

A COMPARISON OF SOLVENT AND WATER-BORNE ALKYD COATINGS &
THE HISTORY OF VOC REGULATION IN THE UNITED STATES

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Molly Elise Burns
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COMMITTEE MEMBERSHIP

TITLE: A Comparison of Solvent and Water-Borne
Alkyd Coatings & The History of VOC
Regulation in the United States

AUTHOR: Molly Elise Burns

DATE SUBMITTED: August 2016

COMMITTEE CHAIR: Raymond Fernando, Ph.D.
Professor of Chemistry, Director of
Polymers and Coatings Program

COMMITTEE MEMBER: Tammy Campbell, Ph.D.
Assistant Professor of Chemistry and
Biochemistry

COMMITTEE MEMBER: Chad Immoos, Ph.D.
Professor of Chemistry and Biochemistry

ABSTRACT

A Comparison of Solvent and Water-Borne Alkyd Coatings and The History of VOC

Regulation in the United States

Molly Elise Burns

Conventional solvent based alkyd coatings have gone out of favor due to concerns over volatile organic compound (VOC) content. However, due to recent focus on renewable raw materials, alkyds are making a comeback in waterborne form. Water based alkyd coatings are known to have poor shelf stability and corrosion resistance, as well as other problems during the formulation process. This part of the project focused on comparing solvent borne to two types of water-borne alkyds, water reducible alkyds and alkyds emulsions. The purpose was to understand the differences between the three types of alkyds in terms of their production and final properties. It was ultimately hoped that the formulations used for this project would prove to solve the problems normally experienced by waterborne alkyds.

After testing several chemical and physical properties, it was determined that the solvent borne alkyd coatings performed better than both water based systems in corrosion resistance, accelerated weathering, and shelf stability but the water reducible and emulsion alkyd coatings performed similarly to the solvent borne alkyd in gloss, contrast ratio, and durability. The VOC emissions for all three alkyd types were as expected; the solvent borne had the highest emission at 253 g/L, followed by water reducible with 166 g/L, and emulsion with 34 g/L.

Following the focus on solvent based alkyd coatings and their potential hazards, a secondary part of this project focused on volatile organic compounds (VOCs) and answering the question of how volatile organic compound regulation in the United States (U.S.) evolved. It quickly became apparent that no comprehensive answer to this question existed. Part two of this project is an attempt to answer this question in a comprehensive manner.

VOC regulations started in California in the late 1970s, and paints and coatings became a nationally regulated emission source by the 1990s. The U.S. government limited harmful emissions, such as smog and compounds contributing to ozone depletion, through Clean Air Acts. The first Clean Air Act was enacted in 1965, but it wasn't until the Clean Air Act of 1990 that VOC emissions became a focus. VOCs are not inherently hazardous but are a source of concern because they serve as a precursor to the formation of damaging ground level ozone.

The Environmental Protection Agency (EPA) has established the minimum VOC emission limits in the Architectural and Industrial Maintenance (AIM) federal rule, but each state or state subdivision can enforce stricter limits within their borders. The strictest limits are set by the South Coast Air Quality Management District (SCAQMD) in Southern California, but other entities exist. This report thoroughly documents the history of VOC regulation in the United States by collecting, combining, organizing, and summarizing information gathered from various industries and government publications, agency members, and industrial and academic professionals.

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A Comparison of Solvent and Water-Borne Alkyd Coatings and The History of VOC Regulation in the United States

1. INTRODUCTION TO ALKYD EXPERIMENT

The paragraphs and contents below detail the information on the part of the project directly relating to “A Comparison of the Solvent and Water-Borne Alkyd Coatings”.

1.1 STATEMENT OF PROBLEM

Alkyd coatings are popular, versatile, and frequently used in the automotive, industrial, and architectural industries.¹ The first alkyds developed were solvent based; however, the abundance of solvents that these coatings contained proved to be harmful to human health and the environment. Partially driven by volatile organic compound (VOC) regulation, water based alkyd coatings were developed as a replacement for the solvent borne technology. The first type of waterborne alkyd coating to be created was a water reducible alkyd; unfortunately, this product still contained relatively high levels of VOCs. With an attempt to develop a very low-VOC paint, alkyd emulsions were developed. This water-in-oil to oil-in-water based technology was formulated at VOC levels significantly lower than the water reducible or solvent borne alkyd coatings. Originally, both types of waterborne alkyd coatings did not possess the properties for which solvent borne alkyds are known for, such as corrosion resistance, hiding power, and shelf stability.²

Currently, water reducible alkyds and alkyd emulsion coatings have properties similar to solvent based alkyd coatings, with the exception of weather and corrosion resistance and shelf stability. These problems need to be resolved for both types of

waterborne alkyd coatings before they can fully replace their solvent based counterparts. This is particularly true for alkyd emulsion coatings, which are not popular commercially available products. This project investigated the magnitude of the performance differences between solvent borne, water reducible, and emulsion based alkyd coatings through direct comparison of representative formulations adjusted to have a similar visual appearance.

1.2 LIST OF TERMS

Alkyd – a resin made from reacting a polyol, dicarboxylic acid, and a fatty acid

DI – deionized (water)

Flats – matte or non-glossy coatings

Non-flats – glossy coatings

NV – Non-volatiles

SB – ‘solvent borne’

VOC – volatile organic compound

WB – ‘water borne’

WR – ‘water reducible’

1.3 PURPOSE OF STUDY

The purpose of this project was to understand the differences and similarities between solvent borne alkyds coatings and two types of waterborne coatings, water reducible alkyds and alkyd emulsions. The formulations used for each type of coating were modified from commercially available starting point formulations. The main reason for altering the starting point formulations was product availability. If the altered formulation improved the properties of the water based alkyd coatings, which were already known to have several inferior properties in comparison to the solvent based counterpart, then an important breakthrough would be made.

In addition to modifying formulations, testing, and comparing the properties of the alkyd coatings, laboratory experiments were designed for the use of the Polymers and Coatings Master's Program. This portion of the project expanded on the purpose of gaining experience with designing formulations and experiments. Four experiments were developed, one each for solvent borne and alkyd emulsion and two for water reducible, and includes instructions on what to test for, how to make each type of alkyd coating, and final requirements in terms of a paper and presentation about the performed experiment. It is hoped that with by conducting these designed experiments, future students will understand how to make alkyd coatings, the problems with water based alkyd coatings, and how to test for particular properties.

2. BACKGROUND ON ALKYD COATINGS

2.1 SYNTHESIS AND USE

The name of alkyd coatings originates from the resin used to create the coating. Originally called an ‘alcid’ for an ‘alcohol’ and ‘acid’, alkyd resins are generally synthesized from an alcohol, dicarboxylic acid, and a fatty acid (see Figure 1).³ The synthesized resin is then mixed with other compounds to form the desired solvent or water based coating. The architectural, industrial, and automotive industries have favored solvent based alkyd coatings for several decades, yet waterborne alkyds have gained much attention for their improvements in air quality and safety. The main types of waterborne alkyds are water reducible alkyds and alkyd emulsions.⁴ Another category of waterborne alkyd coatings are water reducible resins that are copolymerized with other resins such as acrylics or urethanes; this waterborne option will not be discussed.

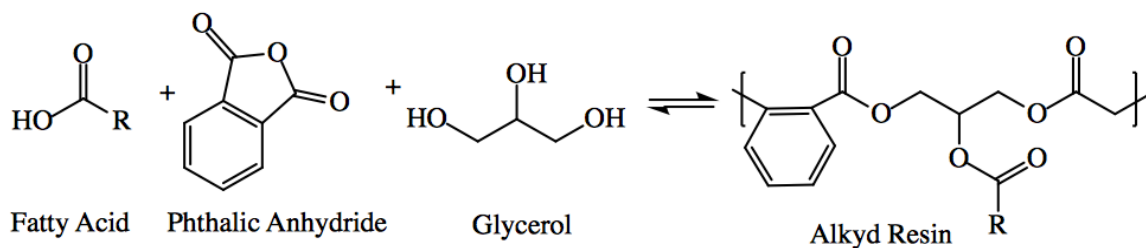


Figure 1. Overall reaction scheme for formulating an alkyd resin.

As previously mentioned, the solvent borne coatings have a few unfavorable properties. They are inherently high in VOCs, emit undesirable odors, and are a health risk for applicators. In contrast, water borne coatings are generally safer to make and handle, are less odorous, and have a reduced impact on the environment. One drawback of water-based paints is that they do not perform as well as their solvent based counterparts.¹

2.2 FORMULATION METHODS AND COMPONENTS

A high performance alkyd coating has many ingredients. In addition to the resin and continuous medium, pigments, dispersing agents, driers, and surfactants are commonly required. Other chemicals for the prevention of a top layer of skin, foam, and microbial growth are usually added, along with chemicals designed to control rheology, wetting, drying, and curing.⁴ The materials included in a formulation are dependent on the target properties and whether the dispersion medium is solvent or water-based.

A common medium used for solvent borne alkyd coatings is mineral spirits. Besides the dispersion medium, the most important component of an alkyd coating is the resin, as it dictates a majority of the properties in the resultant coating.⁵ Resins are not only designed for the medium they are to be dispersed but also depend on if they're to be used in interior, exterior, automotive, wood, or industrial maintenance applications. For an alkyd coating, there are three major resin types: solvent borne, water reducible, and alkyd emulsion. Each of these resins are classified by the type and saturation of the fatty acid used to develop the resin, as these two categories dictate the final coating properties.⁶

As seen in Figure 1, when the fatty acid is mixed with the phthalic anhydride and glycerol, a polyester containing fatty acid side groups is synthesized. This oil portion of the polyester alkyd resin is what undergoes oxidative crosslinking to create a dry film. The rate at which an applied film dries is dependent on the saturation of the fatty acid/oil.⁷ Saturated oils do not contain a double bond in the carbon chain, while unsaturated oils contain double bonds. Double bonds allow for resin crosslinking, and therefore curing, to occur in ambient conditions. Therefore, saturated oils are considered to be 'non-drying' while unsaturated oils are either 'semi-drying' or 'drying'. The difference between semi-

drying and drying classifications depends on the amount of double bonds and rate of cure. Non-drying oils can be cured with heat or certain types of light. Resins are also termed 'short', 'medium', or 'long', depending on the oil content within the resin. Long oil resins contain more than 60% oil, medium oil resins are 40-60% oil, and short oil resins are less than 40% oil.⁷ To summarize, resins are classified by whether they are meant for solvent or water-borne systems, the type of oil, and the amount (or 'length') of the oil. Common environmentally friendly oils include linseed, sunflower, soya, palm, and tung.⁵

To promote the crosslinking of the semi-drying and drying alkyd resins, catalysts are added. These catalysts, also referred to as 'driers', are metal based and can be tailored to promote drying on a coatings surface and beneath it. Surface driers, such as cobalt, manganese, lead, iron, or vanadium salts, are metals with more than one oxidation state and are responsible for the curing process. Through driers, like zirconium, strontium, lead, or lithium, ensure a uniform drying rate throughout the film to prevent wrinkling. Wrinkling is an undesirable defect caused when the film surface cures faster than the rest of the film. Other types of driers include auxiliary and wetting driers. Auxiliary driers such as calcium, barium, zinc, and potassium stabilize pH, decrease yellowing, and decrease the need of surface driers. Wetting driers, such as calcium, strontium, and barium salts, have an affinity for the pigment-resin phase border and stabilizes a coating during storage as a result. When using driers, a mixture of drier types is needed as no single metal is sufficient to catalyze fast and uniform drying.⁸

To prevent a coating from curing while in its canister, and thus to increase its shelf life, anti-skinning agents are added. Anti-skinning agents are oxygen scavengers that prevent the surface of a coating from oxidizing in the presence of air. These additives are

typically used in solvent borne alkyd coatings but is not necessary in waterborne alkyd coatings.⁹ Another way to prevent foam is to add defoamers. Foam is undesirable as it can last for hours or days after product production, reduce pigment grinding, and create defects in the final film. Defoamers work by destabilizing the bi-layer of a surfactant's wall to pop the bubble and release the trapped air. Most defoamers are silicone based and are predominately used in water-based systems.¹⁰

Every type of coating requires the addition of pigments. There are several different types and categories of pigments, including organic, inorganic, and low VOC.¹¹ This project uses titanium dioxide (TiO_2), a common white pigment that is available in different sizes, depending upon the use of the pigment. Similar to the resins, the type of pigment used depends on the continuous medium. In order to disperse the pigment particles into the system, a dispersing agent is used.¹¹ To understand the role of the dispersing agent, the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory can be utilized. DLVO theory was not mathematically determined in this project, but a brief introduction as to the usefulness of the DLVO theory and its application in industry paint formulations will be outlined.

This theory is based on electrostatic stabilization of colloids by determining inter-particle potentials between two particles; here the particles will be considered to be titanium dioxide but any two similar non-volatile particles can be used.¹² DLVO theory describes the van der Waals attraction and electrostatic repulsion forces of two particles of a certain distance away from each other. The range of the DLVO theory is determined by the ionic strength of the solution in which the particles are dispersed, and the thickness of the adsorbed layer of the dispersing agent. The distance between particles can be estimated

from the sizes of the particles, its concentration in solution, and the packing properties.¹² The attractive forces are not limited to van der Waals but also include London Dispersion, Keesom orientation forces, and Debye inductive forces.

The ratio of attractive and repulsive forces evaluated in the DLVO theory dictates the electrostatic stabilization, and charge stabilization, of two particles. The effect of these ratios is shown in Figure 2. At a certain distance, if two unbound or non-interacting particles experience greater attractive forces than repulsive forces, then the particles will become bound. Particles can either be reversibly or irreversibly bound. Two particles can only become irreversibly bound, also known as 'aggregated', when the repulsive forces cannot overcome the attractive forces. This concept is shown as the energy barrier in Figure 2.

The secondary minimum is synonymous with flocculation while the primary minimum indicates aggregation. Flocculated particles can be reversed and re-dispersed by sonication or some other type of agitation. These terms are not universal but mean the same thing. The energy barrier is the electrostatic barrier. The size of the barrier can be changed with ionic strength and distance between the particles; it is possible to not have any energy barrier depending on the type of system. The absence of an energy barrier causes rapid aggregation.

Between the stages of non-interacting and aggregated particles, lies a range of distance in which particles are flocculated. This reversible existence is when the attractive forces are more powerful than the repulsive forces. The degree of attractiveness, distance between the particles, and amount of energy within the system determines if the particles will stay flocculated, become unbound, or become irreversibly aggregated.

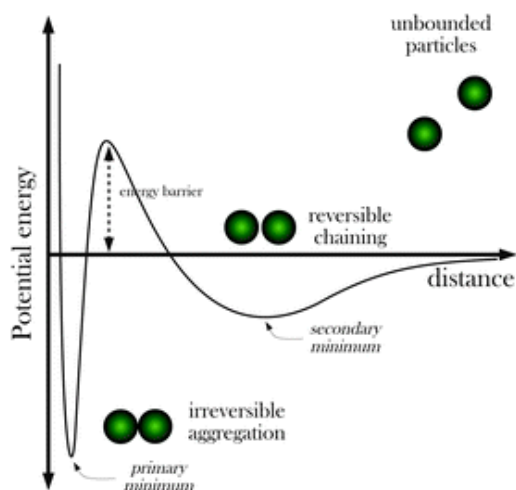


Figure 2.¹³ DLVO theory.

