains dissolved in the water phase while the hydrophobic region solubilizes the particles or wets the the surfaces that would normally be water resistant (hydrophobic).

Solubilization of oil/organic-type particles and wetting of hydrophobic surfaces is made possible because the surfactant molecule lowers the surface energy of the water phase and provides a bridge between the aqueous and non-aqueous phases which would normally be incompatible. The relatively high surface tension of water (~72 mJ/m^2, energy per unit surface area) must be significantly reduced to within range of the lower energy surfaces in order for those surfaces to be wetted or solubilized. Surface energies for many non-porous substrates may range from about 15 mJ/m^2 for fluoronated materials (teflon) to 40 or 50 mJ/m^2 for plastics containing polar groups. The primary substrate involved in these studies was polyethylene terphthalate (PET) film in which the surface tension is known to be about 43 mJ/m^2. Porous substrates and particles must conform to more compex mechanisms of wetting and solubilization. Surfactants provide a multitude of benefits and effects that make certain systems possible that would otherwise be impossible. In particular, systems that require multiple benefits simultaneously often require more than a single surfactant, sometimes acting synergistically, and that concept would likely apply to the system under development here.

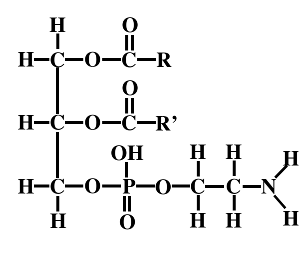
All major surfactant classes were evaluated including anionic, cationic, nonionic and amphoteric materials as advertised by their vendors to be wetting agents, dispersants, adhesion promoters, defoaming agents, viscosity modifiers, drying accelerators, leveling agents, lubricants, fungicides, anti-static agents, etc… Three of the surfactant types provide hydrophillic solution ions (electrolytes) when used in aqueous systems: anionic, cationic and amphoteric. Amphoteric surfactants are monomers or polymers with each molecule containing both a positively charged group and a negatively charge group. A few amphoteric materials were examined during the study but will not be covered here. Cationic surfactants are those in which the molecule contains a hydrophillic nitrogen-based group (generally) that becomes positively charged in solution. While several cationics were tested to observe their behavior in situ and as possible anti-static agents, they will not be discussed here. Ionic and nonionic materials comprize the largest portion of surfactant types in use. As such, surfactants from these two classes were examined more closely and were found to provide great benefits in the binder-solvent formulation which was eventually developed for the project.

Anionic agents are monomers, polymers or complex mixtures containing one or two groups that carry a negative charge. They are the agents historically utilized in soaps. Examples of some of the more common anionic materials include sulfated esters, ethers and alcohols; sulfonated aliphatics, aromatics, and ethers; carboxylated soaps and detergents; phosphated ester alcohols and phenols. Nonionic agents do not ionize but contain hydrophillic polar groups and/or hydrogen bonding capabilities which can provide interactions with water. Common hydrophobic groups used for surfactants (in general) include aliphatic and aromatic hydrocarbons, fatty acids, long chain alcohols, polyalkoxylates, fluorocarbons and silicones. Some of the more common hydrophillic groups utilized for anonic surfactants include sulfates, sulfonates, carboxylates and phosphates. The most common approach for providing hydrophillic properties to synthetic nonionic materials is by incorporating oxyethylene units ($-CH_2-CH_2-O-$) into the molecule. The number and placement of oxyethylene groups incorporated into the surfactant molecule permit great control over the degree of water solubility. Certain glycols, diols and carboxylic acid esters have also been used to impart hydrophillic character. Incorporation of oxyethylenes (more hydrophillic) and oxypropylenes (more hydrophobic) into the same molecule provide a convenient approach to controling the performance of nonionic surfactants. Strategic mixing of these two functionalities within the surfactant molecule can provide some very interesting qualities regarding surfactant capability.

A couple of brief definitions relevant to the discussion will be given here. Emulsions are liquid droplets dispersed within another liquid in which the two liquids are normally insoluble in one another. Use of an effective emulsifying agent promotes a stable dispersion where the droplets remain suspended for long periods of time (such as latex paints). Upon curing, these droplets join (fuse) together or ‘coalesce’ when all the solvent has completely evaporated away leaving the final solid product (cured coating). Emulsions can be classified as either oil-in-water (O/W) or water-in-oil (W/O) dispersions. The most common type is O/W in which a hydrophobic organic (or polymer) entity is stabilized in an aqueous solution containing a dissolved emulsifying surfactant. As will be noted later, the type of emulsion dealt with in this study is somewhat more complex than the simple descriptions given here. One common method of characterizing the nature or activity of surfactants (particularly emulsifying agents), is called the Hydrophile-Lipophile Balance or HLB number. The HLB scale is loosely defined from 1 to 40 in which higher values represent materials of greater water solubility (O/W stabilization), while low valued HLB agents promote W/O systems. In general, surfactant concentrations can range anywhere from 0.001% to 3-5% depending on the particular surfactant type as well as other components and parameters affecting the system. As the surfactant concentration is gradually increased from zero, the molecules localized themselves at the surfaces of interest. At a concentration when the surfaces become saturated with surfactant molecules, the molecules then begin to associate with themselves or aggregate in a new phase of micro-droplets called micelles. This is the Critical Micelle Concenetration or CMC. Above the CMC, the efficiency of the surfactant begins to drop off. Pure surfactants in pure water solutions generally exhibit very low CMC’s (from 10^{-5} % to 0.1% for nonionics). However, the ultimate CMC for a given agent in a mixed solvent systems is highly dependent on the particular molecular interactions between the solvents and may be increased as was the case for the system under development.

