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Improving Aluminum Can Paint Coatings

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MAJOR QUALIFYING PROJECT

Completed in partial fulfillment of the Bachelor of Science degree in Chemical Engineering at
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IMPROVING ALUMINUM CAN PAINT COATINGS

Sponsored by:
Pacific Can Beijing & the Beijing University of Chemical Technology

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ABSTRACT

This project investigated the causes of paint failure on aluminum cans made by Pacific Can Beijing. Hypotheses were proposed as to why paint coatings experienced failure during can production. Paint coating laboratory tests were conducted by the project team to narrow down the possible causes of paint failure. Recommendations were made to increase the performance of paint coatings and decrease the amount of cans that experience paint failure.
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Professors Jianyu Liang and Amy Zeng

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Pacific Can China Holdings Limited

The project team would like to thank Pacific Can and CEO Glenn Yee‘74 for the opportunity to work at a state of the art manufacturing plant like Pacific Can China Holdings Limited Beijing. The project team visited Pacific Can many times to collect data, run tests, and consult with the Pacific Can engineering team. We would like to thank the Pacific Can staff and engineering team, especially Mr. Tan, for the time they sacrificed to explain the production process, answer questions, and collect samples for our testing.

Beijing University of Chemical Technology

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AUTHORSHIP

The Improving Aluminum Can Paint Coatings major qualifying project and paper was equally divided amongst the two project team members, Kevin Kerhulas and Mohammed Babkoor. The project paper went through many stages of writing, editing, and formatting, each of the project partners contributing to the final completion of the project paper equally based on his writing, editing, and formatting skills.
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EXECUTIVE SUMMARY

The beverage manufacturing industry demands a huge quantity of high quality aluminum cans. In fact, the beverage can industry produces three hundred million aluminum cans daily and a total of one hundred billion cans annually (Hosford & Duncan). In the Improving Aluminum Can Paint Coatings project, a team of Worcester Polytechnic Institute (WPI) and Beijing University of Chemical Technology (BUCT) students worked in conjunction with a Chinese manufacturer of the two-piece aluminum can, Pacific Can China Holdings Limited Beijing, to improve the performance of paint coatings on the aluminum can.

The goal of the Improving Aluminum Can paint coatings project was to develop recommendations that would reduce the number of cans that experience paint failure. In order to reach this goal, the project team developed a set of objectives to complete. The objectives of the paint coatings MQP team were to first develop hypotheses as to why the aluminum cans experience paint failures, test our hypothesis with a variety of laboratory techniques used in the paint coatings industry, and develop recommendations that correspond with the test results and observations the project team made at the Beijing production facility. Three hypotheses were developed by the team in order to over the course of the project: the paints fails due to either mechanical forces, chemical attacks, improper curing treatment or any combinations of these three.

As a result, different paint coating industry laboratory testing techniques were conducted to test each of the developed hypotheses. The figure below shows the testing techniques and equipment proposed for each hypotheses.

Figure 1 shows the different experimental techniques/methods proposed for each hypothesis
Due to limitations encountered at the project center and a short, seven-week project duration, the project team conducted a limited amount of tests and eliminated any testing that exceeded the project budget or wouldn’t produce significant enough data that the project team could use to determine the cause of paint failure. Below is table containing the testing that was completed and eliminated during the duration of the project at the BUCT.

The majority of the testing performed were those corresponding to the first hypotheses, paint coating stress tests developed by the American Society for Testing and Materials (ASTM). After testing, the paint coatings team concluded that the paint coatings produced at Pacific Can develop very strong adhesion forces and withstood the stress tests conducted. However, the team was not able to conduct enough testing to conclude whether the other two hypotheses could be potential causes of paint failure. Recommendations were made based on the conducted test results and observations made during the four visits made to the Pacific Can Beijing production facility.

The project team developed short term and long term recommendations. The short term recommendations include decreasing the pH level range of the membrane bath from 3.1 – 3.36 to 2.6 – 3.1 pH and to purchase mixers for the passivation membrane and acidic cleaner barrels feeding the line washer. The long term recommendations are to conduct research into replacing the passivation membrane and applying the label paint coating directly to the aluminum substrate by applying a varnish on the bottom of the can or purchasing anodized aluminum. The goal of the recommendations developed by the paint coatings team were to increase the adhesion forces between the paint coatings and the aluminum substrate, increase the paint coatings performance, and reduce the amount of cans that experience paint failure.
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CHAPTER ONE: INTRODUCTION

One of the most common applications of aluminum is in the beverage manufacturing industry. In fact, the beverage can industry produces three hundred million aluminum cans daily and a total of one hundred billion cans annually. Although the production process may not seem advanced at first glance, it requires a lot of accuracy and precision in order to produce aluminum cans at a rapid, profitable rate. Highly qualified engineers are always in demand in the beverage manufacturing industry in order to optimize can design. Aluminum can production optimization attempts to minimize the amount of materials consumed and energy used while producing more cans and preserving the desired mechanical properties of the can (Hosford/Duncan).

In this project, a team of Worcester Polytechnic Institute (WPI) and Beijing University of Chemical Technology (BUCT) students worked in conjunction with a Chinese manufacturer of the two-piece aluminum can, Pacific Can, to improve the performance of paint coatings on the aluminum can. Pacific Can has developed a state-of-the-art aluminum can making process that produces on the upwards of 7 billion cans a year. Pacific Can is one of the largest producers of the two-piece aluminum can in China with six production plants across the country. In 2010, Pacific Can was awarded with the Can of the Year award and has cornered the beverage packaging industry with major clients like PepsiCo, Coca Cola Beverages, and Anheuser-Busch.

The manufacturing process at Pacific Can starts with sheets of aluminum alloy being fed into a clipper where the amount of aluminum needed to make a single can is cut and enters the body making process. Lubricants, anti-binding agents, and coolants are applied to the aluminum alloy prior to the manufacturing process to minimize friction and thus allow the metal to flow freely through the metal cutting and bending machines. Before any coatings are applied, the aluminum alloy is cleaned in order to remove any oil residues still left on the aluminum substrate. The cans are put through multiple no-rinse washes including a prewash, an acidic cleaning, and a water rinse, all at high temperatures. During the seven-step line washing process, the aluminum is coated with an anti-corrosion agent, a passivation membrane. The purpose of the passivation membrane is to make the aluminum alloy corrosion resistant, maintain the can’s shiny, metallic luster, and provide a proper surface for the organic paint coatings to be applied to. Next, the cans undergo a drying process to allow the primer coat to cure and evaporate any
residual water. After the drying process, the cans are sent to the decorator, where they are printed with the desired beverage labels. After running through another dryer, a lacquer is sprayed on the inside of the can to ensure that the beverage does not corrode the aluminum substrate. The cans pass through an internal dryer and then are sent through a waxes, necker, and flanger where the top of the can is formed. Prior to the packaging of the product onto pallets, the cans are quality tested using X-Ray to look for any faults within each can.

The Pacific Can facility in Beijing has been observing that roughly one in every ten thousand cans experiences paint failure during the filling and packaging processes at Pacific Can’s clients’ beverage factories. Paint failure occurs because the stresses experienced during the filling and packaging processes at beverage factories are greater than the adhesion forces that are created by the can and its paint coatings. As a result, Pacific Can’s clients must recycle these cans because it is not acceptable to supply consumers with an inferior beverage can. Not only does the company lose out on the profit of each failed can, but also the aluminum must be treated to rid the aluminum alloy of paint coatings before it can be recycled. The treatment of cans is a necessary and expensive process. In order to reduce the amount of cans that experience paint failure, the project team analyzed every aspect of the production process to reduce stress or increase adhesion forces between the can and paint coatings.

The cause of paint failure and portion of the can that it occurred in was determined prior to deciding which stress affects each can the most. The project team performed stress tests on aluminum cans with paint coatings to understand the strength of the adhesion forces of the paint coatings. The tests were run to better understand which part of production causes paint failure and the reason behind it in regards to the parameters of production. The can manufacturing process parameters, including temperature, pressure, and pH, was analyzed and optimized in order to ensure a proper environment for can production. The goal of the project was to decrease the amount of cans that experience paint failure at Pacific Can and its clients packaging facilities, decreasing paint treatment and recycling costs while increasing production. The deliverables from the project will increase the efficiency of the can manufacturing process and the performance of the aluminum can paint coatings.