Usually, approximations with the DLVO theory are made from integrating the dispersion forces and geometrical approximations.¹² One of the results of this approximation is the Hamaker constant, which is used to describe the strength of the attractive forces between two particles. More complicated and accurate calculations for the DLVO theory exist, such as the Lifschitz calculations, but most paint formulators use simpler formulas and approximations.¹² In addition, DLVO equations exist for complicated situations such as pigments that are made from more than one material. The equations that exist to determine these DLVO approximations are not listed here, but can be found in Reference 12.

In addition to adding dispersing agents to stabilize the colloids and preventing irreversible aggregation, surfactants are also added to both the solvent and water-borne systems. The surfactants used for these coatings are typically nonionic and/or anionic and are used to increase stability of the colloids and decrease the surface tension of water.^{14,15} Nonionic surfactants are better at stabilizing alkyd emulsions than anionic surfactants by way of improving water sensitivity, increasing colloidal stability, and lowering foam

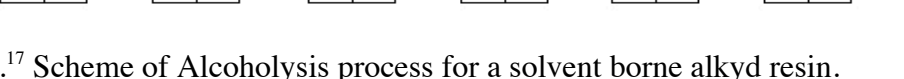
production. Anionic surfactants are used primarily for charge stabilization and can be used in conjunction with nonionic surfactants.¹⁵ Unfortunately, the use of surfactants can be problematic.^{14,15} They increase the VOC content and can deform an applied coating by swelling, pitting, or leaching.

Two additives used in waterborne alkyds but not their solvent based counterpart are co-solvents and bases. The purpose of a co-solvent is to increase resin solubility. Bases, such as ammonium hydroxide, are added to waterborne alkyds to reduce the acidity of the alkyd resin. This partial neutralization is necessary to be able to disperse the alkyd resin in water.¹⁶

Ultimately, when designing and using a coating formulation, it is important to ensure that each component is miscible in each other and will work together to produce the desired properties. This consideration into how each additive will react with each other is part of what makes coatings formulation so delicate, difficult, and rewarding. All alkyd coatings follow a two-step process: (1) developing the resin then (2) incorporation of the resin into the formulation to produce the final coating. The methods of developing each type of alkyd resin is detailed below.

2.2.1 SOLVENT BORNE ALKYDS

There are two main methods to develop a solvent borne alkyd resin. The first method is alcoholysis, also known as the glyceride process, and is based on transesterification of the fatty acid triglycerides into mono- and di- glyceride oils.¹⁷ Once the oil is broken down into a simpler glyceride, it is mixed with an abundance of anhydride to increase the molecular weight. The initial transesterification process is performed in the



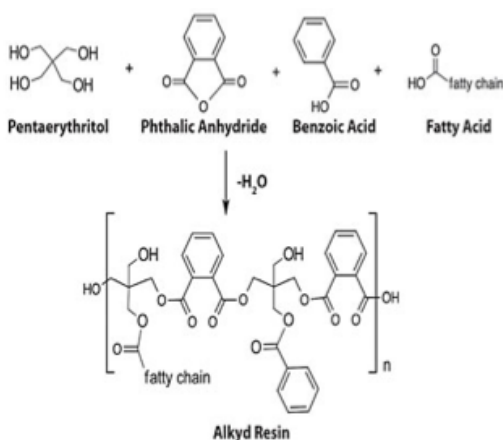


Figure 4.¹⁸ Scheme of fatty acid process for a solvent borne alkyd resin.

Once the solvent borne alkyd resins are made, they are purified and then diluted in solvent. The purification process removes water by heating the resin in an excess of acid or xylene. This process also lowers the viscosity. Once the resin is purified, it is diluted in solvent and ready to be used in a solvent borne alkyd coating formulation.¹⁸

2.2.2 WATER REDUCIBLE ALKYDS

Water reducible alkyds were the first type of waterborne alkyds developed.¹⁶ They contain lower amount of VOCs in comparison to the solvent borne alkyd coatings but still emit large amounts of VOCs. Solvent borne alkyd coatings can contain 400 g/L or more of VOCs; water reducible alkyds typically contain about half of that amount.² In addition to having a high VOC content, water reducible alkyds have short shelf stability due to poor hydrolytic stability.¹

Alkyd resins are highly acidic and need to be neutralized before being used in a waterborne alkyd coating. The base that is used is usually an amine due to its hydrophilic nature. However, hydrolysis of the amine is what reduces the shelf life of the final alkyd

product.² When developing a water reducible alkyd coating, the first step is to mix the resin with the base. Co-solvents are then added to increase the solubility of the resin in water. Figure 5 shows an example of an alkyd resin that has been neutralized with amines.

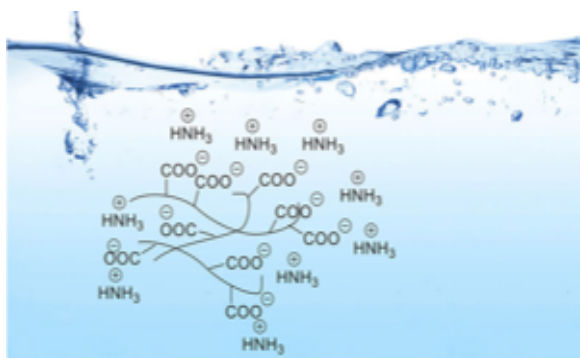


Figure 5.² Basic water reducible alkyd resin.

2.2.3 ALKYD EMULSIONS

Alkyd emulsions are able to have low to near zero VOC content. An alkyd emulsification goes from being an oil-in-water or water-in-oil system to its opposite once a critical point is surpassed. Oil-in-water designates how the emulsion system has a higher oil to water concentration ratio.¹⁵ The surfactant choice is extremely important when designing the formulation. The proper surfactant will have an optimal molecular weight, structure, and hydrophile/lipophile balance (HLB).¹⁵ Visualization of oil-in-water to water-in-oil systems dispersed in a silicone surfactant is shown in Figure 6. However, it's important to note that a water-in-oil to oil-in-water process is also possible.¹⁵

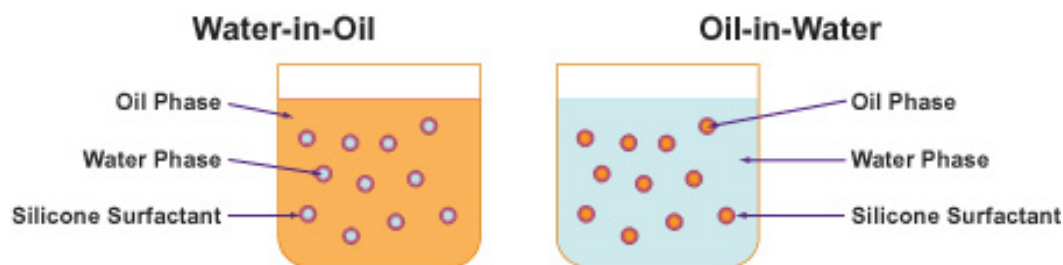


Figure 6.¹⁹ Emulsification process.

One common emulsification process, known as the invert emulsion process, can be made without high shear mixing and with less foam.¹⁵ In a regular emulsification process, the system goes from oil-in-water to being a water-in-oil. However, in the inversion emulsification process, the conversion goes from being a water-in-oil to oil-in-water system. The first step of the inversion emulsification process is to heat up the neat alkyd, either with minimal or no solvent content, until it reaches a manageable viscosity. The system is continuously stirred as to prevent solidification from this point. Prior to this emulsification processes, the amount of base needed to neutralize 40% of the alkyd resin is determined via titration. That determined amount of necessary base is then added into the mixing hot resin in powder form and allowed to disperse for approximately half an hour. A separately heated, molten surfactant mixture is then added to the partially neutralized heated resin. This system is then mixed for another half hour. Water, heated to the temperature of the emulsification system, is added drop-wise. This addition of water forms the water-in-oil emulsion. Eventually, with enough water, the system inverts to an oil-in-water emulsion. Before reaching this inversion point, the viscosity increases. High heat is maintained to control and potentially reduce the viscosity of the system. However, the surfactants used in this process have lower water solubility with higher temperatures.

This emulsification package of alkyd emulsion resin, surfactants, and water, is packaged and used in alkyd emulsion formation coatings like the one used in this project.

2.3 CURRENT INDUSTRIAL RESEARCH

Current industrial research focuses on improving water borne alkyd formulations. One area of investigation is the development of surfactant free, zero-VOC waterborne alkyds; which is being looked into by companies such as Arkema.¹⁶ Companies like Dow have developed their own dispersion method to produce water reducible alkyds with a notable improvement in properties such as corrosion resistance.¹ Other companies such as Ashland and Croda, are supporting the growth of waterborne alkyds by developing dispersing agents and surfactants for this technology.^{20,21} Corrosion inhibitors are being used to prevent rust and increase weathering resistance for water borne coatings.²² Another area of interest involves replacing hazardous cobalt driers with safer metals.^{8,9} While conducting background research for this project, it was discovered that there are very few alkyd emulsion coatings available. One existing product is an alkyd emulsion enamel available through Vista Paint.²³ Improving and commercializing alkyd emulsions is an endeavor of the coatings industry.

3. EXPERIMENTAL METHODS AND MATERIALS

All formulations were modified from commercially available, starting point formulations. Each formulation was selected after considering factors such as the accessibility of certain chemicals, the expected properties based on the type of resin, and complexity of the formulation. Corrosion inhibitors were not included in any formulation, regardless of if they were recommended. This was because the innate corrosion resistance of the three alkyd coating types was to be tested. Each alkyd coating type followed only one formulation. Chemicals and resins were acquired from various companies. A list of all the chemicals used for all three coating methods is listed in Table 1.

A representative coating for each alkyd coating type was formulated in pint sized cans, allowed to rest for 24 hours, and then filtered prior to evaluation. Each coating underwent multiple iterations with minor and major modifications until all coatings achieved a similar and consistent visual appearance. This resulted in a variation between the representative formulations in certain chemical characteristics, such as pigment volume concentration (PVC). The magnitude of these differences is believed not to have significant effects of the coating performance. All paints were filtered with a 125-micron filter to establish a standard appearance.

Table 1. List of supplier companies and chemicals used.

| Chemical | Company | Use |
|-----------------------------|--------------------------------|----------------------|
| Mineral Spirits | Sunnyside | S.B. |
| Bentone SD-1 | Elementis Specialties | S.B. |
| EPS 6603 | Engineered Polymer Solutions | S.B. (resin) |
| X46X60 | Alfa | S.B. (resin) |
| O27T70 | Alfa | S.B. (resin) |
| Setal 11-3616 | Nuplex | S.B. (resin) |
| DA 707 | Patcham (FZC) | S.B. |
| TiPure R706 | Chemours TiPure | S.B., W.R., Emulsion |
| 2-butanone oxime (Skino #2) | TCI America | S.B. |
| 6% Cobalt Drier | EGE Kimya A.S. | S.B. |
| 10% Calcium Drier | EGE Kimya A.S. | S.B. |
| 24% Zirconium Drier | EGE Kimya A.S. | S.B. |
| Setal 41-1390 | Nuplex | W.R. (resin) |
| Kelsol 3961 | Reichhold | W.R. (resin) |
| Ammonium hydroxide (6M) | Chemistry Department Stockroom | W.R. |
| Ammonium hydroxide (conc.) | Chemistry Department Stockroom | W.R. |
| 1-butanol | Chemistry Department Stockroom | W.R. |
| 2-butoxyethanol | Chemistry Department Stockroom | W.R. |
| BYK 022 | BYK Additives and Instruments | W.R. |
| Active 8 | Vanderbilt Minerals, LLC | Emulsion |
| TiPure R960 | Chemours TiPure | S.B., W.R., Emulsion |
| DI Water | | W.R., Emulsion |
| Neosept 91 | Ashland | Emulsion |
| BYK 035 | BYK Additives and Instruments | Emulsion |
| Dispersek 190 | BYK Additives and Instruments | Emulsion |
| Kronos 2130 | Kronos | S.B., W.R., Emulsion |
| Resydrol VAF 6111w/60WA | Allnex | Emulsion |
| Borchi OXY COAT 110 | Borchers | Emulsion |
| Propylene glycol | Chemistry Department Stockroom | Emulsion |
| BYK 346 | BYK Additives and Instruments | Emulsion |
| Strodex KM-0VOC | Ashland | Emulsion |
| Aquaflow XLS-530 | Ashland | Emulsion |
| Aquaflow NMS-450 | Ashland | Emulsion |

3.1 SOLVENT BORNE ALKYD COATING

As a starting point formulation for the solvent borne alkyd coating is listed in Table 2 and was obtained from Engineered Polymer Solutions (EPS). This formulation was specifically for the solvent borne alkyd resin EPS 6603, which was the resin used in this project.

Table 2.²⁴ Starting point solvent borne alkyd coating formulation.

| Material | Type | Pounds | Gallons |
|----------------------|------------------|---------------|----------------|
| Grind | | | |
| Mineral Spirits | Medium | 119.0 | 18.43 |
| Bentone SD-1 | Clay | 0.90 | 2.4 |
| EPS 6603 | Resin | 174.2 | 21.78 |
| Soya Lecithin | Dispersing Agent | 2.00 | 0.23 |
| 6% Calcium Drier | Drier | 3.80 | 0.51 |
| TiPure R902 | Pigment | 300.0 | 8.76 |
| Hegman 7+ | | | |
| Let Down | | | |
| Mineral Spirits | Medium | 46.30 | 7.13 |
| EPS 6603 | Resin | 314.40 | 39.30 |
| 12% Cobalt Drier | Drier | 3.00 | 0.34 |
| 18% Nuxtra LTD Drier | Drier | 5.80 | 0.63 |
| Skino #2 | Anti-skinning | 2.30 | 0.30 |
| Mineral Spirits | Viscosity adjust | 13.00 | 2.00 |
| Total | | 993.09 | 100.00 |

Substitutions to the original solvent borne alkyd formulation resulted in the formulation that was used for this project, shown in Table 3. In addition to the EPS 6603 alkyd resin, 3 other resins were evaluated based on the modified formulation. These S.B. alkyd resins were Alfa X46X60, Alfa O27T70, and Nuplex Setal 11-3616. After producing S.B. alkyd coatings with all 4 resins, it was determined that EPS 6603 had the best visual

appearance, required the least amount of dispersant, and was overall the easiest resin to use (see Appendix A for more information). Due to these reasons, only the EPS 6603 was used.