<u>Results & Discussion:</u>

One of the company’s original solvent-borne formulations did utilize a low HLB surfactant which effectively prevented particle flocculation and provided dispersion stability for magnetic slurries (one of the Centrolex series from Central Soya). This material was from the family of soybean-based, natural lecithin surfactants commonly used in oil/organic systems such as solvent-based paints, cosmetics and foodstuffs. In general, these lecithin surfactants contain neighboring phosphatidyl and amine groups near one end of the glycerol-type molecule which probably interact with the inorganic (slightly charged) particle surface, preventing flocculation, along with complex organic groups (R and R’) which may intertwine with the tertiary structure of the polymer (resin) providing suspension effects. Without this agent (at 1-3%), the solvent-based slurries exhibited significant degrees of instability and generated unacceptable product. Historically, Centrolex- was considered as the ‘magic’ agent responsible for the superior characteristics and success of the product. However, natural lecithins, from any source, and regardless of advertised HLB value, were found to be completely incompatible with any formulation containing even small amounts of water and were thus eliminated as candidates for the system under development.



Now, in addition to the reduced VOC mandate, the proposed water-based resin/solvent vehicle (slurry) was expected to provide several concurrent properties (or conditions) throughout the entire multi-phase process; ball milling, letdown, blending, viscosity reduction, crosslinking, and final web (extrusion) coating process. These properties included:

(1) Wetting/Adhesion – The lower energy substrate (PET film) required the use of an effective wetting agent to reduce the surface tension of water and to promote wetting and adhesion of the aqueous/organic resin vehicle.

(2) Particle Dispersion – A primary requirement was that of providing particle suspension while preventing flocculation and aggregation of highly attractive solid magnetic particles (~ .5-1μ in size) at high loading levels (> 70%).

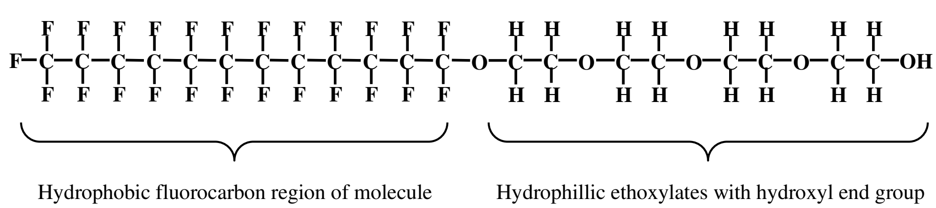
(3) Emulsion Stabilization – This system was expected to exhibit the properties of an emulsion, and as such, agents were needed to facilitate the dispersion of both resins in the aqueous fraction of the solvent system.

(4) Foam Elimination – Excessive foaming was noted for the majority of surfactants that were evaluated. Fortunately, the agents most effective in promoting the above three requirements, also minimized foaming to acceptable levels.

(5) Rapid Flash-Off – Due to multiple calendering of the film immediately after coating deposition, rapid water removal was mandatory in order to prevent sticking to the hot calender surfaces. In this regard, the formulation might be considered to exhibit properties of a 'water-based lacquer', analogous, in a way, to the standard solvent-borne products.

(1) Both the resin vehicle and solvent system were defined earlier (for convenience) in order to focus on the particular surfactants that were explored during the project. Even though all three phases were essentially developed concurrently, the goal of ~ 50/50 THF/water as the solvent system was pursued after it was determined that 100% water was not feasible (given all of the conditions that had to be met). As the work progressed, the ratio 45/55% water/THF by weight (or 48/52% water/THF by volume) was found to demonstrate the greatest producibility and compatibility with the other components. The current factory solvent recovery system was designed to accommodate primarily THF. However, a simple solution of 48/52 water/THF exhibited spreading wetting on the PET substrate that was intermediate between 100% water, which beaded, and 100% THF which readily and rapidly spread across the PET surface (no substrate wetting agents were required for the solvent-based products). While the contact angle for the water/THF mixture was drastically reduced (as compared to 100% water which was >> 90°), an extraordinary surfactant was needed to reduce the contact angle to near zero, similar to 100% THF (and most other volatile organic solvents). Extraordinary because typical water surface-tension-reducing surfactants were ineffective for the mixed solvent system under development.

Several wetting agents commonly used for water surface tension reduction applications were evaluated (such as those from Dow, Niacet, PPG, Union Carbide, 3M, etc..). Measurements were not scientific, but were based on visual observations of spreading/wetting time and apparent surface affinity. The goal was to find the agent and concentration that produced wetting/spreading very close to that of 100% THF. None of the common surfactants were effective including anionic and nonionic families of the polyethoxylates, glycols, acrylates, phosphates, sulfonates, etc… However, the the series of fluorosurfactants produced by 3M exhibited very promising results. In particular, two of these materials demonstrated acceptable effects regarding spreading/wetting of the water/THF solvent on PET. 3M's nonionic FC-170 fluorosurfactant was found to provide exceptional results at very low concentration (0.2-0.3% in slightly basic water prior to dilution with THF). This new solvent system, THF + (water + 0.2% $NaHCO_3$ + 0.3% FC-170), demonstrated a spreading time and wetting affinity for PET substrate that was almost equal (by appearance) to that observed for straight THF. The exact structure and specific chemistry of these fluorinated agents were proprietary and have remained trade secrets of 3M. However, a simplified version might envision a linear block copolymer structure containing a polyfluoroaliphatic hydrophobic section joined to a hydrophillic polyethoxylene section. An abbreviated possible structure is represented below. The fluorocarbon portion of the molecule (teflon-like) provides substrate spreading/wettability and is very insoluble in water (but not necessarily TH), while the ethoxy groups promote water/THF solubility all within a single synergistic molecule that ties the three phases together in a compatible fashion (water, THF and PET).