In this report, the engineering team discussed in detail the research and testing the project team conducted in order to provide Pacific Can Beijing sufficient recommendations in improving the paint coatings in their can making process. The report consists of the following chapters:
literature review, methodology, results and discussions, recommendations, and conclusion. The literature review consists of the research that was conducted by the project team and discusses the different components of paint coatings, how paint works, how paint fails, different types of paint coatings, and how entrepreneurship and innovation were applied to the project. The different tests that were conducted to better understand how paint coatings on the aluminum can and their results were discussed in the methodology and results and discussion. The end of the report includes recommendations for Pacific Can Beijing’s aluminum can production process to increase the performance of their paint coatings and a project conclusion.
CHAPTER TWO: LITERATURE REVIEW

2.1 PACIFIC CAN: COMPANY PROFILE

Pacific Can China Holdings Limited manufactures aluminum beverage cans. The company supplies cans for a wide variety of beverage companies that produce beer, soft drinks, juice, and tea. Pacific Can China Holdings is based in Wan Chai, Hong Kong. Founded in 1991, Pacific Can has established a reputation for offering the highest standard of product quality, technical service, and a growing product range. Pacific Can was established by former managers of the Continental Can Company, headquartered in the United States, an international producer of metal containers and packaging, and former colleagues of Mr. Glenn Yee. In 2003, Pacific Can’s Beijing plant production reached a milestone capacity of one billion cans per year.

In 2009, Pacific Can introduced their innovative two-piece Slick2oo can series. In 2012, Pacific Can was selected as the bronze winner for the Can of the Year award with their Slick 355ml FUSION beer can.

Pacific Can has six “large scale” production facilities (seven total). These plants are located in Beijing, Shenyang, Wuhan, Zhengzhou, Qingdao, and Zhao Qing. These production facilities are all ISO9001 and FSSC 22000:2011 certified. The company has 13 total 2-piece aluminum can production lines.

Innovation has a large influence on the work, research, and design done at Pacific Can. Pacific Can was the first to introduce a 500ml two-piece aluminum can, customized aluminum cans for JDB’s herbal tea brand Wong Lo Kat, and the Slick 200 can series.

2.2 PAINT AND COATINGS

In order to investigate paint failure in regards to the aluminum can, the project team researched the components of paint coatings. Coatings consist of four elements: binders, pigments, solvents, and additives, all playing an important role in the performance of the paint. Along with the different components of paint, the density, weight solid, and binder to pigment ratio greatly affect the performance and features of a paint coating. The components and parameters of paint coatings will be described in the following part of the literature review.
2.2.1 BINDERS

In a paint coating, the binders’ purpose is to act as the glue holding the coating components together. The binding component plays an essential role in the working mechanism of coatings; the binder is responsible for the adhesion of the coating to the substrate. Binders are mostly organic ranging from natural resins and oils to pre-polymers and polymers (Weldon 2-4).

The curing process of binders after the application of a coating is extremely important to the performance of the paint coating in regards to adhesion. As a result, binders are commonly classified on how they cure. Those that cure by solvent evaporation are called thermoplastic while those that cure by chemical reactions after its application are called thermosetting (Weldon 2-4).

One of the most important parameters in the formulation of a paint coating and its binder is viscosity, or a material’s resistance to flow. In order for a coating to be applied by traditional means, by a brush, roller or spray, it must be thin enough so that it can flow. Equally important, the coating must also be thick enough so that sagging does not occur (Weldon 2-4).

2.2.2 PIGMENTS

Pigments are substances that absorb, scatter, or reflect transmitted light. Pigments affect three properties in a coating: corrosion resistance, physical properties, and appearance. In regard to the paint coating as a whole, pigments are minuscule insoluble particles that have a diameter of approximately 1mm (Weldon 4-5). Pigments fall generally into two categories: organic or inorganic. Organic pigments have more complex molecules than inorganic pigments. Although there are a wide variety of organic pigments available in the paint coatings market, they are rarely used as a primer coating, since their main advantage is rich color. The two most well-known inorganic pigments are titanium dioxide and iron oxide. Titanium dioxide is used as a white pigment, commonly for exterior coatings because of its very high refractive index. Iron oxide is the most popular inorganic red pigment (Weldon 4-5).

2.2.3 SOLVENT

Almost all types of coatings need solvents in order to dissolve the binder and adjust the viscosity of the coating. Solvents evaporate after the application of the coating and provide aid in the flow and wetting of the coating during application. An important parameter regarding solvents is their solubility. Some types of binders need specific solvents that commensurate with
their chemical structure. The rate of evaporation of a solvent is another crucial aspect of a paint coating, which could substantially vary from one solvent to another. A solvent that evaporates too quickly is known as a fast or hot solvent, while a solvent that evaporates too slowly is known as a slow solvent. It is very imperative that a solvent has an appropriate evaporation rate. For example, a fast solvent does not allow for a paint coating to flow in a smooth continuous film. As a result, paint failure occurs, known as an orange peel observed in many finishes on automobiles. A too slow solvent also may result in paint failure, known as sagging (Weldon 5).

2.2.4 ADDITIVES

Additives are chemicals that are added to a coating to make it more suitable for the substrate on which it is intended to be applied to. Additives could be surfactants, anti-settling agents, coalescing agents, anti-skinning agents, catalysts, deformers, ultraviolet light absorbers, dispersing agents, preservatives, dries and plasticizers (Weldon 5).

2.2.5 PAINT PARAMETERS

DENSITY
The density of a coating is commonly measured by a pycnometer, an apparatus designed with a fixed volume to be filled with paint. The density is usually reported as pound per gallon.

WEIGHT SOLIDS
This parameter represents the ratio of a very high boiling point or non-volatile materials to the mass of the coating or paint as a whole. For example, consider a batch of paint that has a total mass of 50 kg and consists of 22 kg of solvent, 24 kg of resins, and 4 kg of additives. Then such a batch of paint would have a 56% weight solids. Similarly, the volume solid is the ratio of the volume of the non-volatile materials to the volume of the coating or paint as a whole. This property is relatively more important than weight solids since it determines how much area a certain coating will cover.

PIGMENT TO BINDER RATIO (P/B)
The P/B is simply the ratio of the mass of a pigment to the mass of a binder. For example, a hypothetical type of paint consists of 20 kg pigment and 15 kg of binder. Such a paint or coating would have a pigment to binder ratio (P/B) of 1.33.

PIGMENT VOLUME CONCENTRATION (PVC)
The PVC refers to the ratio of the volume of the pigment \((V_p)\) to the volume of the pigment and the binders \((V_b)\) combined. It is a much more important parameter than the pigment to binder ratio. It could be calculated using the following equation:

\[
PVC = \frac{V_p}{V_p + V_b}
\]  

(1)

In fact, what is really important about the PVC is the CPVC, or the critical pigment volume concentration. It is the PVC at which every single particle of pigment (pigments are very tiny particles that are suspended in the paint rather than dissolved) is coated with the exact amount of binder. Above the CPVC, the concentration of binder to pigment is low while below the CPVC there is excess binder. It is recommended that the PVC should not be higher than the CPVC as many properties such as tensile strength, abrasion resistance, and permeability deteriorate as the CPVC decreases.

2.3 HOW PAINT AND COATINGS WORK

“Coatings are used for one or more of three reasons: (1) for decoration, (2) for protection, and/or (3) for some functional purpose.” (Organic Coatings Science and Technology 25) Every paint coating that is applied to the aluminum can during production at Pacific Can has an important role in the performance of the product, from the lacquer sprayed inside of the can to the beverage label that is rolled on the outside of the can. As one may know, metal is not the best surface to apply paint to, so how does the paint coatings stick to the aluminum alloy surface? According to *Failure Analysis of Paints and Coatings* by Dwight G. Weldon, the five reasons why paint coatings work is due to adhesion, wetting, surface preparation, cohesive strength, and permeability. This next portion of the literature review will go in depth on the five reasons why paint coatings work.