Table 3. Modified solvent borne alkyd coating formulation.

| GRIND: | | | Formula | | Non-Volatile | |
|--------------------------------------|----------------|-----------------|-----------------------|--------------|---------------------|--------------|
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| 0 | 6.45 | Mineral Spirits | 10 | 1.55 | 0 | 0 |
| 70 | 8 | EPS 6603 | 90 | 11.25 | 63 | 7.06 |
| 72 | 8.05 | DA 707 | 6 | 0.75 | 4.32 | 0.48 |
| 100 | 33.33 | TiPure R706 | 90 | 2.7 | 90 | 2.7 |
| Grind Total | | | 196 | 16.25 | 157.32 | 10.25 |
| Pigment Total | | | 90 | 2.7 | 90 | 2.7 |
| Grind (2000 rpm) to Hegman 7+ | | | | | | |
| LETDOWN | | | Formula | | Non-Volatile | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | Grind | 196 | 16.25 | 157.32 | 10.25 |
| 70 | 8 | EPS 6603 | 27.3 | 3.41 | 19.11 | 2.14 |
| 0 | 7.71 | Skino | 2.7 | 0.35 | 0 | 0 |
| 6 | 6.58 | 6% Co Drier | 1.8 | 0.27 | 0.11 | 0.01 |
| 43.5 | 8.18 | 10% Ca Drier | 5.1 | 0.62 | 2.22 | 0.18 |
| 38.6 | 8.06 | 24% Zn Drier | 80 | 9.93 | 30.88 | 2.31 |
| TOTAL | | | 312.9 | 30.83 | 209.64 | 14.89 |
| Paint properties | | | | | | |
| Weight per gallon | | 10.15 | % NV by weight | | 67 | |
| Viscosity | | 112.2 | % NV by volume | | 48.29 | |
| | | | PVC | | 18.13 | |

The alkyd coatings were prepared using a Premier Mill Corp. Laboratory Disperator, Series 2000 Model 90 with a Cowles high shear dispersion blade. Once all components of the grind were added and mixed, the degree of dispersion of the particles was tested with a Hegman Fineness of Grind gauge. The fineness of the grind was to be 7+

and was measured following ASTM D1210-05 (2 Path Apparatus). After letting the grind mix for approximately 5 minutes, the letdown components were added and then mixed for another 5 to 10 minutes.

After the completed coating was mixed, it was sealed and allowed to equilibrate for 24 hours. Following the 24 hours, viscosity measurements were made using a BYK Gardner Brookfield KU-Stormer Viscometer (Serial No. K72740, 2-panel spindle) and density was recorded using ASTM D1475-13 with a 3 milliliter (mL) metal pycnometer. Once these values were recorded, the paint was filtered using a DeVilbiss DeKones 803253 Nylon, Superfine 125-micron mesh cones. No significant amount of paint was lost during the filtration step. After filtering, viscosity and density measurements were recorded and all further sample testing was done using the filtered coating.

Drawdowns were made on Leneta paper opacity charts (2C form, size 7-5/8 x 10 1/4 from The Leneta Co) secured atop a vacuum surface with a 2014 DryFast Vacuum. Drawdowns made using 3 mil and 5 mil steel drawdown bars from BYK Gardner. Additional drawdowns were made onto the cold-rolled steel and aluminum panels for the Q-Fog, QUV, and physical property tests. Drawdowns were made of both the unfiltered and filtered paint to examine visual appearance and the effect of filtering. However, to measure gloss, contrast ratio, and when making the steel and aluminum drawdowns, only the filtered coating was used.

Before testing the VOC content, the solids content needed to be quantified using ASTM D2369. Once value was collected, an Aligent Technologies 689N Network GC System and 5973Network Mass Selective Detector was used to measure VOC content and to determine a materials and coatings VOC emission value. Gloss was measured with a

20°/60°/85° BYK Gardner micro-TRI-gloss. Contrast ratio was determined by a Mercury DataColor P/N1200-1341 Spectrophotometer, the same instrument used to quantify color changes after the QUV experiment. The color values were obtained using a CIE L*a*b* setting in D65 (daylight) and A10 (incandescent) light sources.

To monitor accelerated weathering by heat, moisture, and UV exposure, a QUV chamber was used. Aluminum panels were placed in a Q-Panel Lab Products Model OUV/SE chamber for a minimum of 200 hours, following ASTM C1257 for accelerated weathering resistance testing. Corrosion resistance was tested according to ASTM B117 (salt spray) using a Q-Fog chamber from Q-Lab Corp. Panels were prepared on cold-rolled steel and taped using 3M Scotch Blue Painters tape typical to this application.

Destructive tests of impact and adhesion were conducted using steel panels. For the impact test, a BYK Gardner 111K3 Falling Dart Impact Tester was used. Adhesion (ASTM D3359, Method B) was determined using a BYK Gardner Cross Cutter Tester (Cat. No. 5121, 1.5 mm, 6 blade set) and Elcometer adhesive 99 tape. The shelf stability was determined by visual analysis of the coating(s) within the paint can over the course of one month. Levels of syneresis, color change, and clumps were recorded. If syneresis was evident, the ability of the paint to return to its original state as a result of mixing by hand was tested and noted.

3.2 WATER REDUCIBLE ALKYD COATING

The starting point formulation for the water reducible alkyd coating was obtained from King Industries. In this formulation, shown in Table 4, the company promotes the use of Nuplex Setal 41-1390 and their Narcorr 1389 corrosion inhibitor.

Table 4.²² Starting point water reducible alkyd formulation.

| Material | Type | Control Weight % |
|-----------------------------------|--------------------|-------------------------|
| Grind | | |
| Setal 41-1390 | Resin | 19.2 |
| Ammonium hydroxide (concentrated) | Neutralizing amine | 0.8 |
| 1-Butanol | Solvent | 0.5 |
| 2-Butoxyethanol | Solvent | 0.5 |
| BYK 020 | Defoamer | 0.3 |
| Active 8 | Accelator | 0.1 |
| 5% Cobalt Drier | Drier | 0.6 |
| Titanox R960 | Pigment | 19.0 |
| DI Water | Medium | 17.4 |
| Hegman 7+ | | |
| Let Down | | |
| Setal 41-1390 | Resin | 9.1 |
| Ammonium hydroxide (concentrated) | Neutralizing amine | 0.9 |
| 1-Butanol | Solvent | 0.6 |
| 2-Butoxyethanol | Solvent | 1.7 |
| DI Water | Medium | 29.3 |
| Total | | 100.0 |

After altering the original formulation, a final modified formulation was developed and used, as shown in Table 5. The cobalt drier and corrosion inhibitor were not used. The water reducible alkyd resins tested were Nuplex Setal 41-1390 and Reichhold Kelsol 3961. After making a coating with each resin using the modified formulation, it was determined that the Setal 41-1390 resin had the best appearance and was the easiest to work with.

Table 5. Modified water reducible alkyd formulation.

| GRIND: | | | Formula | | Non-Volatile | |
|-------------------------------|----------------|-----------------|-----------------------|--------------|---------------------|-------------|
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| 70 | 8.70 | Setal 41-1390 | 57.60 | 6.62 | 40.32 | 4.55 |
| 0 | 7.34 | NH4OH | 2.40 | 0.33 | 0.00 | 0.04 |
| 0 | 6.76 | 1-butanol | 1.50 | 0.22 | 0.00 | 0.04 |
| 0 | 7.51 | 2-butoxyethanol | 1.50 | 0.20 | 0.00 | 0.02 |
| 0 | 8.30 | BYK 022 | 0.90 | 0.11 | 0.00 | 0.00 |
| 0 | 7.93 | Active 8 | 0.30 | 0.04 | 0.00 | 0.00 |
| 100 | 32.76 | TiO2 R960 | 57.00 | 1.74 | 57.00 | 1.74 |
| 0 | 8.33 | DI H2O | 52.20 | 6.27 | 0.00 | 0.00 |
| Grind Total | | | 173.40 | 15.52 | 97.32 | 6.39 |
| Pigment Total | | | 57.00 | 1.74 | 57.00 | 1.74 |
| Grind (2000 rpm) to Hegman 7+ | | | | | | |
| LETDOWN: | | | Formula | | Non-Volatile | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| | | Grind | 173.40 | 15.52 | 97.32 | 6.39 |
| 70 | 8.70 | Setal 41-1390 | 27.30 | 3.14 | 19.11 | 2.15 |
| 0 | 7.34 | NH4OH | 2.70 | 0.37 | 0.00 | 0.04 |
| 0 | 6.76 | 1-butanol | 1.80 | 0.27 | 0.00 | 0.05 |
| 0 | 7.51 | 2-butoxyethanol | 5.10 | 0.68 | 0.00 | 0.07 |
| 0 | 8.33 | DI H2O | 55.00 | 6.60 | 0.00 | 0.00 |
| TOTAL | | | 265.30 | 26.58 | 116.43 | 8.70 |
| Paint properties | | | | | | |
| Weight per gallon | | 9.98 | % NV by weight | | 43.89 | |
| Viscosity | | 121.30 | % NV by volume | | 32.75 | |
| | | | PVC | | 19.99 | |

Property testing for the water reducible resins followed the same order and procedure as with the solvent borne alkyd resin, listed in Section 3.1. In addition to making a standard water reducible alkyd coating formulation for this project, the effect of water content added during the letdown stage was evaluated; results of this experiment are given in Appendix 1).

3.3 ALKYD EMULSION

The starting point formulation for the alkyd emulsion coating was obtained from Ashland. This formulation, shown in Table 6, promoted the company's non-ionic synthetic associative thickeners (NSAT) and defoamer but used an Arkema Synaqua 4804 resin. The modified formulation, listed in Table 7, used a Resydrol VAF 6111w/60wA alkyd emulsion resin from Allnex and the NSAT thickeners listed in the starting point formulation. No problems were experienced while formulating this coating.

Table 6.²⁰ Starting point alkyd emulsion coating formulation.

| Material | Type | Amount (kg) |
|-----------------------------|--------------------------|---------------|
| Grind | | |
| Water | Medium | 100.0 |
| Nuosept BIC | Biocide | 2.0 |
| Drewplus TS-4385 | Foam Control | 1.0 |
| Disperbyk 190 | Wetting/Dispersing Agent | 20.3 |
| Kronos 2190 | Pigment | 202.5 |
| Hegman <10 micron | | |
| Let Down | | |
| Water | Medium | 116.4 |
| Synaqua 4804 | Resin | 450.0 |
| Borchi OXY-coat 1101 | Drier | 6.0 |
| Propylene Glycol | Co-solvent | 15.0 |
| BYK 347 | Substrate Wetting | 10 |
| Aquaflow XLS 530 | NSAT Rheology Modifier | 40.1 |
| Aquaflow NMS 450 | NAST Rheology Modifier | 26.7 |
| Total | | 1000.0 |

Table 7. Modified alkyd emulsion formulation.

| GRIND: | | | Formula | | Non-Volatile | |
|--------------------------------------|----------------|--------------------|-----------------------|--------------|---------------------|-------------|
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| 0 | 8.33 | Water | 22.2 | 2.67 | 0 | 0 |
| 0 | 9.6 | Neosept 91 | 0.44 | 0.05 | 0 | 0 |
| 0 | 7.31 | BYK 035 | 0.22 | 0.03 | 0 | 0 |
| 40 | 8.85 | Dispersek 190 | 4.51 | 0.51 | 1.8 | 0.18 |
| 100 | 33.38 | Kronos 2130 | 45 | 1.35 | 45 | 1.35 |
| Grind Total | | | 72.37 | 4.6 | 46.8 | 1.54 |
| Pigment Total | | | 45 | 1.35 | 45 | 1.35 |
| Grind (2000 rpm) to Hegman 7+ | | | | | | |
| LETDOWN: | | | Formula | | Non-Volatile | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | Grind | 72.37 | 4.6 | 46.8 | 1.54 |
| 0 | 8.33 | Water | 28.2 | 3.39 | 0 | 0 |
| 62 | 8.93 | Resydrol VAF | 100 | 11.2 | 62 | 6.94 |
| 1 | 8.68 | BorchiOXY COAT 110 | 1.3 | 0.15 | 0.01 | 0 |
| 0 | 8.66 | Propylene Glycol | 2.2 | 0.25 | 0 | 0 |
| 45 | 8.3 | BYK 346 | 3.3 | 0.4 | 1.49 | 0.18 |
| 40 | 9.3 | Strodex KM-OVOC | 2.2 | 0.24 | 0.88 | 0.08 |
| 28.3 | 8.6 | Aquaflow XLS 530 | 1.29 | 0.15 | 0.37 | 0.04 |
| 28 | 8.6 | Aquaflow NMS 450 | 11.2 | 1.3 | 3.14 | 0.33 |
| TOTAL | | | 222.06 | 19.98 | 110.3 | 8.65 |
| Paint properties | | | | | | |
| Weight per gallon | | 11.11 | % NV by weight | | 49.67 | |
| Viscosity | | 73.62 | % NV by volume | | 43.31 | |
| | | | PVC | | 15.58 | |

Property testing was conducted in the same order and manner as the water reducible and solvent borne alkyd coating trials.

4. RESULTS AND DISCUSSIONS

4.1 COMPARISON OF PROCEDURES

Of the three alkyd coating types, the most difficult to produce was the water reducible alkyd coating. The water reducible alkyd coating was the most delicate for its properties depended on water content. A separate experiment concluded that the addition of 55 mL of water in the letdown stage produced a water reducible coating that matched the standard appearance requirement and had optimal corrosion resistance (see Appendix 1).

The easiest alkyd coating to prepare was the alkyd emulsion coating. The alkyd emulsion resin was the least viscous of the three resins used in this project, and each addition was easily integrated. Both water borne alkyd coatings needed to carefully watched as the change in viscosity would cause the system to stop stirring or cause splattering. The most difficult aspect of the solvent borne alkyd coating formulation process was handling the alkyd resin, which was highly viscous and tacky. In addition, the amount of dispersing agent to add had to be experimentally determined.

Overall, the water reducible and solvent borne alkyd coatings were the most difficult to produce due to the high viscosity of their respective resins and the dependency on the amount of water or dispersant. The alkyd emulsion coating was the easiest to produce.

4.2 COMPARISON OF WET PAINT PROPERTIES

Viscosity measurements and 3 mil paper drawdowns were made for each of the tested coating types before and after filtration. Before filtering the solvent borne, water

reducible, and emulsion-based alkyd coatings, varying amounts of aggregation was visually noticed. Filtering improved the appearance of each coating type by removing most of the aggregates. In each type of alkyd coating, viscosities were reduced after filtering, as shown in Table 8. This confirmed that filtering reduced the amount of aggregates.

Table 8. Viscosity difference.

| Method | Before Filtration (KU) | After Filtration (KU) |
|------------------------------|------------------------|-----------------------|
| Solvent Borne | 116.8 | 112.2 |
| Water Reducible [†] | 79.5 | 77.2 |
| Emulsion | 77.02 | 73.62 |

The solvent borne alkyd coating was the most viscous while the alkyd emulsion coating was the least viscous. This viscosity trend was expected because solids content of each coating showed a similar trend. In addition, the resin viscosity for each coating type followed the same trend. After determining the viscosities, the densities of the filtered coating were measured, as listed in Table 9. The water content percentage was 0, 50, and 50.3 for the solvent borne, water reducible, and emulsion-based alkyd coatings, respectively.