While simple water/FC-170 solutions demonstrated good surface wetting and resin dispersion, resin samples made with FC-170 treated water solutions (but no THF) completely lacked of adhesional wetting since all samples easily de-bonded from the PET substrate after cure. However, incorporation of THF into the solvent system provided the wetting/spreading and adhesional characteristics necessary for the proposed resin/solvent system to be successful. Again, this was most likely due to the synergistics of FC-170 and its ability to enhance compatibility between more than two phases.

It might be noted that the high solubility between water and THF is due chiefly to the polar nature of both molecules. While 100% water exhibits inter-molecular hydrogen bonding resulting in strong cohesive forces (and poor wetting), water/THF mixtures exhibit much weaker interactions between molecules (with improved wetting). When diluted with THF, the water structure is significantly weakened due to reductions in direct hydrogen bonding interactions while the water and THF molecules readily associate with each other as a result of dipole-dipole interactions. Even though the PET substrate polymers contain polar groups which may permit strong interactions with polar surface liquids, the particular solvent ratio optimized for this project (48/52% water/THF by volume) appeared to result in a surface tension that was still higher than the PET substrate. While this ratio is nowhere close to azeotrope concentrations, the reduction in direct hydrogen bond interactions between water molecules enhances their removal (evaporation) during the coating process which addresses condition (5) above. Finally, incorporation of FC-170 into the solvent system reduces the net surface tension of the water/THF mixture below that of the PET substrate resulting in spontaneous wetting/spreading.

A semi-quantitative perspective of these effects can be demonstrated by adapting the well-known spreading equation which is originally derived from the unit-area free energy change that occurs during the wetting process,

$$\frac{-\Delta G}{A} = \gamma_{PET} - (\gamma_{PS} + \gamma_S) = S$$

where S is the spreading coefficient (free energy change per unit surface area wetted, $-\Delta G / A$) which must take on positive values when wetting occurs readily (or spontaneously) and negative values when wetting does not occur; γ_{PET} is the surface tension (energy) of the PET substrate, γ_S is the surface energy of the solvent system and γ_{PS} is the interfacial energy between the PET substrate and the solvent (in all cases, γ takes the units of mJ/m^2 or dynes/cm). Good and Girifalco have proposed an alternative form of this concept by eliminating the interfacial energy and introducing a fractional factor representing the degree of interaction ϕ, which approaches zero when there are no interactions between substrate and solvent, and unity when there are strong interactions:

$$S = 2\gamma_S\left(\phi\sqrt{\frac{\gamma_P}{\gamma_S}} - 1\right)$$

Using literature resources and vendor technical publications, the following approximations were surmised:

$$\gamma_{PET} = 43\ ,\ \gamma_{THF} = 26\ ,\ \gamma_{H_2O} = 72\ ,\ \gamma_{THF/H_2O} \sim 72\times 48\% + 26\times 52\% \cong 48 \text{ and}$$

$$\gamma_{THF/H_2O/FC170} \sim 28\times 48\% + 26\times 52\% \cong 27$$

where solvent volume fractions are used and the resulting surface tension of FC-170/water solution was taken as 28 dynes/cm as suggested from 3M product literature for various liquids. Now the interaction factor ϕ, is very difficult to determine with accuracy. However, for simplified, illustrative purposes, let $\phi \sim 1$, analogous to situations of strong interactions such as hydrocarbon on hydrocarbon or polar on polar systems. Then…

$$S_{H_2O} = 2\times 72\times\left(\sqrt{43/72} - 1\right) = -92.6$$

$$S_{THF} = 2\times 26\times\left(\sqrt{43/26} - 1\right) = +14.9$$

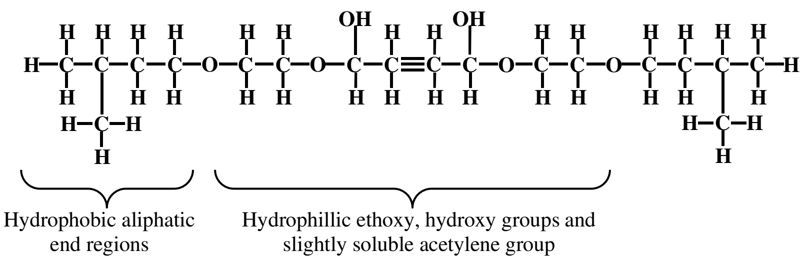
$$S_{H_2O/THF} = 2\times 48\times\left(\sqrt{43/48} - 1\right) = -5.1$$

$$S_{H_2O/THF/FC170} = 2\times 27\times\left(\sqrt{43/27} - 1\right) = +14.1$$

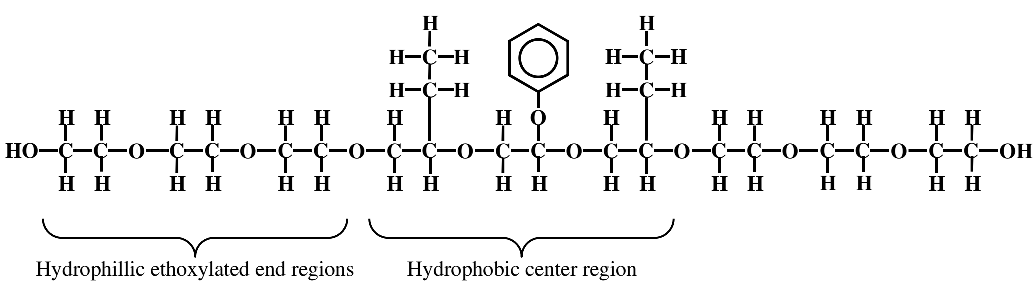
which clearly illustrates the ‘beading’ nature of water on low energy surfaces, the spontaneous wettability of 100% THF, the improvement in wetting/spreading for water/THF mixtures and the enormous improvement when FC-170 is employed.