2.3.1 ADHESION

Adhesion forces can be formed between a paint coating and its desired substrate due to primary, secondary, and mechanical bonding (Weldon 9). Primary chemical bonding consists of ionic, covalent, and metallic bonding. Ionic bonding occurs when electrons are donated from a metal, positive cation, to and a nonmetal, negative anion. On the other hand, in covalent bonding two non-metals share electrons. Even though primary bonding rarely occurs, it is very critical for coatings and paints to establish such kinds of bonding with their respective substrates. Secondary
bonding such as hydrogen and van der waals forces are the forces that mostly responsible for adhesion.

Mechanical forces is the theory that the more pores on a substrate’s surface, the more chemically active sites there will be on the substrate. The chemically active sites on the substrate, pores and voids, allow for mechanical interlocking with the desired paint coating (Weldon 10). The application of mechanical forces applies to the paint coatings in the can making process because the passivation membrane is applied to the can using a spray nozzle. Due to the corrosion aluminum experiences during oxidation, as the passivation membrane is sprayed onto and runs over the can it will be able to grab the aluminum and create strong secondary bonds. Without establishing proper adhesion forces, the paint coatings on the aluminum alloy will simply not be able to stick to the can as it undergoes multiple drying, necking, flanging, and pasteurization stages, causing mechanical and internal stress.

2.3.2 Wetting

During each of the five stages of cleaning and membrane application process, the aluminum can is sprayed for twenty five to thirty seconds using a spray nozzle. “The process of a liquid spreading over a substrate and coming into intimate contact with it is called wetting” (Weldon 10). In order to apply a proper membrane to the aluminum can, the membrane must be applied evenly throughout the entirety of the can. If the membrane is too thick or too thin in any area of the can, especially the top of the can, this can cause paint failure. This section will look at the science behind wetting and how a substrate can be properly covered with a liquid.

To understand wetting, the project team researched the science behind the water molecule and why it beads up. In thermodynamics, it is understood that elements in nature exist in a form where there is minimal free energy and maximal entropy. Therefore, water creating a spherical like structure when poured onto a substrate as a result of the molecule attempting to decrease its free energy. Due to the complicated, ordered structure of the sphere, the shape that water takes when on a substrate does not maximize entropy but is due to water’s high surface tension due to strong hydrogen bonding forces water experiences with other water molecules. In his book *Failure Analysis for Paint and Coatings*, Weldon defines the surface energy as “the excess free energy associated with molecules at the surface compared to molecules in the interior, or bulk, of the liquid Surface energy has the units of joules per square meter, representing the amount.
Surface energy is defined as the amount of work (energy) required to create a unit area of surface, and therefore has units such as joules per square meter or ergs per square centimeter” (Weldon 11). As a result, in order for a liquid to properly wet a substrate the surface energy of the solid must be greater than the surface tension of the liquid. If the surface energy is greater than the surface tension, the contact angle will be near zero allowing for a proper wetting, where as if the surface tension is greater the contact angle will be much higher.

In order to increase the wetting experienced by aluminum cans during the cleaning process and membrane application, we must look into decrease the surface tension of the cleaner. The surface tension of the aluminum alloy cannot be altered for can production because surface tension of a substrate is determined by its composition. Altering the composition of the aluminum can would completely change the production process and is not a risk Pacific Can would be willing to risk. As a result, the project team must look into the parameters that define a liquid surface tension, including temperature, solvents, additives, and resin types (Weldon 11). While taking the surface tension of both the substrate and the liquid into account, we must also consider other aspects of paint coatings that could affect paint application, like viscoelastic forces, contaminated substrate, and temperature. While the difference in surface tension between a liquid and its substrate allow the liquid to properly run along its surface, viscoelastic forces oppose these forces (Weldon 10). In regards to viscoelastic forces, if a substrate and liquid have similar surface tensions, a liquid with a high viscosity will not be able to properly wet a substrate compared to one with a low viscosity. Although the surface tension of metallic substrates is greater than most liquids applied to them, we must understand that during production if the concentration of the liquid bath is altered, paint failure will occur. The concentration of the
cleaner and membrane bath of can be altered due contamination or the end of the “pot life” of the membrane or cleaner supply, resulting in the increase of a liquid bath’s viscosity and the decrease of the bath’s ability to wet a substrate. For example, at Pacific Can, the cleaner and passivation membrane is kept in blue, plastic barrels and then pumped into the production process where it is mixed with water. As the cleaners and chemicals sit in the barrels, the concentration of the chemicals being pumped into production may become altered, especially towards the bottom of the barrel. An altered concentration could result in an improper cleaning or membrane application, both resulting in failure. “It is common in the coatings industry to hear remarks such as ‘even the slightest residue of oil will cause a coating to fail’ (Weldon 13, 14).” A simple way to lower the surface tension and the viscosity of a liquid that will be applied to a substrate is to increase the temperature of the application process. The temperature of the cleaning and membrane application process will be thoroughly examined to ensure proper project recommendations.

2.3.3 Surface Preparation, Cohesive Strength, and Permeability

Along with adhesion forces and wetting, surface preparation, cohesive strength, and permeability play a role in how paint coatings work. At Pacific Can, the process used to prepare the aluminum alloy surface for organic paint coatings is by applying a passivation membrane by conversion coating. It is suggested to use a process called anodizing to apply a passivation membrane to an aluminum substrate (Weldon 23). Anodizing is a type of controlled membrane application where an electric current is run through the metal cleaning process to increase the natural oxide layer around the substrate.

Although not specific to the Pacific Can paint coatings, the final two reasons why paint coatings work are cohesive strength and permeability. Cohesive strength is directly related to the pigment-to-binder ratio (P/B), the molecular weight of the binder, and the cross-link density of the binder (Weldon 23). On the other hand, the permeability of the paint coatings at Pacific Can must be very low, protecting the can from experiencing blistering from water, oxygen, and or salt. The paint coatings chemical resistance to its environment, the pigment-to-binder ratio, the pigment, and cross-link density are the main components that affect the paint coatings permeability (Weldon 23). In regards to Pacific Can, Weldon explains that a thinner
coating not only experience less stress than thicker coatings but also can absorb more solvent, both resulting in paint failure. The permeability of the paint coatings was examined for paint failure due to osmotic or electroendosmotic blistering. To ensure paint failure did not occur due to paint coating thickness, the project team analyzed optimizing the thickness of the paint coatings at Pacific Can.

2.4 HOW PAINTS AND COATINGS FAIL

Prior to the aluminum can being painted with the desired beverage label, the surface of the aluminum alloy must be treated with an oxidizing acidic cleaner and a fluoro-acid membrane. With the membrane, the paint coatings are given a proper surface to be applied to the can, allowing for the proper adhesion bonds to be created between the organic paint coatings and aluminum substrate. The aluminum can’s desired label is applied using a roller (Weldon Chapter 6.4). During this process, the aluminum cans are rotated at the same speed as the application rollers. The application rollers are simultaneously given paint from smaller pickup rollers that have been dipped into paint. This allows the aluminum can to be coated with many layers paint coatings, each one representing a different color, at a very rapid pace. Despite the Alodine 404 membrane that is used at Pacific Can, the employees have been seeing a large number of defective cans due to paint misprints, which cannot be used as a Pacific Can qualified product. As a result, Pacific Can pays a large sum to treat the aluminum to rid it of the label paint so that it can be recycled. In order to increase the adhesion of the membrane and the paint coatings, the MQP must look at why paint coatings fail.

Throughout the entire can making process at Pacific Can, there are many areas of production that can affect the quality of the can. Paint failure occurs when the stresses experienced by the can during the production process, especially during the washing process and heating ovens, are stronger than the adhesion forces that are created between the paint coatings and substrate. “For a variety of reasons, stresses can accumulate in films; if the stresses exceed the tensile strength of the films, failures will result.” (Organic Coatings: Science and Technology 104) The four main reasons why paint coatings fail are due to the misapplication of a coating, a defective coating, the wrong choice of a coating for its desired purpose, or the exposure to an unanticipated environmental excursion. In regards to companies that specialize in paint coatings, or in the case of Pacific Can innovative production process, paint coatings might fail as a result
of one of five types of stresses: mechanical stress, internal stress, chemical attack, weathering stress, osmotic blistering, and electro-endosmotic blistering (Weldon Chapter 2.2). The parameters of production at Pacific Can was analyzed and optimized to ensure that there will be no future paint failure due to misapplication of the coating, defective coating, and wrong choice of coating, or exposure to an unanticipated environmental excursion. Specific to the cans created at Pacific Cans, weathering stress is not a probable cause for a paint failure where mechanical stress, internal stress, chemical attack, and blistering are all serious aspects of the production process that will be examined in this project.