Table 9. Calculated and actual densities.

| Method | Calculated | | Experimentally Determined | |
|-----------------|-------------------|---------------|---------------------------|---------------|
| | Density (lbs/gal) | Density (g/L) | Density (lbs/gal) | Density (g/L) |
| Solvent Borne | 10.15 | 1216.24 | 10.4 | 1245.92 |
| Water Reducible | 10.02 | 1200.66 | 10.5 | 1257.90 |
| Emulsion | 11.11 | 1331.27 | 10.3 | 1233.94 |

The densities of the actual solvent borne and water reducible alkyd coatings were slightly greater than expected. The alkyd emulsion coating showed the biggest difference between the calculated and experimentally determined densities. The change in densities were a result of filtering and solvent evaporation. In the solvent borne and water reducible cases, the evaporation of solvents from the system resulted in an increase in the fraction of non-volatiles to volatiles. In simpler terms, this means that since there was solvent loss, the systems were denser than expected. In the emulsion system, there were no solvents to be evaporated. Here, the lower-than-expected density value was a result of particle loss from filtration. While all three coatings were filtered and experience particle loss, in the water reducible and solvent borne cases, the effect of solvent loss had a bigger impact on density than particle loss. These occurrences which affected the density values, were also considered when evaluating the solids content for each coating.

The percent (%) solids content was determined by doing a weight by difference measurement after less than 1 g of a coating was placed in a 110°C oven for one hour (ASTM 2369). Solids content is a test that needs to be performed in triplicates, therefore the values listed in Table 10 are averages. The standard deviation of the averages was less than 0.7% for each type of alkyd coating.

Table 10. Solids content.

| Type | Expected Values (%) | Actual (%) |
|-----------------|---------------------|------------|
| Solvent Borne | 67 | 69.6 |
| Water Reducible | 44.73 | 49.57 |
| Emulsion | 49.67 | 45.8 |

Once the amount of solids was determined, VOC measurements for the 3 coating types were conducted in duplicates. The VOC content data is shown in Table 11.

Table 11. VOC emissions.

| Method | Density (lb/gal) | VOC (g/L) |
|-----------------|------------------|-----------|
| Solvent Borne | 10.15 | 253.49 |
| Water Reducible | 10.02 | 146.78 |
| Emulsion | 11.11 | 34.15 |

The VOC trend was as expected, with the alkyd emulsion containing the least and solvent borne containing the most amount of VOCs. The VOC content of the alkyd emulsion coating was higher than expected but was not anticipated to somehow effect the other properties. It should be noted that the VOC value recorded is the material VOC, which is the regulated value. Material VOC measures the grams of VOC per liter of coating. An alternative way to record VOC value is with the coatings VOC. This is the grams of VOC per liter of coating minus liter of water content and liter of exempt solvents. The coatings VOC value for the solvent borne, water reducible, and emulsion-based alkyd coatings was 253.49, 402.6, and 90.57 g/L, respectively.²⁵

The shelf stability was tested over the course of one month by visually determining the amount of syneresis, color change, and/or skinning. The coatings were mixed by hand to detect for clumps and to determine if a phase separated coating could return to its original uniform state. In every case that syneresis was observed, the coating returned to its standard appearance shortly after being mixed by hand. Table 12 summarizes the shelf stability for each coating over the course of one month. It should be noted that the stability of the water

reducible alkyd coating was dependent on water content; this experimental result is discussed in Appendix 1.

Table 12. Shelf stability.

| Method | 24 Hours (before filtration) | Week 1 | Week 2 | Week 3 | Week 4 |
|-----------------|--------------------------------|--------------|--------------|--------------|--------------|
| Solvent Borne | N.S., white | N.S., white | N.S., white | N.S., white | N.S., white |
| Water Reducible | L.S., some clumps | L.S., peach | M.S., peach | H.S., peach | H.S., peach |
| Emulsion | L.S., some clumps, air bubbles | L.S., yellow | L.S., yellow | L.S., yellow | M.S., yellow |

N.S., L.S., M.S., and H.S. correspond to no syneresis, light syneresis, moderate syneresis, and heavy syneresis, respectively. As expected, the least shelf stable coating was the water reducible alkyd. This is due to the effect of hydrolysis, as discussed in Section 2.2.2. The most stable coating type was, as expected, the solvent borne alkyd coating. The alkyd emulsion was more stable than the water reducible alkyd coating but wasn't stable in comparison to the solvent borne alkyd coating.

4.3 COMPARISON OF DRY FILM PROPERTIES

The pigment volume concentration (PVC) is the amount of pigment added in relation to the total volume of non-volatiles added. PVC is considered when evaluating gloss. The higher the PVC, the more concentrated the color and, oftentimes, lower the gloss. The lower gloss is attributed to surface roughness and decrease reflection of light.

Gloss was tested at viewing angles for gloss are 20°, 60°, and 85° from vertical. A coating that is glossy is considered to be non-matte or non-flat while a non-glossy coating

is matte and flat. These terms are used semi-interchangeably. A coating is matte if it does not reflect light; this lack of reflection is a result of surface roughness from particles. The PVC and gloss values are listed in Table 13.

Table 13. Gloss.

| Method | PVC | 20° | 60° | 85° |
|-----------------|------------|------------|------------|------------|
| Solvent Borne | 18.13 | 90.7 | 93.7 | 101.9 |
| Water Reducible | 19.99 | 81 | 90.5 | 97.4 |
| Emulsion | 15.58 | 94.6 | 100.65 | 99.43 |

Although the solvent borne and water reducible alkyd coatings had similar PVC values, the water reducible alkyd was noticeably more matte. This occurrence highlights the problems industry is having with reducing problems such as aggregation and surface defects in water reducible systems. The emulsion alkyd had overall the highest values for gloss, as expected since it had the lowest PVC.

After testing the glossiness of each alkyd type, the hiding power was evaluated. Hiding power is determined through contrast ratio and is the ability of a coating to hide a black, or other dark, colors. This is an important consideration in paint manufacturing as consumers do not want to apply multiple layers of paint in order to hide a previous color on a substrate. The contrast ratio for each coating is shown in Table 14. In order to get this ratio, the spectrophotometer used was placed on the white then black portion of the Leneta drawdown paper.

Table 14. Contrast ratio.

| Method | D65 | A10 |
|-----------------|------------|------------|
| Solvent Borne | 0.989 | 0.987 |
| Water Reducible | 0.977 | 0.974 |
| Emulsion | 0.984 | 0.981 |

Where a fractional value of 1.0 corresponds to 100% hiding power, all the coatings had excellent hiding power. The solvent borne coating was the best, at a percentage of 98.9%, followed by the emulsion and then water reducible coating. It should be noted that contrast ratio is usually recorded under the D65 illuminant. The trends of best to worst hiding power follows the same trend of most to least % solids.

4.4 COMPARISON OF DURABILITY-TYPE PROPERTIES

The durability-type properties tested were impact and adhesion, accelerated weathering by QUV, and corrosion resistance with a Q-FOG. The weathering and corrosion resistance testing took at least 200 hours to conduct, and the shelf stability was monitored over the course of one month.

Impact by intrusion and cross hatch adhesion were destructive tests performed using coatings that had been cured for 1 week on steel drawdowns. This duration of cure time ensured both surface and through drying. Results of both tests are shown in Table 15. The adhesion rating was determined using its ASTM standard; the chart used for determining the adhesion strength is listed in Appendix 2.

Table 15. Impact and adhesion.

| Method | Impact | Adhesion |
|-----------------|---------------|-----------------|
| Solvent Borne | Flexible | 5B |
| Water Reducible | Flexible | 5B |
| Emulsion | Flexible | 5B |

In evaluating the results of the three alkyd coatings, it was determined that each method produced a durable alkyd coating. Exceptional and similar results of the water borne alkyd coatings to the solvent borne alkyd coating was not anticipated. These results proved that there was strong cohesion and adhesion for each coating. Each coating was determined to be flexible since there no visible crack, break, or any other form of deformation when being impacted.

To test the resistance against accelerated weathering, drawdowns of the solvent borne, water reducible, and emulsion-based alkyd coatings were made in duplicates on aluminum panels. They remained in the QUV for 200 hours. The color of the drawdowns before and after being placed in the QUV for each alkyd coating type is summarized in Table 16.

Table 16. Color and appearance.

| | | L* | a* | b* | ΔE |
|-----------------|-------------------|--------------|-------------|--------------|--------------|
| Solvent Borne | Before | 96.64 | -1.285 | 3.065 | 0.476 |
| | After | 96.98 | -1.155 | 2.685 | |
| | Difference | 0.255 | 0.13 | -0.38 | |
| Water Reducible | Before | 97.28 | -0.89 | 1.98 | 4.51 |
| | After | 95.71 | -0.27 | 6.16 | |
| | Difference | -1.57 | 0.62 | 4.18 | |
| Emulsion | Before | 96.46 | -1.6 | 3.6 | 0.41 |
| | After | 96.6 | -1.29 | 3.18 | |
| | Difference | 0.14 | 0.31 | -0.42 | |

The corresponding color values for L^* , a^* , and b^* are shown in Figure 7. The ΔE value is calculated by taking the square root of the sum of the squared values of ΔL^* , Δa^* , and Δb^* . If the ΔE value is close to zero, then the coating experienced no detectible change after being exposed to accelerated weathering conditions of UV light, heat, and moisture.

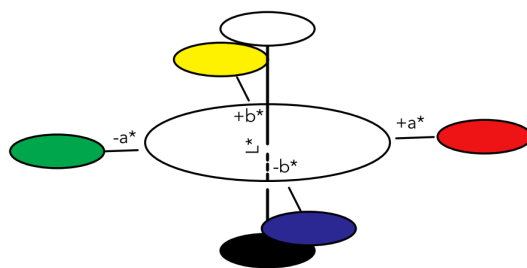


Figure 7.²⁶ Color and appearance using CIE $L^*a^*b^*$ values.

In examining the data collected for this particular property test, it is quickly observed that the water reducible alkyd coating performed the worst while the solvent borne and emulsion coatings were comparable. The solvent borne alkyd coating was expected to have the best weathering resistance, but the resistance of the emulsion coating

was not anticipated to be closely comparable to the solvent borne coating as waterborne coatings do not typically have good weathering resistance. While this result shows that the alkyd emulsion developed using the modified formulation resulted in a durable coating, it is important to consider that most weathering tests are ran for at least a thousand hours.

The corrosion resistance determined after steel drawdown panels were placed in a Q-FOG for 200 hours. Each alkyd coating was tested in triplicate. Figure 8 shows the panel with the highest level of corrosion resistance for each of the alkyd coating types. Every panel placed in the Q-FOG experienced some corrosion as a result of the tape. This deformation is distinguishable by the vertical rust line starting from the top of the visible coating near the tape, and continuing down. This occurrence was regarded as a an artifact of the test procedure and not considered while determining the corrosion resistance of the three alkyd coating types. Corrosion was recorded in terms of amount of rust and blistering both around the vertical scribe and throughout the visible coating area.

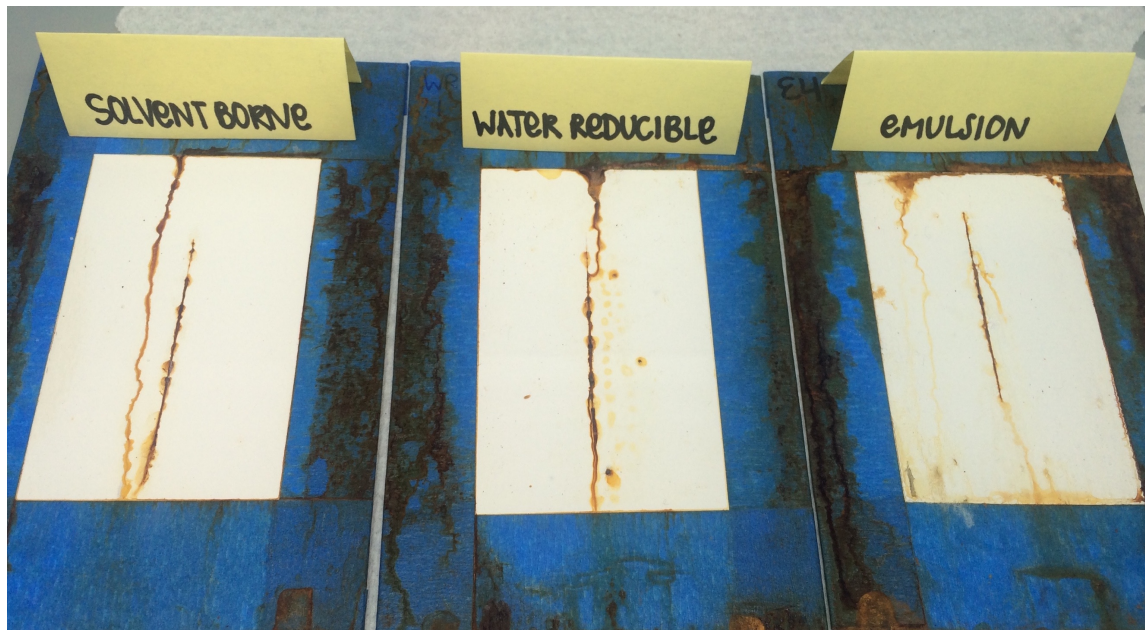


Figure 8. Best corrosion resistance.

All three alkyd coating types showed impressive and nearly similar corrosion resistance. The water reducible alkyd coating was the only coating to not show blistering. In terms of rust resistance, it can be concluded that the emulsion was superior over the solvent borne and water reducible alkyd coatings. However, the emulsion coating was more blistered than the solvent borne alkyd coating.

After comparing the best of the 3 panels tested for the solvent borne, water reducible, and alkyd emulsion alkyd coatings, a comparison of the worst performing panels was also compared, as seen in Figure 9.

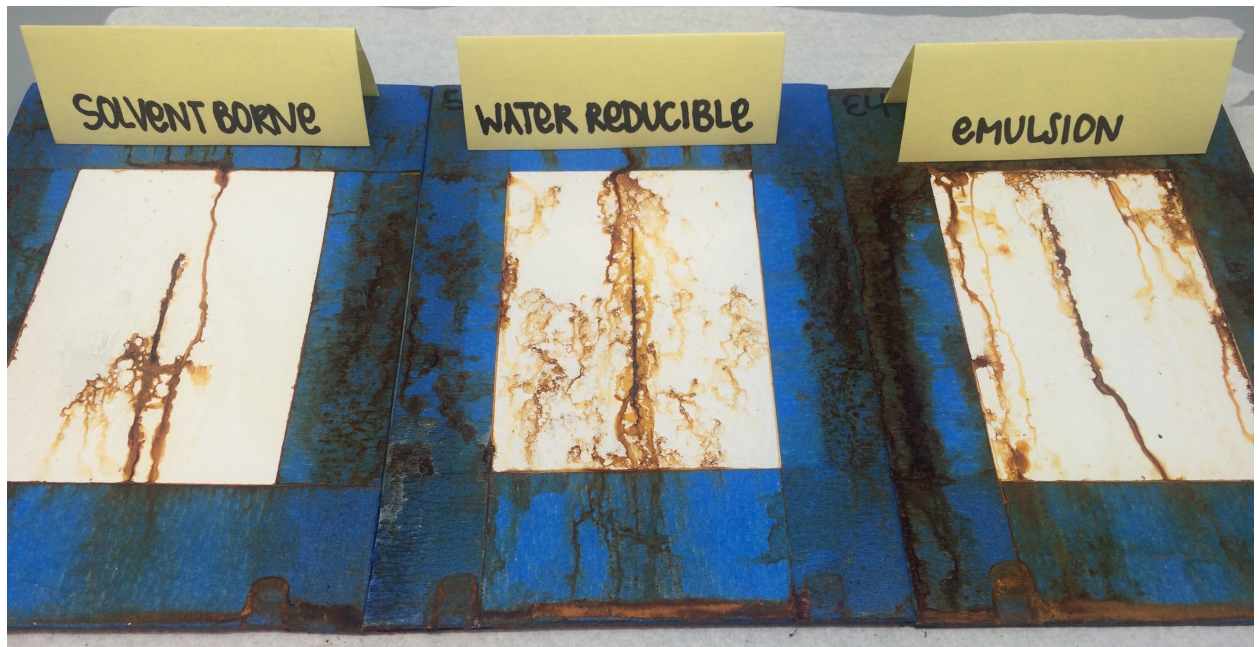


Figure 9. Worst corrosion resistance.