(2) While FC-170 was a mandatory requirement for wetting, spreading and adhesion of the water/THF/resin system, another agent would be necessary to promote suspension and stabilization of the magnetic particulate phase in the formulation. Of all the materials evaluated for providing effective dispersions of γ-Fe_2O_3 particles and preventing their flocculation throughout the milling and grinding processes, Surfynol CT-136 demonstrated the highest efficiency and compatibility with the other formulation components (the Surfynol series of products are manufactured by Air Products & Chemicals). Again, the proprietary structure and chemistry of this material can only indulge one to speculate. AP&C product data sheets describe the material as a high HLB anionic/nonionic adduct mixture that is 52% active. As with other products in the Surfynol series, it is suspected that CT-136 attains its water solubility with the presence of oxyethylene (ethoxy) groups and primary/secondary alcohols, and its hydrophobic character by use of higher alkoxy groups along with the unique actetylene group (carbon-carbon triple bond). There is little doubt that several components in the CT-136 formuation were responsible for the overall properties of this unique material. At least three of the components are the principal agents providing excellent particle suspension and dispersability that was demonstrated with the proposed resin/solvent system for this project. While the acetylene group is generally hydrophobic, it can exhibit a slight affinity for water due to weak hydrogen bonding interactions, and this property most likely played an important role in the benefits observed during fomulation trials. The structural form utilized in many of the Surfynol products incorporates two water-soluble secondary hydroxy groups, one on each allyl carbon between the triple bond which apparently participates in the hydrophilicity of the compound. Thus, it is surmised that two of the principal components can be classified as an aliphatic acetylenic diol and an aliphatic/aromatic ethoxy ethanol both with symmetrically functional structures which act together, synergistically. Simplified, possible structures of these two components are represented below.

Acetylenic Diol



Aromatic/Aliphatic Ethoxylated Alcohol



Both of these compounds are considered to be nonionic. However, the third critical component appears to be a charged polymer phase, perhaps an acrylic or polyester dispersion which imparts a certain degree of anionic character to the material. It is possible this anionic polymer phase may have acted directly at the particle interface synergistically interacting with the other two agents enhancing particle dispersion stability. Other benefits from use of CT-136 included foam reduction and compatibility with the other formulation components (water, THF, FC-170, the primary solvent-based resin and secondary latex resin). It is believed that condition (4) above was adequately addressed due to the de-foaming properties exhibited by both CT-136 and FC-170 and no additional de-foaming agent was required for the formualtion. The product data sheet rated CT-136 as a high HLB material of pH 8. It is suspected that the net HBL value of this material was > ~ 12 in accordance with levels that promote particle dispersion. In addition. the high pH level was inevitably related to the fact that the water/FC-170 solution required basic rendering in order to be effective in the formulation. Anolgous to FC-170, CT-136 was an absolute necessity in the formulation. This component was proven to prevent particle flocculation, enhance the milling (grinding) process and optimize magnetic properties that were required in the end product such as coercivity, remnant magnetization, squareness and orientation ratio (for further discussions in associated magnetic concepts, see the project report, “Particle Size Reduction & Control During Milling of Magnetic Slurries” and the publication, “Magnetic Characterization of Thick Film Chromium Dioxide Coatings”).

(3) The exact nature of this emulsion was not certain. Variations in either solvent of about 10% beyond the 52/48% ratio resulted in slurries that were inadequate for coating operations. However, increased additions of THF appeared to produce more devastating results (in terms of emulsion stability) than did additions of water/FC-170 solution (dilution to a certain point with any solvent will de-stabilze an emulsion). Thus, it is probably acceptable to say that this system could be classified as an oil-in-water emulsion. It might be noted that the primary resin (Vylon) was a functionalized polymer that exhibited complete and rapid dissolution in THF with a slight tendency to emulsify in FC-170/water solution (at low concentration), while the secondary resin *was* a dispersion/emulsion that displayed poor results upon dilution with THF. There is no doubt that both CT-136 and FC-170 played dominant roles in the emulsion stability of the formulation at this point. Samples prepared with all the components discussed thus far demonstrated results that were essentially identical to company's solvent-based counterpart in terms of processability and formulation stability. Slight phase separations could sometimes be seen during sample drawdowns and coating trials, and the ultimate magnetic properties were not believed to be fully optimal. However, these conditions were occasionally addressed with the solvent-based products due to inadvertant formulation and processing variations.