2.4.1 MECHANICAL STRESS

In order to analyze the mechanical stresses that the aluminum can experiences during the can production process, the project team began with analyzing the application of the first paint coating, the Alodine 404 membrane. After the aluminum can is cleaned of all of the oils and contaminants, the passivation membrane Alodine 404 is applied using conversion coating followed by a final water rinse and drying process. The Alodine 404 membrane is considered what is called a viscoelastic solid. A viscoelastic solid is a material that has properties of both viscous liquid and elastic solids (Weldon 39). Although the membrane is applied to the can using an aqueous liquid bath, the purpose of the membrane is exist in its’ solid form as an adhesive agent. During the drying of the can the Alodine 404 turns from a viscous liquid to a viscous solid. The temperature and rate of the production affects whether the membrane takes either the properties of the viscous solid or liquid. The amount of stress that the aluminum can experiences, the force applied to the can, directly affects the amount of strain that the can undergoes. As a result the modulus, the ratio of stress to strain, or stiffness of the paint membrane will remain constant. A substance’s modulus remaining constant is described as displaying a Newtonian behavior. Due to conservation of energy, “this stress has to be relieved, and how the coating (or coating system) does this will determine whether or not it fails, and the mode of failure” (Weldon 41). The entire process of labeling an aluminum can involves a multi coat system of the membrane with separate layers of organic paint for the different colors that are displayed on the cans. If the paint-membrane adhesion has strong cohesive forces then the stress experienced during the manufacturing process will not cause the paint to fall off of the can itself. Failures occurs at the weakest point due to mainly three reasons: inappropriate application of the membrane to the can, lack of surface preparation, and/or partial corrosion of the body of the can.
At Pacific Can, the can undergoes the most physical forces during the necking and flanging processes of production as well as the can’s movement along the production line on conveyor belts and can tracks. As the forces from these stages of production act on the can, the stress is experienced throughout each layer of the paint coatings but primarily affects the primer on the substrate. When these forces are applied to a can that has a flaw within its substrate structure of paint coating, failure occurs through the delamination of the paint coatings from the can itself, sometimes taking the membrane along with it (Weldon 2.2.1). The membrane’s elastic component depends on whether the paint coatings on the aluminum will experience failure or not. Mechanical stress is experienced at Pacific Can through the physical forces applied to the can through the necking and flanging process and through the cans movements through the production process. When the structure of the can has been compromised or a paint coating has not been properly applied or cured onto the can, the aluminum can paint coating may experience paint failure. The project team analyzed the reduction of mechanical stress throughout the production line at Pacific Can.

2.4.2 Internal Stress

The aluminum can undergoes three different drying processes where its’ paint coatings cure, after the application of the membrane, after the beverage label is rolled onto the can, and one last time after the inside of the can is sprayed with lacquer. During these processes, the paint coatings’ molecules move very fast as the solvent evaporates and the remaining paint coating components bind the aluminum can. “Internal stress is the consequence of a coating’s inability to shrink. If the coating shrinks, this is actually a form of stress relaxation, and the stress or internal energy has been dissipated (much like a crack forming in a brittle coating which dissipates the stress that has built up or has been applied to that coating)” (Weldon Chapter 2.2.2). As the solvent component of the paint coating evaporates, cross-linking causes the paint coatings to shrink. As a result of the solvent evaporation, the covalent bonds being created while the cans are being dried are much shorter. “In the early stages of solvent evaporation and/or cross-linking, the coating is often above its glass transition temperature ($T_g$) and the polymer chains have sufficient mobility to allow for shrinkage. However, as film formation via solvent evaporation or continual cross-linking proceeds, the $T_g$ will continue to rise; the polymer chains will have reduced mobility, and internal stress will result from the coating's inability to undergo further shrinkage” (Weldon Chapter 2.2.2). As paint coatings are added onto the label of the can and
then dried, the can experiences what is called shrinkage stress. Shrinkage stress is the force applied to the primary coating of paint due to the top layer of paint coating shrinking (Weldon Chapter 2.2.2). The primer adhesion to a substrate will fail if its cohesive forces cannot withstand the shrinkage stress of the top coatings of paint, in the case of the aluminum can causing the paint label to fall off. During the process of painting the aluminum can internal and shrinkage stress occurs as the membrane is dried, the paint label is dried, and the lacquer applied to the inside of the can is applied. Each time that the aluminum can enters a drying oven, the weakest points on each can are tested to see if their cohesive forces can withstand the internal and shrinkage stress.

2.4.3 Chemical Attack

There are many chemicals that are applied to the aluminum can throughout the production process each having a specific purpose, but the combination of all of these chemicals depends on the performance of the paint coatings of the end product. The stages of production that could affect the performance of the paint coating if contaminated is the washer bath, membrane bath, beverage paint label, lacquer application, and waxer application. Chemical attack is considered a stress because it does not allow for the proper adhesion bonds to be created and as a result doesn’t allow the proper performance of the paint coating. The reactivity of a paint coatings depends on the polarity of the bond since most paint coatings are organic and subject to chemical reactions (Weldon 31). “In practical terms, coating binders consisting primarily of carbon–carbon single bonds, or ether (C–O–C) linkages, are relatively stable towards chemical attack. Binders containing alcohol, carboxylic acid, ester, amine and amide groups, and those containing conjugated carbon–carbon double bonds, will be more susceptible to aggressive chemicals such as acids, bases and oxidizing agents” (Weldon 32). Also, carbon-carbon double bonds are more susceptible to chemical attack than carbon-carbon single bonds due to their degree of delocalized electrons. The double bond is more susceptible because the more delocalized electrons there are the more electrons are able to react. Due to contact with acids and or bases, pigments along with binders can cause paint coating failure due to chemical attack. In the case of Pacific Can the aluminum can is amphoteric, react as an acid or a base depending on the chemicals present in an environment (http://study.com/academy/lesson/amphoteric-definition-properties-examples.html). As a result of this amphoteric characteristic, aluminum can be subject to rapid deterioration known as the
aluminum flake (Weldon 32). The possibility of contamination of the paint coatings used at Pacific Can was thoroughly researched and analyzed through testing.

### 2.4.4 Blistering

During the cleaning process of the aluminum can prior to the passivation membrane application, the aluminum can experiences both oxidation and corrosion due to the high temperature at which water is sprayed onto the can. The passivation membrane is then sprayed on using an aqueous solution followed by two water rinses. After the application of the membrane it is critical that water does not penetrate the membrane surface in order to assure paint quality. Despite the membrane and paint coatings acting as barriers to water, the water molecule can pass through most modern paint coatings due to its small size. When water passes through the paint coatings to the water-soluble coating, the Alodine 404 membrane will begin to dissolve. If a portion of the membrane dissolves on the can and the aluminum alloy is exposed, this location on the can acts as an osmotic cell (Weldon Chapter 34-36).

“An osmotic cell consists of a semipermeable membrane (the coating) separating a solution of high concentration (the submicroscopic droplets of dissolved material) from a solution of low concentration (e.g. relatively pure potable water in an elevated water tank). This is a non-equilibrium condition and the two solutions have different values of free energy or chemical potential. There will be a strong driving force to make these two concentrations, and hence the chemical potential of the solvent (water in this example), equal. In practice, more water than 'normal' will permeate the coating in an attempt to dilute the concentration of the soluble species within or behind the coating film. The driving force for this is the concentration gradient and hence chemical potential gradient, across the coating membrane. The consequence is a water-filled blister. Such blisters are fairly common, and are referred to as osmotic blisters. The term 'osmotic pressure' refers to the pressure that is building up inside or behind the coating as more and more water accumulates there. The water is not accumulating because it is being forced through the coating under pressure; it is accumulating in an attempt to eliminate the concentration gradient. In fact, it will continue to do so until the pressure being exerted inside the forming blister is energetically equivalent to the
chemical potential difference across the coating due to the concentration gradient” (Weldon 48).