In comparing the panels with the least corrosion resistance, it is evident that the water reducible alkyd coating again performed the worst. The solvent borne and emulsion panels shows significant amounts blistering. The paint around the scribed showed heavy rusting in the solvent borne and emulsion coating cases, however the area of rust did not deviate far from the scribe in the case of the emulsion coating in comparison to the solvent borne coating. After inspecting these panels, it was determined that the emulsion coating had the greatest amount of rust resistance while the water reducible coating had the highest level of blistering resistance.

4.5 COMPARISON SUMMARY

The wet paint tested included viscosity, density, % solids content, amount of VOCs, and shelf stability. The dry film properties tested were gloss, and contrast ratio. The gloss and contrast ratios of the two waterborne alkyd coatings were similar, but a bit lower in value, in comparison to the solvent borne alkyd coating. At this point, it was determined that the coating with the best properties was the solvent borne alkyd, but that the alkyd emulsion coating outperformed the water reducible alkyd coating. The solvent borne alkyd coating was more shelf stable than the waterborne alkyd coatings, with the emulsion alkyd being more stable than the water reducible alkyd coating.

In evaluating the durability-type properties of the three alkyd types by impact and adhesion, weathering resistance, and corrosion resistance, it was concluded that there were some surprising results. Both waterborne alkyd coatings performed better than expected, especially in regards to impact and adhesion. The solvent borne and emulsion-based alkyd coatings performed similarly in both weathering resistance and corrosion resistance. The water reducible alkyd coating was inferior to the solvent borne alkyd and alkyd emulsion coatings in terms of weathering and corrosion. However, the water reducible alkyd coating did not blister in the corrosion resistance property test. Both the solvent borne alkyd and alkyd emulsion coatings showed corrosion resistance after 200 hours, with the alkyd coating becoming the most blistered but least rusted. This result was not expected. Overall, the solvent borne alkyd coating proved to be the most durable after various property tests, followed by the alkyd emulsion coating, and ending with the water reducible coating. The effect of water content on the properties of the water reducible alkyd coatings is summarized in Appendix 1. The 55 mL water reducible alkyd coating sample used for

comparison against the solvent and emulsion alkyd coatings performed the best among the other water reducible formulations.

5. FUTURE WORK

There are several parts of this project that can be more thoroughly explored in the future. The problems experienced with the solvent borne and water reducible resins that we're considered to be unfit for comparison in this project should be investigated with more detail. Another aspect that needs to be addressed is the small difference in the PVC of the three formulations. The solvent borne and water reducible alkyd coatings can also be compared to commercially available products; once alkyd emulsion coatings are commercially available they should be compared as well.

The practice of filtering a paint is not desirable in an industrial setting. Therefore, making each coating with different titanium dioxide, more amount of or use of a different dispersing agent, increased speed, or a combination of all three possible remedies should be examined. Constant mixing speed was not possible during any procedure due to the small size of the paint can and the type of disperser used; this problem can only be solved by either increasing the batch size or using a different disperser. Overall, it is proposed that in the future, more work needs to be done to solve the problems that were experienced in this project and to perform a more in depth comparison of each of the solvent borne, water reducible, and emulsion-based alkyd coatings.

6. CONCLUSION

Alkyd coatings are used in automotive, architectural, and industrial industries. These coatings were traditionally made in a solvent medium, but concern over air quality and VOC content encouraged the development of waterborne alkyd coatings. There are two main waterborne alkyd coating types: water reducible and alkyd emulsion. Both types of waterborne alkyd coatings are considered to be inferior to the original solvent based alkyd coatings in properties such as weather resistance, corrosion resistance, and shelf stability. The purpose of this project was to develop a formulation and produce a solvent borne, water reducible, and emulsion-based alkyd coating then to compare their properties.

Property testing was divided into categories of wet paint/film properties and long term properties. The tests performed in the first category were carried out to determine and compare viscosity, density, solids content, VOC content, gloss, and contrast ratio. After conducting these trials it was found that the trends of intrinsic physical properties matched industry reported data on the three alkyd types. The gloss and contrast ratio were very high for all three alkyd coating types, but the solvent borne outperformed the waterborne alkyd coatings. Destructive durability testing involved impact, adhesion, and weather and corrosion resistance. Impact and adhesion tests showed that all three coating types were equally flexible and adhesive. After 200 hours each of QUV and Q-FOG testing, it was determined that the solvent borne had the highest weather resistance, was unexpectedly comparable in corrosion resistance to the alkyd emulsion coating, and more stable than either of the waterborne alkyd coatings. In terms of shelf stability, the solvent borne alkyd coating was the most stable over the course of a month, followed by the alkyd emulsion

and water reducible alkyd coatings. The water reducible alkyd coating performed the worst in all three long term property tests.

Future work should focus on solving the problems experienced for the water reducible alkyd coatings and a more thorough exploration of how certain additives affect the visual appearance of the tested alkyd coatings. The results of the alkyd emulsion coating should be repeated and expanded to determine if the formulation developed in this project could become a commercially produced and available product.

The History of VOC Regulation in the United States

7. INTRODUCTION TO THE HISTORY OF VOC

The paragraphs and contents below detail the information on the part of the project directly relating to “The History of VOC Regulation in the United States”.

7.1 PURPOSE OF STUDY

This project started when my Committee Chair, Dr. Ray Fernando, was asked ‘how VOC regulations started in the United States,’ by a particular Chinese paint company. After conducting a bit of research, it became apparent that there was no solitary place to find a complete and detailed list regarding VOC regulations. Acknowledging the benefit to the coatings industry both domestically and internationally, it was decided that I would research, compile, and report a summary of the history of VOC regulations in the United States. The importance of such a summary is that it will provide an understanding on current VOC regulations nationwide and regionally, explain why and how VOC regulations came about, as well as outline methods of VOC testing and provide other pertinent information. This report was presented as a poster at the American Coatings Association Conference in Indianapolis, Indiana in April of 2016.

7.2 LIST OF TERMS

AIM – Architectural, Industrial, and Maintenance

CAA – Clean Air Act

CARB – California Air Resource Board

EPA – Environmental Protection Agency

Flats – matte or non-glossy coatings

HAPS – Hazardous Air Pollutants

LADCO – Lake Michigan Air Directors Consortium

NAAQS – National Ambient Air Quality Standards

Non-flats – glossy coatings

OTC – Ozone Transport Commission

SCAQMD – South Coast Air Quality Management District

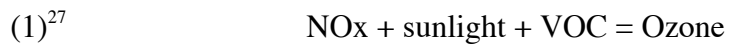
VOC – volatile organic compound

8. ABSTRACT

Improvement of air quality has been a concern and goal in the United State since the 1950s. In 1955 the first Clean Air Act (CAA) was implemented. This Act would eventually be the influence for the start of volatile organic compound (VOC) restriction and limitation in coatings. Numerous revisions of CAA, new legislation, and government entities have been established since 1955, all of which work on improving overall air quality. However, as a direct result of VOC limitation, air quality and human health have improved due to a decrease in ground level ozone. The United States must, at minimum, follow the Environmental Protection Agency Architectural and Industrial Maintenance (EPA AIM) federal rule on VOC limits though some states and regions have their own stricter rules. Typically, the most stringent regulations are those developed by the South Coast Air Quality Management District (SCAQMD) in California, which is often regarded as the leader in VOC limitation and prevention. In the past half-century, coatings in the US have gone from containing over 400 g/L to near zero, in some cases.

9. ABOUT VOLATILE ORGANIC COMPOUNDS

There are several reasons why VOC regulation is important. As outlined before, improving air quality means improving the health of humans and livestock, of preventing negative impacts to food supply and the exterior of buildings, and ensuring that there isn't an increase in the formation of harmful chemicals in the atmosphere. Beyond the worry of creating human health problems as a result of inhaling chemicals that paint can emit, VOCs react with the atmosphere to form dangerous ground level ozone. A simplified equation outlining how VOCs react with nitrogen oxide to create ozone can be seen in Equation 1.



The exact method of how and why chemicals in paint were dangerous was not fully understood until the research conducted during the several Acts since the 1950s.

10. HISTORICAL BACKGROUND

Concern over air quality is not new. In 1306, King Edward I of England banned the use of sea coal due to its heavy smoke production, and 250 years later Queen Elizabeth I implemented a similar ban.^{28,29} In 1952, 4,000 London residents died from an event known as the “Killer Smog” which caused pneumonia, bronchitis, tuberculosis, asphyxiation, heart failure, asthma, lung inflammation, and respiration cell damage.³⁰ In the late 19th century, Cincinnati and Chicago attempted to regulate coal burning to no avail. In 1948 serious attention was drawn to air quality concern when smog in Dorona, Pennsylvania caused 20 deaths and thousands to seek medical attention. At that time smog levels in Los Angeles were also dangerously high.²⁸ As a result of the deadly air quality events the United States enacted the first air regulation act: the Air Pollution Quality Act of 1955.

11. CLEAN AIR ACTS

Regarded as “an act to provide research and technical assistance relating to air pollution control,” the Air Pollution Control Act of 1955 (Public Law 159) did not achieve much in the way of improving air quality, but it did set the course for being more aware of air quality problems and how to solve them.³¹ While eventually this Act would evolve into legislation that would set limits on harmful emissions and outline national standards for how to test for these said emissions, this particular Act focused more on finding the cause(s) of poor air quality over methods on how to resolve air pollution. Specifically, this Act focused on the dangers to agricultural crops, livestock, property, and overall air quality as a result of transportation source emissions. The United States surgeon general and the Secretary of Health, Education, and Welfare were tasked with determining the health risks as a result of automotive exhaust through a research program budgeted at \$5 million. According to the Act, “nothing contained in this Act shall limit the authority of any department or agency of the United States to conduct or make grants-in-aid or contracts for research and experiments relating to air pollution under the authority of any other law.”³¹ The research conducted under this Act ultimately showed that motor vehicles pose a danger to human health, agriculture crops and livestock, and results in the deterioration of property.^{31,29}

At the time, focus on air and water quality was highlighted with a public movement over environmental concern, also known as the Environmental Movement.³² This concern was not only over motor vehicle emissions but the use and disposal of chemicals. Rachel Carson, a conversationalist and influential scientist, famously raised concern over the impact of pesticides and contamination of water with her 1962 book *Silent Spring*.^{32,33} In

the book, she opposed the use of long lasting chemicals such as dichlorodiphenyltrichloroethane (DDT) and the disposal of chemicals into the environment. *Silent Spring*, written in such a way that the general public could understand her scientific findings, highlighted the fact that once biocides enter the food chain, they poisoned not only insects but the hierarchy.³³ Before *Silent Spring* sold millions of copies, however, New York Democratic Rep. James Delaney added a statement into a bill about the FDA stating ‘no additive shall be deemed safe if it is found to induce cancer when ingested by man or animal’ in 1958.³⁴ This ‘Delaney Amendment’ was a result of discovering that a aminotriazole herbicide was cancerous.³⁵ James Delaney and Rachel Carson’s incitation of the Environmental Movement raised awareness on the dangers of certain chemicals and influenced legislation to start protecting and improving air quality and the environment.³²

Recognizing the concerns highlighted by the Environmental Movement, the United States Congress passed the first major legislation on air pollution *control* with the Clean Air Act of 1963 (Public Law 88-206).³⁶ Two revisions of this Act were later made in 1970 and 1990. It should be noted that ‘revisions’ refer to entirely new Acts while ‘amendments’ correspond to modifications on a particular act. The purpose of the 1963 Act was “to improve, strengthen, and accelerate programs for the prevention and abatement of air pollution.”³⁶ Whereas the previous Act focused on transportation emissions, this Act set emission standards for stationary sources such as power plants, steel mills.²⁹ A research program meant for the development of improved and cost-effective techniques for removing sulfur from fuels, such as gasoline, was a major focus.³⁶ Amendments to this Act were made in 1965, 1966, 1967, and 1969. These amendments saw the formation of the

Motor Vehicle Air Pollution Control Act, Air Quality Control Regions (AQCRs) to monitor ambient air, and State Implementation Plans (SIPS) for states to make their own timetable of air quality improvement.²⁹

The Clean Air Act of 1970 (Public Law 91-604) was “an Act to amend the Clean Air Act to provide for a more effective program to improve the quality of the Nation’s Air.”^{29,37} This Act was more ambitious in its air quality goals and subsequent deadlines.²⁹ This goal of revision was to improve knowledge of air pollutants and their effects on all aspects of human health, control and improve vehicle emissions, and produce new synthetic fuels. In addition, this Act established the National Ambient Air Quality Standards (NAAQS), New Source Performance Standards (NSPS), and after an amendment in 1977, the Prevention of Significant Deterioration (PSD).^{29,37} Along with these new programs, the Act gave citizens the right to take legal action against companies, persons, organizations, and governments who violated emission standards.²⁹ These emission standards included the new ambient air quality standards, performance standards for new stationary sources, definitions of hazardous air pollutants (HAPS), and motor vehicle emission standards.³⁷ Hazardous air pollutants are pollutants that cause cancer and other serious health impacts; these are different from VOCs, which are carbon-based compounds that react with other chemicals in the air to produce ozone.³⁸ No specific VOC limits in coatings, or other products, were included in this Act.

The latest Clean Air Act was enacted in 1990 (Public Law 101-549) for the purpose of being “an Act to amend the Clean Air Act to provide for attainment and maintenance of health protective national ambient air quality standards, and for other purposes.”^{29,39} This Act amended the problems of the previous Acts as well as focused on new issues. It instilled

the Best Available Control Technology (BACT) to reduce the amount of air toxics and both called for and encouraged a reduction of use of chlorofluorocarbons (CFCs) and low-sulfur fuels to prevent ozone depletion and acid rain, respectively.²⁹

From the time of the establishment of the first air quality Acts to the eventual implementation of the latest Clean Air Act of 1990, the United States saw a distinguishable improvement to air quality and human, environmental, and property health. As a results of these Acts, VOC regulation and limitation became important. While motor vehicle emissions, HAPs, and other sources and types of emissions also became a concern and an area of focus, this paper will emphasize only on the history and impact of VOC regulation in the United States.

12. VOC REGULATION

An understanding of VOCs reactivity was gained, in part, though research funded by the various air pollution control acts. Along with government funded research, acknowledgement should be given to research groups around the U.S. which either accidentally or purposely discovered the risks and methods behind VOC emissions. A timeline showing when the major laws and governmental agencies involved with VOC regulations is given in Figure 10.