At this point in the project, performance of the formulation was impressive. Tweaking of the existing component concentrations, the formulation sequence and the milling/mixing/blending process provided even further improvements. However, trials were continued in efforts to identify any possible agents that could further enhance the system. It was felt that a third and final agent would be of great benefit to further stabilize the emulsion nature of our formulation (resin droplets dispersed in water/THF). Of all the materials sampled, Rhone Poulenc's Colloid 226/35 demonstrated noticeable benefits in short and long-term emulsion stability, which ultimately resulted in smoother slurry processing and coating operations, and very impressive magnetic properties (indicating superior particle dispersion). Colloid 226/35 is described as an anionic acrylic polymer and is believed to be strongly absorbed at resin-solvent interfaces. Thus, the enhanced stabilization that was observed by addition of Colliod 226/35 could very well be a result of any or all three effects: (a) resin-solvent interfacial tension reduction, (b) a mechanical or viscous barrier around droplets retarding coalescence, and (c) charges imparted to the droplets from the anionic Colloid 226/35 molecules form an electrical double layer retarding droplet flocculation and coalescence.

Conditions (4) and (5) were satisfied and addressed in previous paragraphs. It is believed that all surfactants utilized were well below their CMC for this particular formulation. In addition, there were no signs of incompatible interactions between the three surfactants or between the surfactants and the resin/binders such as viscosity increases, surfactant aggregation, particle flocculation, premature coalescence, sustaining phase separations, creaming or breaking. While subsequent coating runs on company production lines proved the water/THF formulation to meet or exceed the standard THF-based product in terms of processibility and product performance, the details and results will not be addressed here. The final formulation worksheet can be viewed in the project report "An Original Water-Based, Lacquer-Latex Flexible Coating Formulation". Details concerning candidate resins that were researched and evaluated for the formulation can be reviewed in the project report "Innovative Polymers & Hybrids for Elastomeric Resin Binder Systems".

An almost complete list of the surfactant materials evaluated for this study is given in the following table.

FORMULATION ADDITIVES

Vendor/Supplier	Trade Name	Advertised Function	Chemical Type
ADM Ross & Rowe	Yelkinol G	wetting agent / dispersant	nonionic lecithin form
Air Products and	Surfynol 104 E	wetting agent / defoamer	nonionic proprietary acetylenic diol HLB 4
Chemicals Inc.	Surfynol 104PG-50	wetting agent / defoamer	nonionic proprietary acetylenic diol HLB 4
	Surfynol 420	wetting agent / defoamer	nonionic ethoxylated acetylenic diol HLB 4
	Surfynol 440	wetting agent / defoamer	nonionic ethoxylated acetylenic diol HLB 8
	Surfynol 465	wetting agent / defoamer	nonionic ethoxylated acetylenic diol HLB 13
	Surfynol 485	wetting agent / defoamer	nonionic ethoxylated acetylenic diol HLB 17
	Surfynol 502	wetting agent / defoamer	nonionic modified acetylenic diol
	Surfynol SE-F	wetting agent / defoamer	nonionic ethoxylated acetylenic diol
	Surfynol TO	wetting agent / grinding aid	nonionic modified acetylenic diol HLB 10
	Surfynol GA	dispersant / grinding aid	nonionic modified acetylenic diol HLB 13
	Surfynol CT-131	dispersant / grinding aid	nonionic/anionic solvent free proprietary mixture
	Surfynol CT-136	dispersant / grinding aid	anionic proprietary mixture for high HLB
	Surfynol CT-141	wetting agent / dispersant	anionic proprietary mixture for high HLB
	Surfynol CT-324	wetting agent / dispersant	anionic proprietary mixture for high HLB
	Surfynol DF-58	anti- foaming agent	nonionic organo — modified silicone
	Surfynol DF-75	anti- foaming agent	nonionic organic— based