In respect to the aluminum can, osmotic blistering occurs due to the application of the membrane with an aqueous solution. Due to the high rate at which the aluminum cans are manufactured, the passivation membrane is dried at a very fast rate, meaning the solvent must evaporate during this period. “Solvent, depending on its evaporation rate and the temperature and air flow during application, initially evaporates rapidly from a coating. However, as the coating begins to dry and harden, solvent evaporation drops off rapidly. It has been reported [19] that up to 10-20% of the original solvent may be retained within the coating, and that in some cases, up to 5-10% of it may be retained for years” (Weldon Chapter 49). The surface preparation of the aluminum can is critical to how well the passivation membrane is applied to the can. With an improper cleaning or corroded can, the passivation membrane will not wet the entirety of the can. As a result the parts of the can where a proper membrane wasn’t applied will develop osmotic cells when sprayed with water. When the adhesion forces are surpassed by the stress caused by blistering, paint failure will occur.

2.5 ALUMINUM CORROSION

2.5.1 METALS IN NATURE

No metals exist uncombined in nature. Gold, silver, copper and platinum are the only exception to this rule. All metals are found combined with other metals and elements. Such combinations are known as ores and minerals. Ores and minerals naturally form in the earth’s crust. For example, aluminum is most abundantly found in an aluminum ore known as Bauxite, which consists of many elements. Bauxite is a mixture of hydrous aluminum oxides, aluminum hydroxide, clay minerals, and some insoluble materials. Aluminum minerals in Bauxite may encompass gibbsite (Al (OH)₃), boehmite ((γ-AlO (OH))) and diaspore (AlO (OH)).

In order to obtain a pure metal, the metal has to be separated from its ore or mineral. This separation process, or extraction, requires a tremendous amount of energy and is highly endothermic. Extracted metals are in an unstable state due to the huge amount of energy transferred to them. On the other hand, metals tend to be highly stable in their natural ore and minerals and always try to revert to this stable state when possible.
This reversion process is what is known as corrosion. Corrosion is a naturally occurring process in which metals convert back to the way they exist in nature when they are exposed to the environment. Corrosion is usually not desirable due to the fact that it deteriorates the desired properties of the metals in general.

2.5.2 Types of Corrosions

There are many types of corrosion, each of which has its own mechanism. This section of the literature review discusses these types briefly.

Uniform Corrosion

Also known as chemical attack corrosion is the most ubiquitous type of corrosion, caused by chemical or electrochemical reactions. Such corrosion leads to the deterioration of a metal surface. If the metal is not protected against corrosion, the metal will eventually reach mechanical failure. Although uniform corrosion is responsible for the majority of deterioration in metals, it is often regarded as the safest type of corrosion because it is foreseeable and preventable.

Localized Corrosion

In a limited area of a metal and is classified to three types as follows:

1. Pitting Corrosion. Industrial metals are coated with corrosion-resistant agents. However, a metal sometimes partially loses its passivation in some areas. As a result, a metal undergoes partial corrosion, or localized corrosion while de-coated area becomes anodic and the rest of the metal becomes cathodic. This results in a galvanic reaction, which deteriorates the attacked area. Pitting corrosion is considered highly dangerous because it is often hard to detect due to the relatively small area where it occurs.

2. Crevice Corrosion. Occurs as a result of exposing the metal to a still microenvironment. Exposing metals to acidic conditions might result in this kind of corrosion.
3. Filiform Corrosion. Happens when water attacks a coating. Water penetrates areas where coating defects are present, resulting in the deterioration of the metal structure.

**GALVANIC CORROSION**
Requires the presence of two different metals that are exposed to an electrolyte. One metal undergoes oxidation, the anode; while the other metal undergoes reduction, the cathode. Considering the metals are exposed to an electrolyte, a galvanic couple forms. The anode, as a result, corrodes faster than it does when it’s in its natural environment. In contrast, the cathode deteriorates slower than it does naturally.

**ENVIRONMENTAL CRACKING CORROSION**
Caused by environmental parameters that collectively lead to the deterioration of metals. Chemical and mechanical conditions are the result of stress corrosion cracking, fatigue corrosion, hydrogen-induced cracking, and liquid metal embrittlement.

**FLOW–ASSISTED CORROSION (FAC)**
Occurs after the dissolution of a substrate’s passivation membrane, exposing a substance directly to its environment.

**INTER–GRANULAR CORROSION**
The attacking of a metal’s grain boundaries by a chemical or electrochemical reaction. The corrosion is due to impurities in metal. These impurities exist close to grain boundaries, and are as a result more susceptible to corrosion than the rest of the metal.

**DE–ALLOYING**
Corrosion happens in the part of an alloy of where there is a high concentration of metal that is more inclined to corrosion.

**FRETTING CORROSION**
Caused by wearing, weight, and vibration on an unevenly rough surface. It is usually found in rotation and impact machinery and bearings.

**HIGH-TEMPERATURE CORROSION**
Fuels that used in metal turbines and diesel engines contain vanadium or sulfates. Such compounds undergo a series of reactions during the combustion process and as a result form new compounds that are highly corrosive. This type of corrosion may also happen by high temperature oxidization.
2.5.3 **Redox Reactions**

Redox reactions are involved in almost all kinds of corrosion. Redox reactions are also called oxidation-reduction reactions. Similar to acid-base reactions, redox reactions are matched set reactions, meaning that they always happen simultaneously. Each reaction is called a halfway reaction, and together they form a complete reaction. Oxidation means the loss electrons while reduction means the gaining electrons. An example of a half-reaction that involves oxidation is as follows: \( \text{Cu} (s) \rightarrow \text{Cu}^{2+} + 2e^- \). What is happening in the above reaction is that the copper is undergoing oxidation (losing electrons), and thus becoming a cation. The symbol \( e^- \) represents a free electron and since copper is being oxidized, the electron is present in the right side of the chemical equation.

Oxidation is always associated with reduction reaction. To further explain redox reactions, consider the following reduction reaction:

\[
2 \text{Ag}^+(aq) + 2e^- \rightarrow 2\text{Ag}(s) \quad (1)
\]

The silver is initially in an aqueous solution and exists as sliver ions. It then undergoes a reduction reaction by receiving the electrons lost by copper, forming a solid sliver. The two half-reactions can be added together to give the complete reaction.

\[
\text{Cu} (s) \rightarrow \text{Cu}^{2+} + 2e^- \quad (2)
\]

\[
2 \text{Ag}^+(aq) + 2e^- \rightarrow 2\text{Ag}(s) \quad (3)
\]

\[
\text{Cu} (s) + 2 \text{Ag}^+(aq) + 2e^- \rightarrow \text{Cu}^{2+}(aq) + 2e^- + 2\text{Ag}(s) \quad (4)
\]

By simplifying

\[
\text{Cu} (s) + 2 \text{Ag}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + 2\text{Ag}(s) \quad (5)
\]

As shown above, the two half-reactions are added up together to give the complete reaction. The two electrons in both side of the equation cancel each other out. Since copper is being oxidized. As a result the copper loses an electron, what is known as a reducing agent, causing other substances to gain electrons. That is also why copper can be called an electron donor. Similarly, silver is considered an oxidizing agent because it causes other substances to lose electrons, making silver an electron acceptor.
**Oxidation Number (ON)** Whenever redox reactions are discussed, the oxidation number should also be discussed. The oxidation number is defined as the effective charge of an atom in a compound. This charge is calculated in accordance to a set of rules. An increase in the oxidation number is followed by an increase in the oxidation state. On the other hand, a decrease in the oxidation number is followed by a decrease in oxidation state and eventually leads to reduction. Therefore, the tendency of a metal to be oxidized or reduced can be inferred from its oxidation number. The rules of assigning an oxidation number are as follows:

1. The oxidation number of a substance in its natural state is zero.

2. The oxidation number of simple ions is equal to the charge on the ion. For example, in aluminum oxide (Al₂O₃), the oxidation number of Al³⁺ ion is +3, and the oxidation number of oxygen in the O²⁻ ion is -2, making the total charge of the compound natural (having a oxidation number of zero).