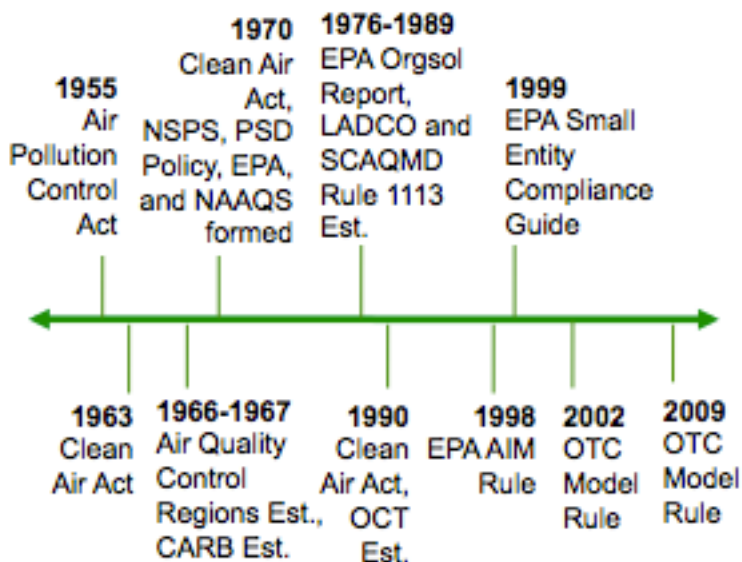


Figure 10. Timeline of major VOC Acts.

In the 1970s, VOC regulation became a major focus. As a result of the Clean Air Act of 1970, the Environmental Protection Agency (EPA) and National Ambient Air Quality Standards (NAAQS) were formed. The NAAQS named 6 categories of pollutants: nitrogen oxide (NO_x), carbon monoxide (CO), sulfur oxide (SO_x), lead (Pb), ozone (O₃), and particulate matter (PM).⁴⁰ The idea behind creating categories was to better focus on

specific classes of pollutants, instead of combating air problems as a whole. VOC regulation falls under the regulation of nitrogen dioxide. This is because VOCs react with ultraviolet (UV) light to create free radicals, which then react with nitric oxide (NO) to produce ozone. The free radicals can continue to make NO₂ from NO, which perpetuates the cycle of NO₂ reacting to sunlight to create NO and ozone.⁴¹ In addition to creating categories, they also created a system for how ozone was to be recorded based on 1- and 8- hour time intervals.⁴⁰

The EPA later formed several divisions with report systems to oversee and manage air quality, such as the Total Exposure Assessment Methodology (TEAM) and the Report on the Environment (ROE). TEAM is in charge of measuring indoor VOC and was created in 1985; while this division is important, indoor VOC is not a focus of this paper.⁴² The ROE, official since 2001, reports on trends and how human health in the United States changes over time within 5 different categories: Air, Water, Land, Human Exposure and Health, and Ecological Condition.⁴³

Along with the EPA, several other air quality organizations such as the Ozone Transport Commission (OTC), South Coast Air Quality Management District (SCAQMD), California Air Resource Board (CARB), and Lake Michigan Air Directors Consortium (LADCO) were formed.⁴⁴ Smaller state and county-wide organizations were also created. The EPA regionalized the United States to better monitor and handle air quality control. A map of these regions can be seen in Figure 11. It is important to know that states must, at minimum, follow the EPA federal rule but are allowed to follow stricter air quality standards such as LADCO, OTC, and SCAQMD. The difference between each air quality agency will be discussed later in this report. It should be noted that the difference between

the strictness of each region is the result of a mixture of politics, public influence, amount of urbanization, danger of pollution from other countries as a result of air flow, and weather.

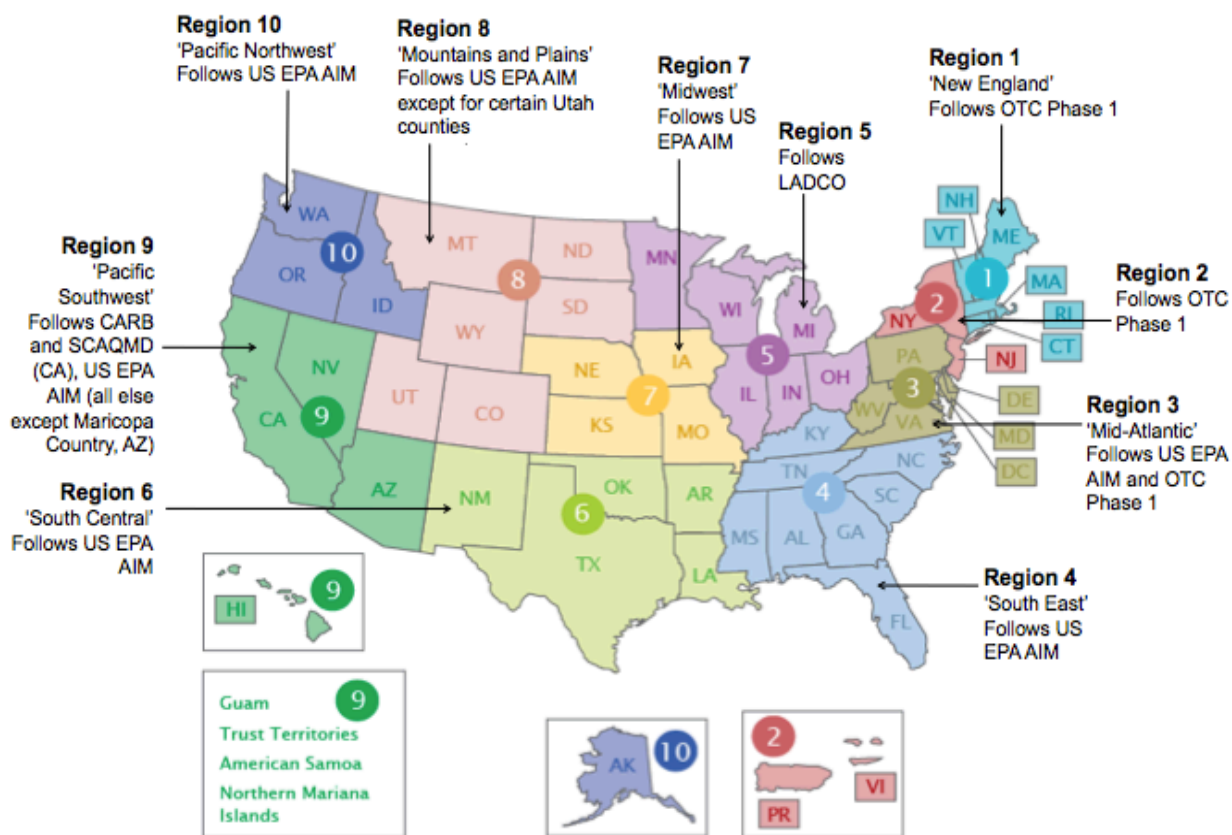


Figure 11.⁴⁵ EPA map of regions.

The trade-off between lowering VOC limits and performance has always been a concern and a challenge. Early on, the technology to create high-performance coatings with low VOCs was not possible; there was a sacrifice between either meeting the limit requirements or having a well-performing product. Due to recent advances in research there have been breakthroughs and improvements with lower VOC coatings, but there is still a

challenge in making having these coatings perform as well as their solvent-borne counterparts.

One of the biggest, and earliest, plans to reform VOCs in coatings came in 1977 and 1978 when the California Air Resource Board (CARB) had an objective to ban solvent borne coatings.⁴⁶ Before carrying out this objective, CARB contracted a company to conduct research and form a conclusion as to the feasibility of banning solvent borne coatings. This company, named Orgsol, submitted a report which advised against the banning of solvent borne paints but suggested that architectural coatings should contain no more than 250 g/L of VOCs;’ a limit which CARB then implemented as a rule. A timeline for companies to meet these requirements for their paints were also given.⁴⁶

However, in 1979 through 1986, the EPA reevaluated the Orgsol report with a different hired company named Acurex. Acurex reported that by decreasing the amount of VOCs in these architectural coatings, the performance of the coatings also decreased.⁴⁶ The weathering and corrosion resistance of these exterior coatings were impacted and resulted in the need to reapply a new coat every few years or to use several coats initially. Thus, while there was a decrease in VOCs, the amount of paint needed, and thus the amount of chemicals required, ultimately saw no change and even an increase in environmental damage. While current VOC limits for architectural coatings were at 250 g/L or less at the time, these limits did not match the technology available. After reviewing Acurex’s report, the EPA drafted new regulations with a company known as Engineering Science.²⁰ These new regulations did not apply to non-flat, i.e. glossy, or specialty coatings. That same year, in 1981, SCAQMD admitted that a VOC limit of 250 g/L for non-flat coatings was too low to produce a suitable coating, and raised the limit to 450 g/L. They also claimed that it

would not make any more VOC regulations until it actually proved to reduce ozone pollution. At that point, CARB adopted SCAQMD's Rule 1113 with amendment that non-flat coatings could have 380 g/L and that solvent-borne coatings could be made. However, even though solvent borne coatings could be made, they did not perform as well as before VOC regulation. By the end of 1987, SCAQMD amended its Rule 1113 to 380 g/L VOC for non-flats after having Eastern Michigan University, CalCoast Analytical Labs, and Coatings Technology Inc. conduct studies on VOC limits.²⁰

In 1981 the Architectural Coatings Task Force (ACTF) was formed to conduct studies on architectural coatings and to recommend low limits with good performance and minimal product usage.²⁰ Between 1987 and 1989 Region 9 forced local districts to implement low limits via 4 procedural devices: 1) EPA to disapprove extensions and relaxations, 2) threat of persecution of unenforced/outdated laws, 3) ACTF's specially coatings recommendations approved, 4) pressured local districts to implement stricter rules.²⁰ In 1990 the Clean Air Act Reauthorization was implemented and set a goal of 2005 to drastically improve air quality.

In 1993 the SCAQMD published the Air Quality Analysis Guidance Handbook, mainly for lead regulation, and the Mobile Assessment for Air Quality Impacts (MAAQI), for emissions from land use projects.⁴⁷ In 2000, SCAQMD changes its VOC regulations again and in 2001 they adopted Title V after EPA finalized its deliberation since 1997. In 1998 the EPA published the federal rule of Architectural, Industrial, and Maintenance Coatings (AIM) to limit the amount of VOCs that manufacturers and importers can put into coatings, impose container labeling requirements, and listed more exemptions to the VOC regulations. These exemptions were for coatings made before 9/13/1999, exported

coatings, aerosol containers, small (<1 L) volume, and paint exchange. They also made the exceedance fee \$1.27 per pound of VOC over the limit. The final corrections to the EPA AIM Rule (63 FR 48848 under section 183e of the Clean Air Act) for architectural coatings were made in 1999 under the Federal Registrar. The exceedance fee was increased again in 2000 and 2015. In 1999 the Small Entity Compliance Guide was written by the EPA to meet the requirement by the Small Business Regulatory Enforcement ACT (SBREFA).⁴⁸

In 2000 SCAQMD changed its VOC limits to 50 g/L for flats, non-flats, quick dry enamels, and floor paints; to 100 g/L for other coatings such as industrial maintenance, rust preventative, primers, sealers, undercoats, and recycled flat and non-flat coatings. The limits also decreased to 250 g/L and 450 g/L for other coatings not including those used for swimming pools, shellacs, wood preserves, and some water-repellent coatings. This was a large change from the previous and then most recent 1987 limits of 350 g/L for primers and sealers, 400 g/L for quick dry enamels, 680 g/L for lacquers. The previous limits were 500 g/L for varnishes and 400 g/L for primers, sealers, and undercoats in 1984; 500 g/L for industrial topcoats and primers in 1985, and an increase to 420 g/L for the paints in 1984 and 1985. In 2015, SCAQMD amended its air quality significant threshold and in 2016 they began developing a new and revised Air Quality Analysis Handbook Guide to replace the 1993 version.⁴⁹

The OTC was created by the Clean Air Act of 1990 along with the Reasonably Available Control Technology (RACT) to measure and control ground level ozone in the Northeast and Mid-Atlantic regions of the United States.⁵⁰ The OTC's first set of VOC regulations was titled RACT Phase 1, and the NOx Memorandum of Understanding (MOU) to further control NOx within its domain. In 2002 the OTC wrote and enforced a

Model Rule (of 2002) which gave rules and regulations for consumer products, solvents and cleaners, AIM coatings, and additional NO_x control measures. A more recent version of the Model Rule was made in 2009 but there has yet to be a state to adopt it.⁵¹

LADCO was established in 1989 for the main purpose of “providing technical assessments for and assistance to its member states on problems of regional air quality, including ozone, fine particles, regional air haze and air toxics; and to provide a forum for its member states to discuss regional air quality issues.”⁵² Similar to OTC’s MOU, LADCO established the Lake Michigan Ozone Study (LMOS) to fulfill a 1989 Memorandum of Agreement which oversaw the collection of various air quality data and to develop a model system for its states. The study found that air transport, literally how air moves in the atmosphere, saw continuous reactions with ozone precursors such as NO_x and VOCs and henceforth revised their regional SIPs to reduce NO_x and thus VOC emissions in 1990. In order to support the new regional goals the Midwest RPO (MRPO) was formed in 1999 with serious work on improving air quality by 2001.

Maricopa County in Arizona follows the federal Clean Air Act while some counties of in Utah follow Utah Administrative Rule R307-361 for Architectural Coatings.^{53,54} These counties have VOC limits for 250 g/L, 50 g/L, and 50 g/L for architectural maintenance, flats, and non-flat coatings respectively. A table of VOC limits for each Regions’ ruling air quality districts can be seen in Table 17.

Table 17. Overview of VOC limits.

| Entity | Year | Industrial Maintenance (g/L) | Flats (g/L) | Non-Flats (g/L) |
|---------------|-------------|-------------------------------------|--------------------|------------------------|
| EPA | 1998* | 450 | 250 | 380 |
| CARB | 2000 | 250 | 100 | 150 |
| | 2007* | 250 | 50 | 100 |
| SCAQMD | 1977 | ---- | ---- | 250 |
| | 1981 | ---- | ---- | 450, 380 |
| | 1984-87 | 500, 420 | 550, 420 | 420, 400 |
| | 2008* | 100 | 50 | 50 |
| OTC | 2002* | 340 | 100 | 150 |
| | 2009 | 250 | 50 | 100 |
| LADCO | 2014 | 340 | 100 | 150 |

As of February 2016, SCAQMD proposed amendments to Rule 1113 to “lower some VOC limits; carve out new categories and establish VOC limits,” amongst other changes. The proposed changes are to be taken into effect in 2019. The VOC limits for industrial maintenance, flat, and non-flat coatings do not change.⁵⁵

13. METHODS OF VOC MEASUREMENT

There are several different methods to measure VOC content and techniques that need to be used depending on if the coatings are water borne or solvent borne. EPA Method 24 is the most common technique, although not accurate for most water borne coatings, and measures VOC by weight content.²⁵ Through work between California Polytechnic State University – San Luis Obispo and ASTM International, ASTM D6886 was developed primarily to overcome the limitations of EPA Method 24 by providing an accurate determination of VOC content in water borne coatings with the use of gas chromatography. Karl Fisher titration for water borne coatings can also be used. However, this method can have high uncertainty values depending on the sample size and solvents used within the coating.³⁰

14. RELEVANT INFORMATION

Limiting VOC emission has impacts not only in manufacturing and development, but also importation, exportation, total allowable emissions for a manufacturing plant, and exempt solvents. A VOC limit designates amount of VOCs a paint can contain. To clarify, a paint container holding a matte coating will have 50 g/L of VOCs or less if sold in Region 9. On a larger scale, manufacturing plants and companies are held to a total emissions limit so that while producing paints at a single stationary source, there is a maximum emissions threshold. Before being banned by SCAQMD, a concept of averaging was frequently used to record VOC emission. This meant that it was possible to manufacture coatings with high emissions, or high VOCs, as long as low VOC coatings were also being produced. The average of these high and low emissions was the number that a company or entity would report as their emission level. This practice is no longer allowed.