	Surfynol DF-110D	anti— foaming agent	nonionic acetylenic— based
	Surfynol DF-695	anti — foaming agent	nonionic silicone — based
Albright and Wilson	Briquest 301-50A	deflocculant /complexer	amino tri(methylene phosphonic acid)
Americas Inc.	Eltesol SX 93	dispersant / coupling agent	sodium xylene sulfonate NaSO3C8H10
	Empicol LZ/D	dispersant / complexer	sodium C12— C18 alkylsulfate
	STPP	dispersant / complexer	sodium tripolyphosphate Na5P3O10
	KTPP	dispersant / complexer	potassium tripolyphosphate K5P3O10
	Albrite TBPO4	plasticizer/ flame retardant	tri butyl phosphate C12H2,PO,
Angus Chemical Co.	AMP -95	dispersant / emulsifier	2 - amino —2 — methyl— 1 — propanol
	NiPar 640	wetting agent / dispersant	nitro ethane + nitro propane
	Alkaterge— E	wetting agent / dispersant	ethyl hydroxymethyl oleyl oxazoline
	Alkaterge-T	dispersant / anti— corrosive	heptadecenyl ethyl oxazoline methanol
BKY Chemie	BKY - P 104 S	wetting agent / dispersant	unsaturated polysiloxane/polycarboxylic acid
	BKY - 155	polymeric dispersant	anionic sodium salt of acrylic acid copolymer
	BKY - 156	polymeric dispersant	anionic ammonium salt of acrylic copolymer
	Disperbyk	wetting agent / dispersant	alkylol ammonium salt of polycarboxylic acid
	Disperbyk - 110	wetting agent / dispersant	copolymer with acidic groups
	Disperbyk - 160	wetting agent / dispersant	blocked copolymers with pigment affinity groups
	Disperbyk- 181	wetting agent / dispersant	anionic alkanlammonium salt of funtional polymer
	Lactimon - WS	wetting agent / dispersant	anionic polycarboxylic acid with amine in silicone
Buckman Laboratories	Busperse 39	wetting agent / dispersant	sodium neutralized polyacrylate
Inc.	Busperse 47	wetting agent / dispersant	anionic fatty acid in DMF
	Busperse 203	wetting agent / dispersant	proprietary polyacrylate
	Busperse 229	wetting agent / dispersant	Busperse 39 + Busperse 47
	Busperse 275	wetting agent / dispersant	un— neutralized polyacrylate
Central Soya	Actiflo 68 -UB	wetting agent / dispersant	nonionic lecithin complex HLB 2
	Centrolex-P	wetting agent / dispersant	nonionic lecithin complex HLB 7
	Blendmax 322- D	wetting agent / dispersant	nonionic lecithin complex HLB 8
	Centrol CA	wetting agent / dispersant	nonionic lecithin complex HLB 6
	Centrobake 100 -L	wetting agent / dispersant	nonionic lecithin complex high HLB
	Centrolene A	wetting agent / dispersant	nonionic lecithin complex HLB 10
	Centrolex-P	wetting agent / dispersant	nonionic lecithin complex HLB 7
	Centromix— E	wetting agent / dispersant	nonionic lecithin complex HLB 12
	Centrophase 31	wetting agent / dispersant	nonionic lecithin complex HLB 4
	Centrophase C	wetting agent / dispersant	nonionic lecithin complex HLB 4
	Centrophase NW	wetting agent / dispersant	nonionic lecithin complex HLB 4
Chartwell International	B-515	adhesion promoter	aluminum — amino complex
Inc.	B-515.1	adhesion promoter	bimetallic— amino complex
	B-525	adhesion promoter	aluminum— carboxyl complex
	B-525.1	adhesion promoter	bimetallic— amino complex
Cook Composites and	Coroc A-620-A2	leveling agent / grinding aid	polyacrylate in solvents
Polymers	Coroc A-2201-M	leveling agent	polyacrylate in solvents
	Coroc A-2678-M	leveling agent / grinding aid	water reduced polyacrylate
	Coroc A-3661-E3	dispersant / grinding aid	polyacrylate in solvents
	Coroc R-1623-M3	leveling agent	polyester microgel in solvents
	Coroc A-2SSO-W	leveling agent	aqueous acrylic microgel
	Coroc A- 4023- M 3	leveling agent	acrylic microgel in solvents
Daniel Products Co.	Disperse Ayd 1	wetting agent / dispersant	surfactant alkyd dispersion in spirits
	Disperse Ayd 6	wetting agent / dispersant	anionic dispersants in xylene
	Disperse Ayd 8	welting agent / dispersant	surfactant alkyd dispersion in spirits
	Disperse Ayd 15	wetting agent / dispersant	acrylic dispersion in glycol acetate
	Disperse Ayd W-22	welling agent /dispersant	nonionic/anionic synergistic blend
	Disperse Ayd W-28	wetting agent / dispersant	nonionic/anionic synergistic blend
	Dapro W-77	wetting agent	nonionic/anionic synergistic blend