3. The oxidation number of hydrogen is +1 when it is combined with a nonmetal like the case in CH₄.

4. The oxidation number of hydrogen is -1 when it is combined with a metal such the case in LiAlH₄.

7. Oxygen usually has an oxidation number of -2. Exceptions include molecules and polyatomic ions that contain O-O bonds, such as O₂, O₃, H₂O₂, and the O₂²⁻ ion.

8. The sum of the oxidation numbers in a neutral compound is zero.

\[
\text{H}_2\text{O}: 2(+1) + (-2) = 0
\]

9. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.

10. Elements in the bottom left corner of the periodic table have more tendency to have positive oxidation numbers than their counterparts in the upper right corner. For instance, in SO₂ since the compound is neutral and we know that oxygen is always assigned an oxidation number of -2, sulfur has to have an oxidation number of +4.
2.5.4 CORROSION IN ALUMINUM

Aluminum is the most abundant metal in the earth’s crust. Like most metals, aluminum does not exist in nature in its pure form. It is found as an aluminum ore, combined with other elements. Bauxite, which consists of many elements, is the most present aluminum ore in nature. It is a mixture of hydrous aluminum oxides, aluminum hydroxide, clay minerals, and some insoluble materials. Aluminum minerals in Bauxite may encompass gibbsite (Al (OH)₃), boehmite ((γ-AlO (OH))) and diaspore (AlO (OH)).

Aluminum is regarded as one of the most important metals used in industrial operation due to its extraordinary physical and mechanical properties. Its relatively high tensile strength, ductility, and low density make aluminum a good candidate in many industrial-manufacturing applications. Furthermore, aluminum has a relatively low extraction cost because iron’s melting temperature is 660.323 C, while that of aluminum is 1538 C. Also, an oxide layer naturally forms on the surface of aluminum when exposed to environments where oxygen is present, making aluminum corrosion-resistant. However, the film cannot resist highly corrosive environments like high temperature and pH environments where the thin film is attacked and dissolved.

2.5.5 CORROSION PROTECTION: PASSIVATION

Corrosion is undesirable because it causes metals to deteriorate, eventually leading to mechanical failure. As a result, understanding corrosion and its prevention has been a developing field for a long time, especially in the paint coatings industry. Many chemical compounds have been developed in order to prevent corrosion. Such chemical compounds are coated on the surface of a metal, making the surface chemically inert to its desired environment. The process of applying a thin layer of film over the surface of the metal is called passivation. “Passivation is the process of making a material “passive,” usually by the deposition of a layer of oxide on its surface. In air, passivation affects the properties of almost all metals – notable examples being aluminum, zinc, titanium, and silicon. In the context of corrosion, passivation is the spontaneous formation of a hard non-reactive surface film that inhibits further corrosion. This layer is usually an oxide that is a few nanometers thick.” (Passivation of Aluminum) There are three different types of passivation that are used today: alclading, conversion coating and anodizing.
**ALCLADING** is the process of coating a metal alloy with a thin layer of pure metal that is resistant to corrosion. An example of this is the passivation of aircraft parts that are made of aluminum with pure aluminum.

**CONVERSION COATING** is a protective surface layer on a metal that is created by chemical reaction between the metal and a chemical solution. This type of passivation is the most common in the protection of aluminum cans against corrosion.

**ANODIZING** is an electrochemical process that converts the metal surface into a decorative, durable, corrosion-resistant, anodic oxide finish. Anodizing is the creation of a thick metal oxide passivation layer by immersing a metal substrate into an acid electrolyte bath and passing an electric current through the medium.

Examples of passivation membranes used in the industry for the protection of aluminum cans are discussed in detail in the following section.

**PASSIVATION OF ALUMINUM CANS**

The passivation membrane applied to aluminum can allows for a proper surface for the organic paint coatings to be rolled onto the can’s surface, making up the desired beverage label. The purpose of the aluminum can is not just to hold and contain a beverage but also to promote the product, with the beverage label. As a result of this, Pacific Can cannot sell misprinted cans as their product and instead pay a lot of money to treat and recycle the painted, waste metal from production. The passivation membrane that is used in Pacific Can’s manufacturing process is Bonderite M-NT 404 Conversion Coating, also known as Alodine 404. The company Henkel, a leader in laundry/ home care, beauty care, and adhesive technologies industries, patented the conversion coating process of applying the Alodine 404 membrane on aluminum cans. Henkel supplies Pacific Can with their passivation membrane along with their acid cleaners, Ridoline 120 and 550. Henkel’s safety data material sheets and technical process bulletins for Alodine 404, along with their acid cleaners Ridoline 120 and 550, were used as primary sources in our research. The chemical composition of the Alodine 404 passivation membrane is 1-5% hexafluorozirconic acid, 1-5% ammonium nitrate, and .1-1 % hydrogen fluoride in an aqueous solution. The specific concentration of the compounds found in the Alodine 404 passivation
membrane are unknown due to it being a Henkel company secret although approximate concentrations of the membrane were given.

The recommended process from Henkel of applying the passivation membrane consists of the following processes: pre wash, cleaning, water rinsing, treating the can with the Alodine 404 passivation membrane, water rinsing, deionized water rinsing, and the drying of the can. In 200 gallons of membrane bath with a pH of 2.6 to 3.1, 2 gallons of Alodine 404 is applied to the aluminum cans using spray nozzles from 15 to 130 seconds at temperature ranging from 85° to 110° Fahrenheit. The membrane is a colorless liquid that is very acidic, less than 1.5 pH. The membrane has a boiling point of over 212° Fahrenheit and a specific gravity of 1.02 to 1.05.

The application of the passivation membrane to the aluminum can is completely essential in the function of the can as both a container for beverages and an item of marketing for the beverage company. The passivation membrane restores the quality of the can after it has experienced corrosion, provides a proper surface for further paint coatings to be applied to, and makes the aluminum alloy corrosion resistant.

**2.6 ENGINEERING INNOVATION AND ENTREPRENEURSHIP**

Pacific Can has shown great accomplishments in engineering and business, receiving the first place in the Can of the Year Award in 2009 and the High-Tech Enterprise Certificate in 2010. Awards like these could not have been won without Pacific Can’s leading innovation in the production of the Aluminum cans and entrepreneurship. The team of engineers at Pacific Can are committed to modifying the production of aluminum cans to achieve the maximum rate of production, maximizing profit. Working with the team of engineers, a team of entrepreneurs allows Pacific Can to thrive as a business, creating points of contact throughout China with some of the largest beverage companies like Coca Cola and Pepsi. Selling their soda cans at such a cheap rate due to their state of the art manufacturing process, Pacific Can creates value for beverage companies, allowing them to pay less to package their drinks.

While at the Beijing University of Chemical Technology and Pacific Can, the MQP team must analyze how innovation and entrepreneurship apply to the project and improving the paint coatings on aluminum cans. Through research and testing, the MQP team has developed a set of innovative recommendations that will decrease the number of paint failure cans produced. Entrepreneurship applies to the paint coatings project through trying to convince Pacific Can, a thriving manufacturing company, to accept and apply the project team’s recommendations to the
production process. Through applying innovation and entrepreneurship to chemical engineering projects of all kinds, project teams will increase the impact that they can have on the world, the ultimate goal of any engineer.

2.6.1 Innovation at Pacific Can

In order to maintain a market for a company’s product, engineering teams across the world are concentrating on modifying their products and processes to increase net profit of the organization. The quality of the product, production cost, and the market are all concerns for engineering teams as they try to innovate in the favor of the company. After the invention of an early entrepreneur, the followings acts to improve said invention, whether it be a process or product, while maintaining its’ original purpose by an organization is innovation (Becker and Whisler, 1967, Baregheh, Rowley, Sambrook 1329). Innovation can range from a new product, service, or process based on that of an original invention, to modify it to reduce cost, increase quality, and or make a process more efficient. Without Glenn Yee’s innovative process to develop aluminum cans at a high rate, the MQP project would not be able to exist. The MQP team’s purpose is to innovate and improve the current paint coatings on the aluminum can to increase adhesion forces and reduce stress. As a result of the desired innovation from the project, the team was able to make recommendations to improve the aluminum can paint coatings and reduce the number of defective cans due to misprints. “Innovation represents the core renewal process in any organization. Unless it changes what it offers the world and the way in which it creates and delivers those offerings it risks its survival and growth prospects” (Baregheh, Rowley, Sambrook 1324). Innovation must be a part of every company’s business plan to ensure future markets still have interest in their product. Although there will always be a demand for aluminum cans in the beverage industry, Pacific Can must ensure that they offer beverage companies a quality aluminum beverage container at the cheapest price. With the desired deliverable from our project, Pacific Can will be able to decrease the amount of misprinted cans, resulting in more product and less money wasted on treating painted metal. As a result of the increase in profit, Pacific Can may be able to offer their can at a cheaper rate.