Following the practice of being able to produce any coating so long as it is below the overall threshold emissions limit, is the issue of importing and exporting. As long as a company is below the emissions limit set by their Region, they can export any coating. For example, if a company in Region 2 is selling paint to a country or state with looser VOC limits, they are allowed to export that high VOC containing product so long as it is not used in areas with strict(er) limits. Congruent to this, shipping products that contain VOC amounts higher than the limit for that Region is not allowed. Due to this, it is not uncommon for companies to manufacture coatings that meet the strictest regulations, usually SCAQMD within Region 9, rather than making several different paints to comply with different regional requirements. In short, by meeting the strictest limits, companies

can sell their product everywhere within the United States. Other companies have decided to sell and manufacture only in certain Regions as to avoid particular VOC limits.

VOC limitations do not signify the inability to use solvents in coatings. Solvents that do not participate in atmospheric photochemical reactions which can ozone are classified as VOC exempt solvents. The EPA definition of VOC compounds even addresses the exemption of certain compounds: “Volatile Organic Compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by the EPA as having negligible photochemical reactivity.”⁵⁶ Chemicals such as acetone, methane, ethane, certain perfluorocarbon compounds, and others are exempt compounds. In order to be considered as an exempt compound, a chemical must contain more than 12 carbons, have a vapor pressure of less than 0.11 mm/Hg at 20°C, and a melting point higher than 20°C without subliming. There have been 3 recent noteworthy compounds that the EPA deemed to have negligible photochemical activity: t-butyl acetate (t-BA) in 2004, dimethyl carbonate (DMC) in 2011, and 2-amino-2-methyl-1-propanol (AMP) in 2015. It should be noted that AMP is the only amine classified as being VOC exempt and was quickly approved as an exempt solvent.⁵⁷⁻⁵⁹

Maximum Incremental Activity (MIR), developed by Dr. William P.L. Carter from University of California, Riverside, numerates the potential of emitted VOCs to react with NO_x. The EPA designates a compound as having negligible reactivity if the MIR is less than or equal to the reactivity of ethane. Compounds with an MIR above this threshold is considered to be a VOC emitting compound and is subject to VOC limitation.⁶⁰

Dunn-Edwards, a prominent coatings company in the South-West, has developed a new type of VOC labeling. Reactivity Activated VOC (RAVOC) is a rating that “adjust(s) the VOC content to reflect the potential air quality impacts of the specific VOCs used, relative to the average mix of all VOCs in the air. For example: If the VOC content of a product is 100 g/L, and the RAVOC rating is 50 g/L, (then) the VOCs used in this product have only half the air quality impact of an equivalent amount of average VOCs.”³⁵

To summarize, the classification of VOC exempt compound is important to the paint industry. Since the VOC limits established in the 1950s were ahead of the technology available, paint formulators weren’t able to use necessary solvents; this resulted in paints with properties that were negatively comparable to their solvent borne counterparts. Exempt VOCs compounds has partly resolved this problem by allowing the use of solvents which were proven to not form ground level ozone.

15. CONCLUSION

Attempts to improve air quality in the United States were made as early as 1800's. However, it wasn't until 1955 with the Air Pollution Quality Act that serious and national attempts to improve air were made. After this air quality Act, other acts such as the Clean Air Acts of 1963, 1970, and 1990 were enforced; with each new Acts requiring stricter VOC emission limits. Currently the United States, must at minimum, follow the federal rule of EPA AIM, but some regions within the United States adhere to stricter VOC emission limits. These regions follow entities such as SCAQMD, LADCO, OTC, CARB, and other more local county-wide groups. The leader in VOC regulation is SCAQMD, located in California, with limits as low as 50 g/L in comparison to 250 g/L to the federal rule (for flat coatings specifically). Initially, the decrease of VOCs in coatings resulted in adverse paint qualities and inferior products. However, recent developments in resin and additive technology have minimized these effects in most cases. In fact, quality products are now being manufactured and sold at VOC levels well below the federal limits. The regulation of VOCs in coatings has resulted in a decrease in harmful ground level ozone and an improvement on human health and the environment. Future regulations will likely lower VOC limits for many types of coatings nationwide.

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APPENDICES

A. Water Reducible Water Content Experiment Results

While determining the best way to formulate the water reducible alkyd coating, it was discovered that the amount of water added to the system during the letdown stage had a noticeable impact on several properties. This information was not immediately important to the focus of the main purpose of this Part of the project. However, these sets of experiments lead to the determination of the optimal water content for the water reducible alkyd coating which was later used to be compared to the solvent borne and alkyd emulsion alkyd coatings. After evaluating the following data, it was concluded that adding 55 mL of water to the system in the letdown stage provided the most optimal properties overall.

Since this evaluation of water concentration was not a focus of this project, some property tests weren't completed, specifically only in the case of VOC content for the 65 mL and 80 mL W.R. coatings. The property tests are separated by the categories of wet paint properties, dry film properties, and durability-type properties.

Table 7.1A. Wet paint properties for the water reducible water content experiment. The VOC content for the 65 mL and 80 mL was not recorded as, at this point, it was determined to be unnecessary.

| Water | Viscosity (KU) | | Density (lbs/gal) | % Solids Content | | VOC content | Shelf Stability (Week 4) |
|--------------|----------------|-------|-------------------|------------------|--------------|-------------|--------------------------|
| | Before | After | | Calculated | Experimental | | |
| 45 mL | 125.7 | 123.5 | 10.06 | 45.61 | 30.16 | 186.85 | Moderate syneresis |
| 50 mL | 79.5 | 77.2 | 10.02 | 44.73 | 28.4 | 146.77 | Moderate syneresis |
| 55 mL | 121 | 121.3 | 9.98 | 43.89 | 37.96 | 165.79 | Heavy syneresis |
| 65 mL | 112.2 | 111.6 | 9.91 | 42.29 | 33.63 | ---- | Heavy syneresis |
| 80 mL | 80.4 | 79.7 | 9.82 | 40.11 | 30.44 | ---- | Heavy syneresis |

Table 7.1B. Dry Film properties for the water reducible water content experiment. The values have been simplified and presented as being either ‘best’, ‘fair’, or ‘poor’ when that particular paint was compared against the other water concentrations.

| | PVC | Gloss | Contrast Ratio |
|--------------|-------|-------|----------------|
| 45 mL | 19.99 | Fair | Best |
| 50 mL | 19.99 | Best | Fair |
| 55 mL | 19.99 | Best | Best |
| 65 mL | 19.99 | Best | Fair |
| 80 mL | 19.99 | Fair | Poor |

Table 7.1C. Durability-Type properties for the water educible water content experiment.

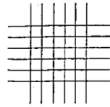
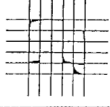
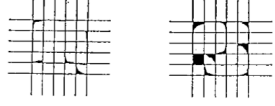
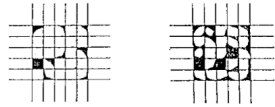
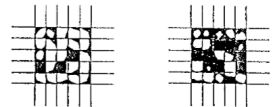
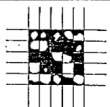
To simplify the results, the coatings are concluded as being ‘best’, ‘middle’, ‘poor’, or ‘worst’ as compared to the other water concentrations.

| | Impact | Adhesion | QUV (200hrs) | Q-Fog (200hrs) |
|--------------|---------------|-----------------|---------------------|-----------------------|
| 45 mL | Flexible | 3B | Poor | Best |
| 50 mL | Flexible | 5B | Poor | Best |
| 55 mL | Flexible | 5B | Best | Middle |
| 65 mL | Flexible | 4B | Poor | Poor |
| 80 mL | Flexible | 4B | Poor | Worst |

It is important to note that the fluctuation of properties as a result of changing water concentration highlights the problems industry is currently experiencing with water reducible coatings.

B. Adhesion Chart, ASTM D3359

The following ASTM given chart was used to determine the level of adhesion:

| CLASSIFICATION | PERCENT AREA REMOVED | SURFACE OF CROSS-CUT AREA FROM WHICH FLAKING HAS OCCURRED FOR SIX PARALLEL CUTS AND ADHESION RANGE BY PERCENT |
|----------------|----------------------|---|
| 5B | 0% None |  |
| 4B | Less than 5% |  |
| 3B | 5 - 15% |  |
| 2B | 15 - 35% |  |
| 1B | 35 - 65% |  |
| 0B | Greater than 65% |  |

C. Experiments for the Polymers and Coatings Master's Program

C.1 Purpose of Study

The purpose of developing these laboratory experiments was to contribute to future Polymers and Coatings Master's students' knowledge of coatings formulation, and to gain experience with designing experiments. These experiments are intended to be used in such a way that different laboratory groups complete different experiments. Each group will then present a formal presentation to the class so that the other groups learn the details about how to make each of the 3 types of alkyd coatings; solvent borne, water reducible, and alkyd emulsion. An outline for how the labs should be incorporated by the instructor(s) and completed by the students is described in Section 9.2, as written from the point of view of an instructor to the students.

C.2 Anticipated Plan of Integration

These experiments are designed to be completed over the course of a quarter. This time allocation takes into account the accessibility of the paint mixing equipment as well as provides ample time to make and test each coating. All of the coatings made for solvent borne alkyd, water reducible alkyd, and alkyd emulsion experiments should be made within the fume hood for safety purposes. After completing the requirements for formulating and testing the coating(s), students are expected to write an individual short report and prepare a 10 to 15-minute presentation with their group. The purpose of the presentation is to have the students explain the intricacies of formulating a coating and background information on a specific coating to their peers. The paper is designed to encourage thorough research

into the intended purpose of each a component in a formulation, why certain alkyd coating types are problematic, and potential ways to solve any experienced problems or difficulties.

C.3 Solvent Borne Alkyd Coatings Experiment

Chem 5XX: Solvent Borne Alkyd Lab

Objective: The purpose of this lab is to highlight how to make a solvent borne alkyd coating and to understand the importance of using the correct materials in a formulation.

Experiment: In this experiment you will make at minimum 3 paints. You will be comparing how different resins, each of which is meant for a solvent borne alkyd coating, behave differently. The resins you will use are:

Paint 1: EPS 6603 (long oil alkyd resin, soya oil)

Paint 2: X46X60 (medium oil alkyd resin, vegetable oil)

Paint 3: Nuplex Setal 11-3616 (long oil alkyd resin, linseed oil)

The basic formulation is as follows:

| SOLVENT BORNE | | | | | | |
|----------------------|---------|-----------------|----------------|-------|---------------------|-------|
| <u>GRIND:</u> | | | <u>Formula</u> | | <u>Non-Volatile</u> | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| 0 | 6.45 | Mineral Spirits | 10.00 | 1.55 | 0.00 | 0.00 |
| 70 | 8 | EPS 6603 | 90.00 | 11.25 | 63.00 | 7.06 |
| 72 | 8.05 | DA 707 | 6.00 | 0.75 | 4.32 | 0.48 |
| 100 | 33.33 | TiPure R706 | 90.00 | 2.70 | 90.00 | 2.70 |
| Grind Total | | | 196.00 | 16.25 | 157.32 | 10.25 |
| Pigment Total | | | 90.00 | 2.70 | 90.00 | 2.70 |

| | | | | | | |
|-------------------------------|---------|--------------|-----------------------|-------|---------------------|-------|
| Grind (2000 rpm) to Hegman 7+ | | | | | | |
| <u>LETDOWN:</u> | | | <u>Formula</u> | | <u>Non-Volatile</u> | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| | | Grind | 196.00 | 16.25 | 157.32 | 10.25 |
| 70 | 8 | EPS 6603 | 27.30 | 3.41 | 19.11 | 2.14 |
| 0 | 7.71 | Skino | 2.70 | 0.35 | 0.00 | 0.00 |
| 6 | 6.58 | 6% Co Drier | 1.80 | 0.27 | 0.11 | 0.01 |
| 43.5 | 8.18 | 10% Ca Drier | 5.10 | 0.62 | 2.22 | 0.18 |
| 38.6 | 8.06 | 24% Zn Drier | 80.00 | 9.93 | 30.88 | 2.31 |
| TOTAL | | | 312.90 | 30.83 | 209.64 | 14.89 |
| <u>Paint properties</u> | | | | | | |
| Weight per gallon | | 10.15 | % NV by weight | | 67.00 | |
| Viscosity (KU) | | 112.2 | % NV by volume | | 48.29 | |
| VOC (g/L) | | 253.59 | PVC | | 18.13 | |

Safety: All coatings will be mixed, and all additions will be weighed, in the fume hood.

NO EXCEPTIONS! Paints will only be removed from the fume hood for viscosity testing and to make drawdowns. Drawdowns will be placed in the hood to dry.

Helpful hints: The resins are very sticky, it is recommended that two gloves be worn while handling the resins so that the top layer can be removed after weighing and adding the resin and safe formulation can continue afterwards with the remaining glove. Carefully move

the blade to the side of the can and slow the speed considerably when adding the resin and pigment. This is to prevent the resin from wrapping around the spin rod and the pigment from escaping the canister. After adding both components, mix at an increasing speed until full integration. Add each addition stepwise with about a 30 seconds in between each addition. Mix the grind for about 5 minutes and the letdown for about 5 to 10 minutes, both at high speeds.

Experimental: Before making the coatings, determine the paint properties left blank in the formulation. After making the paint, seal it with a lid then let it sit for a minimum of 24 hours (make a note about how the coating looks immediately after making it vs. after letting it sit for some time). After 24 hours make sure you do the following for each coating:

- 1) Determine the viscosity
- 2) Make 3 mil and 5 mil draw downs
- 3) (minimum of) 3 steel drawdowns of each for impact, adhesion, and flexibility tests

Discussion: As discussed, a paint formulation is very specific since everything needs to work cohesively. Evaluate the different types of resins (what they're used for, what solvents they're in, the visual viscosity difference, etc.) and explain the results of each paint. What differences or similarities did you find in the viscosity, gloss, contrast ratio, hiding power, adhesion, impact, and flexibility? What difficulties did you experience while making each coating and were they overcome? If you were to make a solvent borne alkyd coating, what resin would you use? What other modifications might you make to the formulation to improve the coating or process

C.4 Water Reducible Alkyd Coatings Experiment

C.4.1 Difference in Water Concentration

Chem 5XX: Water Reducible Alkyd Lab

Difference in Water Content

Objective: The purpose of this lab is to highlight how to make a water-borne water reducible alkyd coating and to understand the importance of using the correct materials in a formulation.