FORMULATION ADDITIVES

Dexter Chemicals	Strodex PK-80A	wetting agent / dispersant	anionic ethoxylated alkyl phosphate ester
	Strodex PK-95G	wetting agent / dispersant	anionic ethoxylated alkyl phosphate ester
	Dextrol OC-15	wetting agent / dispersant	anionic ethoxylated alkyl phenoxy phosphate
	Dextrol OC-20	wetting agent / dispersant	anionic ethoxylated alkyl phenoxy phosphate
	Dextrol OC-50	wetting agent / dispersant	anionic ethoxylated alkyl phenoxy phosphate
	Dextrol OC-70	wetting agent / dispersant	anionic ethoxylated alkyl phenoxy phosphate
Dow Chemicals	Dowfax 2A1	wetting agent / dispersant	anionic aliphatic diphenyl oxide disulfonate
	Dowfax 2EP	wetting agent / dispersant	anionic aliphatic diphenyl oxide disulfonate
	Dowfax 3B2	wetting agent / dispersant	anionic aliphatic diphenyl oxide disulfonate
Harcross Organics	T-Mulz 565	wetting agent / dispersant	anionic phosphate ester blend
	T-Mulz 598	wetting agent / dispersant	anionic phosphate ester blend
	T-Det N-4	wetting agent / dispersant	nonionic ethoxylated nonyl phenol HLB 9
	T-Det N-8	wetting agent / dispersant	nonionic ethoxylated nonyl phenol HLB 12
	T-Det N-12	wetting agent / dispersant	nonionic ethoxylated nonyl phenol HLB 14
Henkel Corp.	Disponil SMO 100 F-I	dispersant	nonionic ethoxylated sorbitan oleate HLB 4
	Hyonic GL 400	wetting agent / dispersant	nonionic ethoxylated nonyl phenol HLB 18
	Hyonic PE 260	wetting agent / dispersant	nonionic ethoxylated nonyl phenol HLB 13
	Lomar PWA	dispersant	anionic ammonium naphthalene sulfonate
	Nopco 1186 A	wetting agent	anionic dioctyl sodium sulfosuccinate
	Nopcosperse 44	dispersant / wetting agent	anionic polyelectrolyte
	Disponil 05	wetting agent / dispersant	nonionic proprietary surfactant
	Texaphor 963	dispersant / grinding aid	polycarboxylate and amines in aromatics
	Texaphor 3061	wetting agent / dispersant	polycarboxylate in aromatic solvents
	Texaphor VP 3098	wetting agent / dispersant	polycarbonic acid in xylene
	Texaphor Special	anti— settling agent	mixture of anionic surfactants in solvent
	Perenol F 40	leveling agent	acrylate copolymer solution
ICI Americas	Atmer 110	anti— static agent	polyoxyethelene sorbitan laurate
	Atmer 163	anti— stat neutralizing agent	N, N-Bis (2 — hydroxyethyl) alkylamine
	Hypermer LP6	particle dispersant	proprietary polymer
	Hypermer LP7	particle dispersant	proprietary polymer
	Hypermer LP8	particle dispersant	proprietary polymer
	Hypermer PS3	particle dispersant	proprietary polymer
King Industries	K-Sperse 152	dispersant/wetting agent	organo zinc sulfonate
	Dislon KS-281	anti -floating agent	nonionic /anionic amine salts of polyesters
	Dislon 873 N	wetting agent / dispersant	nonionic/ anionic amine salts of polyesters
	Dislon 3600 N	anti-sag/anti-settling agent	nonionic polyether / ester thixotrope
	Dislon 4200-10	anti — sag / anti — settling agent	wax— based polyolefin thixotrope
	Dislon 6500	anti— sag /anti— settling agent	nonreactive polyamide thixotrope
	Dislon 6900-20X	anti — sag / anti — settling agent	nonreactive polyamide thixotrope
	Dislon 7004	wetting agent / dispersant	anionic polyether / ester
	Dislon L-1983	level agent / defoamer	nonionic polyacrylate low polarity
	Dislon L-1982	leveling agent	nonionic polyacrylate medium low polarity
	Dislon L-1984	leveling agent	nonionic polyacrylate medium high polarity
	Dislon L-1980	leveling agent / dispersant	nonionic polyacrylate high polarity
	Dislon OX-70	anti — foaming agent	nonionic polyacrylate low polarity
	Dislon OX- 60	anti-foaming agent	nonionic polyacrylate medium low polarity
	Dislon 1950	anti — foaming agent	nonionic polyacrylate medium high polarity
	Dislon 1970	anti-foaming agent	nonionic polyacrylate high polarity
Lubrizol Corp.	Lubrizol 2061	adhesion promoter	anionic acid of alkyl phosphate ester
	Lubrizol 2062	adhesion promoter	anionic acid of alkyl/aryl phosphate ester
	Lubrizol 2063	adhesion promoter	anionic acid of carboxy phosphate ester
	Lubrizol 2152	dispersant/wetting agent	anionic calcium sulfonate
	Lubrizol 2155	dispersant/wetting agent	nonionic alkyl amide alkene amine
	Lubrizol 2401	surfactant monomer	alkene amido sulfonic acid
	Lubrizol 2405	surfactant monomer	alkene amido sodium sulfonate
	Ircosperse 2170	dispersant/wetting agent	hydroxy ethylated amino ethyl amide
	Ircosperse 2171	dispersant / wetting agent	polyolefin anhydride
	Ircosperse 2172	dispersant/wetting agent	polyolefin amide alkene amine
	Ircosperse 2174	dispersant / wetting agent	alkyl amino polyester
	Ircosperse 2177	dispersant / wetting agent	hydroxy alkylated amine phenol
Monsanto Corp.	Modaflow Resin	leveling /wetting agent	alkyl ester acrylate copolymer
	Multiflow Resin	leveling / wetting agent	alkyl ester acrylate copolymer
	Madaflow 2100	leveling / wetting agent	alkyl ester acrylate copolymer
3M Industrial Chemical	Fluorad FC-99	wetting / leveling agent	anionic perfluoroalkyl sulfonates
Products Div.	Fluorad FC-120	wetting / leveling agent	anionic perfluoroalkyl sulfonates
	Fluorad FC-129	wetting / leveling agent	anionic fluoro alkyl carboxylates
	Fluorad FC-170C	wetting / leveling agent	nonionic fluoro polyoxyethylene ethanols
	Fluorad FC-171	wetting /leveling agent	nonionic fluoro alkyl alkoxylates
	Fluorad FC-430	wetting / leveling agent	nonionic fluoro alkyl esters
Niacet Corp.	Niaproof 4	wetting agent / penetrant	sodium tetradecyl sulfate
	Niaproof 8	wetting agent / penetrant	sodium 2-ethylhexyl sulfate