In order to innovate the performance of the paint coatings used at Pacific Can on the aluminum can, the MQP team must conduct research and testing, “Innovation concerns processes of learning and discovery about new products, new production processes and new forms of economic organization (Dosi, 1990, p. 299)” (Baregheh, Rowley, Sambrook 1329). The MQP
team will look at all aspects and parameters of the production process, the chemicals used, theory behind adhesion, as well as why paint coatings work and fail. Once conducting research on how to increase the adhesion of the membrane to the aluminum can and the membrane to the paint, the project team was able to develop and design a set of recommendations to increase the performance of Pacific Can’s paint coatings. At the conclusion of the project, the team will fulfill Plessis’ definition of innovation, “Innovation as the creation of new knowledge and ideas to facilitate new business outcomes, aimed at improving internal business processes and structures and to create market driven products and services. Innovation encompasses both radical and incremental innovation” (Baregheh, Rowley, Sambrook 1326). In order to achieve this goal we must follow the innovation process steps shown below.

The MQP team worked on the development and adoption stages of innovation, making recommendation to alter the production process, allowing the Pacific Can team of engineers to decide whether or not to implement them.

2.6.2 ENTREPRENEURSHIP AT PACIFIC CAN

Although innovation is a very important part of any company, it is just as important to be able to properly advertise, connect, market, and distribute your product, process, or service to the outside world. “When an individual combines an entrepreneurial mindset with engineering and professional skills, and positive character attributes, they become a powerful agent for change. They will impact the world” (KEEN Student Outcomes 2). Having an entrepreneurial mindset is essential in innovation engineering in order to be able to describe, portray, and explain

Figure 3 shows an innovation diagram (Baregheh et al; 2009).
how your product, process, or service will be appealing to an industry, company, or general public. Being able to connect to the correct market is essential in having a successful, innovative product. While on MQP, the team must have an engineering mindset along in order to ensure that the project has an successful impact on Pacific Can. KEEN Engineering Unleashed describes a person with the entrepreneurship mindset is one who is curious, creates connections, and creates value.

With the engineering mindset, the project team considered the character of each team member, collaboration, engineering thought and action, and communication to both the advisors and Pacific Can representatives. As a group, it was essential to meet deadlines with data, conclusions, and recommendations with the team’s best effort to provide the best solution for Pacific Can’s problem. In order to solve this problem, the team collaborated with each other and members of Pacific Can and the BUCT in order to understand the full can-making process at Pacific Can and theory behind different aspects of the process. With the help of the advisors and Pacific Can staff, the project team will be able to use engineering thought and action to develop a modification of the can production process to increase the performance of paint coatings. After the conclusion of the project, the MQP team must be able to communicate the project’s findings in order to convince them to adopt our recommendations and make an impact on Pacific Can (KEEN Engineering Unleashed Example Behaviors). When working on a engineering project, one must take into consideration the innovative and entrepreneurship aspects of the project to ensure the project team’s efforts impact the sponsor.
CHAPTER THREE: METHODOLOGY

The project was conducted in a series of three stages, the preparation stage (PQP), the project stage (MQP – BUCT), and the extension of the project (MQP - WPI). The stages of the project are shown below in a flow chart with a brief description as to what the project team accomplished in each stage.

The goal of the Improving Aluminum Can paint coatings project was to develop recommendations that would reduce the number of cans that experience paint failure. As a result of reaching this goal, the project team would decrease the amount of cans Pacific Can’s clients recycle due to paint failure during the filling and packaging process. The goal of the project will strengthen the integrity of Pacific Can’s product, ensuring the performance of the aluminum can’s paint coatings. In order to reach this goal, the project team developed a set of objectives to complete. The objectives of the paint coatings MQP team were to first develop hypotheses as to why the aluminum cans experience paint failure, test our hypothesis with a variety of laboratory
techniques used in the paint coatings industry, and develop recommendations that correspond with our test results. The recommendations provided would alter the production process parameters or recommend the addition or elimination of a process at Pacific Can.

The preparation stage occurred during D term at WPI, March – April 2015. PQP was a brainstorming stage where the problem statement, goals, and objectives of the project were identified. Scientific papers and books regarding the problem statement were researched; many of the sources proved to be very helpful to the project team during the actual project stage. Laboratory testing techniques used in the field of paint coatings were reviewed during the preparation stage in order to be utilized at the project center. The project team performed as many laboratory techniques as possible in order to find out the cause of the paint failure on the aluminum cans and reach our goal of the project. During the preparation stage, a final presentation and written proposal were developed and presented to the advisors.

Conducting the MQP project at the Beijing University of Chemical Technology occurred during E term, June – August 2015. A gant chart of the project team’s work, progress, and testing while in Beijing is provided below.

![Improving Aluminum Can Paint Coatings - MQP Schedule](image)

*Figure 5 shows the timeframe of the project.*

While in Beijing, the project team continued to research the problem statement and work on the project paper. The project team visited Pacific Can four times to analyze the production process
parameters, run tests, ask the Pacific Can engineers questions, and take pictures of the production plant. The project team conducted some of the desired paint coating laboratory techniques that we requested. The project team conducted two final presentations, one to the staff at Pacific Can and another time at the Beijing University of Chemical Technology. Due to the lack of testing, the project team decided to extend the project to a term at WPI, in order to conduct the appropriate testing to provide Pacific Can with significant recommendations. While in Beijing, the project team was able to experience a different way of processing and thinking in regards to engineering and take in the Chinese culture.

In this chapter, the analytical techniques and testing used by the project team are presented. The purpose and working mechanism of each method is described. Some of the methods are described more than others. This is because of their possible unfamiliarity to the reader. However, it also should be noted that the description of the methods in this chapter are intended to simply give a basic idea of how the test/equipment works, and how it applies to the analysis of paint coating failure.

3.1 **LIGHT MICROSCOPY**

In the failure analysis of paints and coatings, light microscopy is widely used. Though it might seem to be a very simple tool, light microscopy provided valuable insight about the cause of paint coating failure. By simply looking at samples of aluminum cans that have experienced paint failure, it was possible to determine the place on the can where failure occurred, the type of failure that occurred, and the extent of which paint failure occurred. Based on this information, hypothesis regarding the causes of the failure of the label paint were identified. After observing the can with the naked eye, a microscope with the following specifications was used to observe the paint failures on the defective aluminum cans: 10 – 50 X magnification, 2 X auxiliary lens, light source, and a camera.

Using the microscope, aluminum cans without a passivation membrane, with a passivation membrane, beverage label paint coatings, and beverage label paint coatings that have experienced failure were observed. The aluminum can samples were observed while lying flat on a transparent microscope slide and vertically, looking at the layers of each paint coating. Can samples were examined for voids and globules. Voids are trapper gases between the paint coating and substrate that would result in paint failure. Globules would be seen through the light
microscope if there was an application error in the production process, either over-spray or dry-spray (Weldon 141-145). Observations seen with the light microscope were used to obtain a better idea behind paint failure and were not used to determine the actual cause of failure or make any conclusions. In his book *Failure Analysis of Paints and Coatings*, Dwight Weldon states “Field observations and simple visual observations can sometimes be misleading in this regard. Occasionally, even microscopic observations can lead to the wrong conclusion” (Weldon 145). Light Microscopy was an important tool in narrowing down the wide range of causes in which paint failure could have occurred in regard to the aluminum can.