Experiment: This experiment requires the formulation of at least 4 paints. You will be comparing how the amount of water used in the LETDOWN stage will impact the final coating's properties. The water concentrations to be evaluated are:

Paint 1: Add 45 mL

Paint 2: Add 50 mL

Paint 3: Add 65 mL

Paint 4: Add 80 mL

The basic formulation is as follows:

| WATER REDUCIBLE | | | | | | |
|-----------------|---------|-----------------|----------------|------|---------------------|------|
| <u>GRIND:</u> | | | <u>Formula</u> | | <u>Non-Volatile</u> | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| 70 | 8.7 | Setal 41-1390 | 57.60 | 6.62 | 40.32 | 4.55 |
| 0 | 7.34 | NH4OH (concen.) | 2.40 | 0.33 | 0.00 | 0.04 |
| 0 | 6.76 | 1-butanol | 1.50 | 0.22 | 0.00 | 0.04 |

| | | | | | | |
|----------------------|-------|-----------------|--------|-------|-------|------|
| 0 | 7.51 | 2-butoxyethanol | 1.50 | 0.20 | 0.00 | 0.02 |
| 0 | 8.3 | BYK 022 | 0.90 | 0.11 | 0.00 | 0.00 |
| 0 | 7.93 | Active 8 | 0.30 | 0.04 | 0.00 | 0.00 |
| 100 | 32.26 | TiO2 R960 | 57.00 | 1.74 | 57.00 | 1.74 |
| 0 | 8.33 | DI H2O | 52.20 | 6.27 | 0.00 | 0.00 |
| Grind Total | | | 173.40 | 15.52 | 97.32 | 6.39 |
| Pigment Total | | | 57.00 | 1.74 | 57.00 | 1.74 |

Grind (2000 rpm) to Hegman 7+

| <u>LETDOWN</u> | | | <u>Formula</u> | | <u>Non-Volatile</u> | |
|----------------|---------|-----------------|----------------|-------|---------------------|------|
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| | | Grind | 173.40 | 15.52 | 97.32 | 6.39 |
| 70 | 8.7 | Setal 41-1390 | 27.30 | 3.14 | 19.11 | 2.15 |
| 0 | 7.34 | NH4OH (concen.) | 2.70 | 0.37 | 0.00 | 0.04 |
| 0 | 6.76 | 1-butanol | 1.80 | 0.27 | 0.00 | 0.05 |
| 0 | 7.51 | 2-butoxyethanol | 5.10 | 0.68 | 0.00 | 0.07 |
| 0 | 8.33 | DI H2O | 50.00 | 6.00 | 0.00 | 0.00 |
| TOTAL | | | 260.30 | 25.98 | 116.43 | 8.70 |

Paint properties

| | | | |
|--------------------------|--------|-----------------------|-------|
| Weight per gallon | 9.98 | % NV by weight | 43.89 |
| Viscosity (KU) | 121.30 | % NV by volume | 32.75 |

| | | | |
|-----------|--------|-----|-------|
| VOC (g/L) | 146.78 | PVC | 19.99 |
|-----------|--------|-----|-------|

Safety: All coatings will be mixed, and all additions will be weighed, in the fume hood. NO EXCEPTIONS! Paints will only be removed from the fume hood for viscosity testing and to make drawdowns. Drawdowns will be placed in the hood to dry.

Helpful hints: Add each addition step wise. Carefully move the blade to the side of the can and slow the speed considerably when adding the resin and pigment. This is to prevent the resin from wrapping around the spin rod and the pigment from escaping the canister. After adding both components, mix at an increasing speed until full integration. Mix the grind for about 5 minutes after complete addition and the letdown for about 5 to 10 minutes.

Experimental: Before making the coatings, determine the paint properties left blank in the formulation. After making the paint, close it with a lid then let it sit for a minimum of 24 hours (make a note about how the coating looks immediately after making it vs. after letting it sit for some time). After 24 hours make sure you do the following:

- 1) Take its viscosity and density, then make a 3 mL drawdown on paper and at least two 5 mL steel panel drawdowns.
- 2) Filter the paint into another pint paint canister (use the spatula to carefully press paint through the filter if necessary; more than one filter may be needed)
- 3) Take the viscosity and density of the filtered paint, then make a 3 mil drawdown on paper and at least two 5 mil steel panel drawdowns.

Discussion: As discussed, what is added into a paint formulation is very specific. Water reducible coating properties are very dependent on their water content. Compare the 4 paints in terms of viscosity, density, gloss, contrast ratio, impact, and adhesion. Are the differences you see what you expected? Why or why not? Research how water reducible coatings typically behave in terms of water content and compare this against your results. If you were to make a water reducible alkyd coating with this formulation, how many mL of water would you add in the letdown stage. Lastly, what did you notice about the viscosity changes while mixing the coatings? What problems did you experience and how were they overcome?

C.4.2 Use of Driers and Ammonium Hydroxide

Chem 5XX: Water Reducible Lab

Use of Driers and Ammonium Hydroxide

Objective: The purpose of this lab is to highlight how to make a water borne alkyd coating and to understand the importance of using the correct materials in a formulation.

Experiment: In this experiment, you will make a minimum of 4 paints. You will be comparing the effect of driers and base concentration. In water borne coatings, it is important to control the pH and driers are necessary to advance dry time. The types of paint you will be making is as follows:

Paint 1: Using 6M Ammonium hydroxide (without driers)

Paint 2: Using concentrated ammonium hydroxide (without driers)

Paint 3: Using all the driers (with concentrated NH_4OH)

Paint 4: No driers added ((with concentrated NH_4OH)

The basic formulation is as follows:

| WATER REDUCIBLE | | | | | | |
|-----------------|---------|------------------------------|----------------|------|---------------------|------|
| <u>GRIND:</u> | | | <u>Formula</u> | | <u>Non-Volatile</u> | |
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| 70 | 8.7 | Setal 41-1390 | 57.60 | 6.62 | 40.32 | 4.55 |
| 0 | 7.34 | NH ₄ OH (concen.) | 2.40 | 0.33 | 0.00 | 0.04 |
| 0 | 6.76 | 1-butanol | 1.50 | 0.22 | 0.00 | 0.04 |
| 0 | 7.51 | 2-butoxyethanol | 1.50 | 0.20 | 0.00 | 0.02 |

| | | | | | | |
|----------------------|-------|-----------|--------|-------|-------|------|
| 0 | 8.3 | BYK 022 | 0.90 | 0.11 | 0.00 | 0.00 |
| 0 | 7.93 | Active 8 | 0.30 | 0.04 | 0.00 | 0.00 |
| 100 | 32.26 | TiO2 R960 | 57.00 | 1.74 | 57.00 | 1.74 |
| 0 | 8.33 | DI H2O | 52.20 | 6.27 | 0.00 | 0.00 |
| Grind Total | | | 173.40 | 15.52 | 97.32 | 6.39 |
| Pigment Total | | | 57.00 | 1.74 | 57.00 | 1.74 |

Grind (2000 rpm) to Hegman 7+

| <u>LETDOWN</u> | | | <u>Formula</u> | | <u>Non-Volatile</u> | |
|----------------|---------|-----------------|----------------|-------|---------------------|------|
| % NV | Lbs/Gal | Material | Lbs | Gal | Lbs | Gal |
| | | | | | | |
| | | Grind | 173.40 | 15.52 | 97.32 | 6.39 |
| 70 | 8.7 | Setal 41-1390 | 27.30 | 3.14 | 19.11 | 2.15 |
| 0 | 7.34 | NH4OH (concen.) | 2.70 | 0.37 | 0.00 | 0.04 |
| 0 | 6.76 | 1-butanol | 1.80 | 0.27 | 0.00 | 0.05 |
| 0 | 7.51 | 2-butoxyethanol | 5.10 | 0.68 | 0.00 | 0.07 |
| 0 | 8.33 | DI H2O | 50.00 | 6.00 | 0.00 | 0.00 |
| TOTAL | | | 260.30 | 25.98 | 116.43 | 8.70 |

Paint properties

| | | | |
|--------------------------|--------|-----------------------|-------|
| Weight per gallon | 9.98 | % NV by weight | 43.89 |
| Viscosity (KU) | 121.30 | % NV by volume | 32.75 |
| VOC (g/L) | 146.78 | PVC | 19.99 |

Safety: All coatings will be mixed, and all additions will be weighed, in the fume hood. NO EXCEPTIONS! Paints will only be removed from the fume hood for viscosity testing and to make drawdowns. Drawdowns will be placed in the hood to dry.

Helpful hints: Add each addition step wise. Carefully move the blade to the side of the can and slow the speed considerably when adding the resin and pigment. This is to prevent the resin from wrapping around the spin rod and the pigment from escaping the canister. After adding both components, mix at an increasing speed until full integration. Mix the grind for about 5 minutes after complete addition and the letdown for about 5 to 10 minutes.

Experimental: Before making the coatings, determine the paint properties left blank in the formulation. After making the paint, close it with a lid then let it sit for a minimum of 24 hours (make a note about how the coating looks immediately after making it vs. after letting it sit for some time). After 24 hours make sure you do the following for each coating:

- 1) Determine the viscosity and take note of appearance
- 2) Make 3 mil and 5 mil drawdowns of each coating
- 3) Make glass and (2) aluminum drawdowns of Paint 3 and Paint 4. Make note of any film deformation and dry time. Measure adhesion after 24 hours.

Discussion: As discussed, what is added into a paint formulation is very specific as everything needs to work cohesively. Explain why pH control is necessary and how driers affect the system. Explain the results of each paint in terms of differences or similarities did you find in the appearance, viscosity, gloss, contrast ratio, hiding power, and adhesion. Paints 1 and 2 are to be compared directly, same with Paint 3 and 4. What difficulties did

you experience while making each coating and were they overcome? What further experiments would you conduct to determine the best way to make a water reducible alkyd with this particular resin? Keep in mind that industrial alkyds require other additives, therefore please limit hypothesis testing to small scale paints similar to what was made in this lab.

C.5 Alkyd Emulsion Coatings Experiment

Chem 5XX: Alkyd Emulsion Lab

Objective: The purpose of this lab is to highlight how to make a water-borne emulsion alkyd coating and to understand the importance of using the correct materials in a formulation.

Experiment: This experiment requires the formulation of at least 3 paints. You will be comparing how the type of titanium dioxide added will affect the final film. The titanium dioxide pigments you will be using are:

Paint 1: Use TiO₂ 960

Paint 2: Use TiO₂ 760

Paint 3: Use Kronos 2310

The basic formulation is as follows:

| EMULSION | | | | | | |
|-------------|----------------|-----------------|------------|------------|--------------|------------|
| GRIND: | | | Formula | | Non-Volatile | |
| <u>% NV</u> | <u>Lbs/Gal</u> | <u>Material</u> | <u>Lbs</u> | <u>Gal</u> | <u>Lbs</u> | <u>Gal</u> |
| 0 | 8.33 | Water | 22.20 | 2.67 | 0.00 | 0.00 |
| 0 | 9.60 | Neosept 91 | 0.44 | 0.05 | 0.00 | 0.00 |
| 0 | 7.31 | BYK 035 | 0.22 | 0.03 | 0.00 | 0.00 |
| 40 | 8.85 | Dispersek 190 | 4.51 | 0.51 | 1.80 | 0.18 |
| 100 | 33.38 | Kronos 2130 | 45.00 | 1.35 | 45.00 | 1.35 |
| Grind Total | | | 72.37 | 4.60 | 46.80 | 1.54 |

| | | | | | | |
|-------------------------------|----------------|--------------------|-----------------------|------------|---------------------|------------|
| Pigment Total | | | 45.00 | 1.35 | 45.00 | 1.35 |
| Grind (2000 rpm) to Hegman 7+ | | | | | | |
| | | | | | | |
| LETDOWN: | | | Formula | | Non-Volatile | |
| <u>% NV</u> | <u>Lbs/Gal</u> | <u>Material</u> | <u>Lbs</u> | <u>Gal</u> | <u>Lbs</u> | <u>Gal</u> |
| | | Grind | 72.37 | 4.60 | 46.80 | 1.54 |
| 0 | 8.33 | Water | 28.20 | 3.39 | 0.00 | 0.00 |
| 62 | 8.93 | Resydrol VAF | 100.00 | 11.20 | 62.00 | 6.94 |
| 1 | 8.68 | BorchiOXY COAT 110 | 1.30 | 0.15 | 0.01 | 0.00 |
| 0 | 8.66 | Propylene Glycol | 2.20 | 0.25 | 0.00 | 0.00 |
| 45 | 8.30 | BYK 346 | 3.30 | 0.40 | 1.49 | 0.18 |
| 40 | 9.30 | Strodex KM-OVOC | 2.20 | 0.24 | 0.88 | 0.08 |
| 28.3 | 8.60 | Aquaflow XLS 530 | 1.29 | 0.15 | 0.37 | 0.04 |
| 28 | 8.60 | Aquaflow NMS 450 | 11.20 | 1.30 | 3.14 | 0.33 |
| TOTAL | | | 222.06 | 19.98 | 110.30 | 8.65 |
| <u>Paint properties</u> | | | | | | |
| Weight per gallon | | 11.11 | % NV by weight | | 49.67 | |
| Viscosity (KU) | | 73.62 | % NV by volume | | 43.31 | |
| VOC (g/L) | | 34.15 | PVC | | 15.58 | |

Safety: This experiment may be conducted using the grinder on the benchtop. Drawdowns may be placed on the benchtop to dry.

Helpful hints: Add each addition step wise. Carefully move the blade to the side of the can and slow the speed considerably when adding the resin and pigment. This is to prevent the resin from wrapping around the rotor and the pigment from escaping the canister. After adding both components, mix at an increasing speed until full integration. Mix the grind for about 5 minutes after complete addition and the letdown for about 5 to 10 minutes.

Experimental: Before making the coatings, determine the paint properties left blank in the formulation. After making the paint, close it with a lid then let it sit for a minimum of 24 hours (make a note about how the coating looks immediately after making it vs. after letting it sit for some time). After 24 hours make sure you do the following:

- 1) Take its viscosity and make both a 3 mil and 5 mil drawdown.
- 2) Filter the paint into another pint paint canister (use the spatula to carefully press paint through the filter if necessary; more than one filter may be needed)
- 3) Take the viscosity of the filtered paint, then make both a 3 mL and 5 mL drawdown.

Discussion: As discussed, what is added into a paint formulation is very specific. Evaluate the different types of titanium dioxide used (what they're used for, particle size, and any limitations on mixing speed) and explain what was seen both before and after filtration of all the alkyd emulsions. How did viscosity, gloss, hiding power, contrast ratio, and overall film appearance change, or were similar, between the 3 types of TiO_2 . Did filtration make a difference? How would you improve the coating in terms of TiO_2 choice or what TiO_2 would you use if you were going to use this coating? Lastly, what did you notice about the

viscosity changes while mixing the coatings? What problems did you experience and how were they overcome?