FORMULATION ADDITIVES

OM Group	Dri-Rx	drying accelerator	glycol ether metal complexer
	Co Hydro -Cure	drying accelerator	cobalt napthenate in mineral spirits
	Mn Hydro -Cure	drying accelerator	manganese carboxylates in mineral spirits
	Zr Hydro -Cem	drying accelerator	zirconium carboxylates in mineral spirits
	Spurso	anti— floating / dispersant	proprietary alkyd in mineral spirits
Paint Chemicals	No. 901 G.D.A	grinding aid / dispersant	nonionic acetylenic diol in solvents
	ASASWA	wetting /anti— sagging agent	cationic non- acrylic polymer
	Chem-Rez J-50	wetting / leveling agent	nonionic acetylenic diol in solvents
	HSWADA	wetting agent / dispersant	nonionic acrylic polymer
	WRAPA	wetting / leveling agent	anionic water reducible non— acrylate
PPG Industries	Avanel S-74	wetting agent / dispersant	anionic proprietary cleaning surfactant
	Macol OP-10 SP	wetting agent / dispersant	nonionic octyl phenol ethoxylates
	Mapeg 400 ML	wetting agent / dispersant	nonionic polyethylene glycol ester
	Maphos 60 A	wetting agent / dispersant	anionic aliphatic phosphate ester
	Mazclean EP	wetting agent / dispersant	nonionic emulsifier for d— limonene
	Maztreat 76	anti -foaming agent	nonionic proprietary organic blend
	Mazsperse 85 B	wetting agent / dispersant	nonionic ethoxylated sorbitan trioleate
	Mazsperse 264 A	anti-static agent	cationic quarternary ammonium etho sulfate
	Mazsperse 1525-90	wetting agent / dispersant	nonionic proprietary ethoxylate
	Mazwet DF	wetting agent / dispersant	nonionic proprietary ethoxylate
	S-Maz 85	wetting agent / dispersant	nonionic sorbitan trioleate
	T-Maz 85	wetting agent / dispersant	nonionic ethoxylated sorbitan trioleate
	Mazon SAM-211	wetting agent / dispersant	anionic polyalkoxy sulfate monomer
Rhone Poulenc	Colloid 102	wetting agent / dispersant	anionic acrylic polymer MW 3400
	Colloid 204	wetting agent / dispersant	anionic acrylic polymer MW 10000
	Colloid 225	wetting agent / dispersant	anionic acrylic polymer
	Colloid 226/35	wetting agent / dispersant	anionic acrylic polymer
	Colloid 270 D	wetting agent / dispersant	anionic acrylic polymer MW 3200
	Colloid 284	wetting agent / dispersant	anionic acrylic polymer MW 2200
	Colloid 286	wetting agent / dispersant	anionic acrylic copolymer
	Manchem APG X	coupling agent / dispersant	zircoaluminum — organic complex
	Manchem APG -2	coupling agent / dispersant	zircoaluminum — organic complex
	Manomet 10	coupling agent / dispersant	zinc /aluminum— organic complex
Riceland Foods	Lecigran MT-2	wetting agent / dispersant	granule soybean lecithin complex
	Lecigran MT-3	wetting agent / dispersant	powdered soybean lecithin complex
Synthetic Products	Synpro 303	anti-settling thixotrope	aluminum salt of stearic acid (Al distearate)
Troy Chemical	Troysol AFP	wetting /anti-floating agent	CaCO, with surfactants and dispersants
	Troysol 98 C	wetting agent / dispersant	amphoteric fatty amine
	Troysol CD-1	dispersant / wetting agent	polymeric oil derivative
	Troysol CD -2	dispersant / wetting agent	modified vegetable oil derivative
	Troysol LAC	wetting / leveling agent	anionic proprietary surfactant mixture
	Troysol Q 148	defoamer/ leveling agent	modified siloxane copolymer
	Troysol S366	wetting / leveling agent	nonionic siloxane copolymer
	Troysol U.G.A	dispersant /grinding aid	nonionic proprietary surfactant mixture
	Troysperse W 516-2	wetting agent / dispersant	amphoteric proprietary surfactant mixture
Union Carbide	Silwet L-77	wetting / leveling agent	nonionic Si ethoxylate low HLB MW 600
	Silwet L-7210	dispersant / leveling agent	nonionic Si ethoxylate low HLB MW13000
	Silwet L-7602	wetting agent / dispersant	nonionic Si ethoxylate low HLB MW 3000
	Silwet L-76&4	wetting agent / dispersant	nonionic Si ethoxylate high HLB MW 4000
	Triton N-57	wetting agent / dispersant	nonionic nonyl phenol ethoxylate HLB 10
	Triton N-101	wetting agent / dispersant	nonionic nonyl phenol ethoxylate HLB 13
	Triton X-45	wetting agent / dispersant	nonionic octyl phenol ethoxylate HLB 10
	Triton X-100	wetting agent / dispersant	nonionic octyl phenol ethoxylate HLB 14
	Tergitol 15-S-5	wetting agent / dispersant	nonionic alkyl ethoxylate MW 420 HLB 11
	Tergitol 15-S-7	wetting agent / dispersant	nonionic alkyl ethoxylate MW 508 HLB 12
	Tergitol 15 -S- 9	wetting agent / dispersant	nonionic alkyl ethoxylate MW 596 HLB 13
	Tergitol 15-S-15	wetting agent / dispersant	nonionic alkyl ethoxylate MW 860 HLB 16
	Tergitol TMN-6	wetting agent / dispersant	nonionic alkyl ethoxylate MW 543 HLB 12
	Tergitol XJ	wetting agent / dispersant	nonionic alkyl alkoxylate MW 2506
	Tergitol D-683	wetting agent / dispersant	nonionic alkylphenol alkoxylate MW 990
Witco Organics Div.	Emcol 4500	wetting agent / dispersant	anionic sodium dioctyl sulfosuccinate
	Petro 425	dispersant / wetting agent	sodium alkyl napthalene sulfonate
	Witflow 901	wetting agent / dispersant	sodium dioctyl sulfosuccinate
	Witflow 902	wetting agent / dispersant	sodium oleoyl isopropanol amide sulfosuccinate
	Witflow 912	dispersant / anti— corrosive	proprietary mixture of surfactants
	Witflow 918	dispersing agent	alkylaryl isopropylamine sulfonate
	Witflow 934	wetting agent / dispersant	modified fatty acid diethanolamide
	Witflow 950	wetting agent / grinding aid	polypropoxy amino quaternary NH4 Cl
	Witflow 953	wetting agent / grinding aid	polypropoxy alkyl quaternary NH4 Cl
	Bubble Breaker 748	defoaming agent	silicone— free surfactant blend
	Bubble Breaker 3056 A	defoaming agent	reacted silica in mineral oil / surfactant blend
	Kemamine P-999	dispersant /anti-static agent	unsaturated fatty amine mixture