### 3.2 Differential Scanning Calorimeter

During the production process at Pacific Can, the aluminum cans undergo rapid heating processes in three separate ovens, post washing and membrane application, post label paint application, and post lacquer application. The degree to which the paint coating cures when passing through these three ovens directly reflects how well the paint coatings will perform due to the degree to which the paint coatings cure. Recall that most coatings used in the industry are thermosetting, which cure by chemical reactions during or after application. If the coatings do not fully cure, the coatings will not create proper adhesion bonds with the coating or substrate beneath, which could result in paint failure. The theory behind the curing of a paint coating lies upon the concept of the glass transition temperature $T_g$. “Glass Transition is an endothermic event, a change in heat capacity that is depicted by a shift in the baseline. It is considered the softening point of the material or the melting of the amorphous regions of a semi-crystalline material.” ([Differential Scanning Calorimetry: A Beginner's Guide](#)) Below the glass transition temperature paint coating molecules are very rigid and cannot move, known as the glassy state. Above this temperature, the molecules move freely around the substrate. As they leave the ovens, they undergo substantial decrease in their temperature, enough to transfer the molecules to the glassy state. If the coatings are not fully cured as they suddenly enter the glassy state, their molecules will try to move but will not be able to, since they are already in below $T_g$. Therefore, this creates stress within the coatings, which might be finally relieved by cracking.
One of the most widely used tools in the analysis of the glass transition temperature is the Differential Scanning Calorimeter (DSC). Given the fact that it has the ability to identify glass transition temperature, changes in heat flow and heat capacity, the DSC is considered a very powerful tool in the field of material science. According to a beginner guide about DSC published by PerkinElmer, a company that manufactures DSCs, “The information these instruments [DSCs] generate to understand amorphous and crystalline behavior, polymorph and eutectic transitions, curing and degree of cure, and many other material properties used to design, manufacture, and test products”. Due to the importance of the thermosetting paint coatings at Pacific Can, it is crucial that we understand how a paint coating is cured through using a differential scanning calorimeter.

**Sample Preparation**

The preparation of a test sample for a Differential Scanning Calorimeter is prepared by first creating .5-100 mg of test samples. Record the mass of the desired test samples. Using forceps, place the test sample into the one half of an aluminum DSC pan. Again using the forceps, place the top half of the aluminum DSC pan on the bottom half of the pan. Crimp the sample aluminum DSC pan. Using forceps, create a control sample by placing the top half of the aluminum DSC pan on the bottom half and crimping it, this will allow the user to see if there is any mistakes within the test run (http://faculty.olin.edu/~jstolk/matsci/Operating%20Instructions/DSC%20Operating%20Instructions.pdf).
3.3 **Infrared Spectroscopy**

Spectroscopy is the study of the interaction of light with matter. Light is a form of energy, electromagnetic radiation that travels through space at a speed of $2.99792458 \times 10^8$, mostly known as $c$. From classical physics, light possesses the properties of waves, as suggested by Huygens in the late seventeenth century in order to explain the diffraction and refraction of light. Almost a century after this proposition, Einstein observed another phenomena of light called the photoelectric effect, which led him to conclude that light is electromagnetic radiation that travels as packets or bundle of energy, known as photons. Both suggestions, Huygens’ and Einstein’s, are complementary. Representation of the wave-like nature of light is shown in Figure 8 which shows how light travels through space as waves that are made of oscillating electronic and magnetic fields.
Figure 8 shows the full electromagnetic light spectrum (Weldon, 2010).

One of the most important parameters of light is the wavelength ($\lambda$). It is defined as the distance between two consecutive crests or troughs (a cycles). Another equally important parameter is the frequency $v$, which is the number of cycles per seconds. The mathematical relationship of wavelength and frequency is as follows where $C$ is the speed of light:

$$C = \lambda v$$  \hspace{1cm} (2)

Another useful relationship when discussing light is that of energy and frequency. The following relationship shows how energy and frequency are inextricably intertwined, where $h$ is the Planck constant and has a value of $6.626 \times 10^{-34}$ J/s:

$$E = h v$$  \hspace{1cm} (3)

From the above relationship, it is obvious that the higher the frequency, the higher the energy is associated with it. The electromagnetic spectrum, which is depicted in Figure 8 consists of multiple regions, each has a different frequency and wavelength. As the regions of the spectrum have different energy, they interact with light differently. Infrared radiation is low in energy compared to other light waves. Stretching vibration and bending the molecules are the basis of infrared radiation. The first is about change in the length of a bond, while the second is about a change in the angle of a bond. The vibrations of bonds happen at specific frequencies. However, vibrations are commonly reported in wave number, obtained by the division of the frequency by the speed of light. Irrespective of the compound they are present in, the stretching of molecules depends on two factors: the type of the atoms and the type of the bond. For example, the stretching of the O-H bond occurs between 3650-3200 cm$^{-1}$ regardless of the kind of substance it is present in. Spectra of common functional groups are shown in Figure 9.
The vibrations within chemical bonds, shown in Figure 9, occur at certain frequencies or wave number. Exposing any molecules to a frequency that is identical with its molecular vibration results in the absorption of energy by the molecules. This is, in fact, constitutes the basis of infrared spectroscopy. Within the infrared spectrum, each molecule has its particular distinctive fingerprint, which is basically a very narrow range of wave number at which the vibration occurs.

**SAMPLE PREPARATION**

There are a few different ways to prepare a paint coating sample for infrared spectroscopy testing. For solids, the most common way to prepare a sample is by potassium bromide (KBr). Crushing the sample either manually or mechanically, and mixing it with KBr, in a powder, high purity form is known as the pallet technique. The mixture is then put in a die and exposed to a pressure of several tons per square inch using a hydraulic laboratory press. The sample is then placed in the optical path of the spectrometer. A transmission spectrum is obtained after the infrared radiation is directed through the sample. A different method to prepare a sample is by creating a mull, or scattering a ground sample in a small amount of mineral oil of high purity. The mixture is then placed within two pieces of NaCl or KBr crystals. A good method for preparing a viscous liquid or solid sample for infrared spectroscopy is ATR. This method involves pressing the sample against a crystal that has a high refractive index.
APPLICATION

There are many reasons why infrared spectroscopy is used in the analysis of paints and coatings. The four most common purposes for infrared spectroscopy are the following: determining whether the wrong choice of coating was used, mix ratio failure, detection of contaminants, and evaluation of the degree of cure. Because the first two don’t apply to our problems, they are not discussed here.

DETECTION OF CONTAMINANTS

A common reason for paint coating failure is because of the interruption of a paint coating by contaminants. It is often possible to detect the presence of contamination of a disbanded piece of paint through the use of a microscope. A microscope can easily detect the contaminants dirt, concrete laitance, mill, mildew and rust in a paint coating. However, it is sometimes not possible to identify contaminants via the use of a microscope, and thus the use of infrared spectroscopy is the next solution. However, detecting contaminants by the use infrared spectroscopy is not as easy as it appears. It is very tempting to conclude that a paint coating has failed because it basically produced unexpected spike within a particular wave number range. The best way to analyze for contaminants in a paint coating using infrared spectroscopy is to run test for both a failing and non-failing chip of paint. Obtaining a control, a panel that is pre-made in the laboratory for the coating, could also help in contaminate detection.
An example from the literature of how infrared is used to detect contaminants is as follows. Epoxy coating sometimes experience what is called an amine blush. According to the author of the book *Failure Analysis of Paint and Coating*, “This [amine blush] refers to the exudation, or blushing, of some of the low-molecular weight amine-or amide-curing agents to the surface of the epoxy.” Both blushed and non-blushed IR spectra are shown in Figure 10. It can be seen that the blushed epoxy has a more intense band near 1650 cm⁻¹.

**DEGREE OF CURE:**

Paint coating failure could also occur due to drying process that is used, not allowing the coating to properly cure. The degree of cure can be tested using the MEK-rub test, a differential scanning calorimeter, and infrared spectroscopy. As previously mentioned, there are two kinds of coatings: thermosetting and thermoplastic. The first, which is more commonly used, cures by a chemical reaction during or after application. Therefore, as the coating is curing, some particular bands correspond to the particular functional groups as they disappear and or new ones appear. As a result, it is very possible to monitor the curing process of a particular type of paint.

An example of how this is achieved is urethane coatings, which are made by the reaction of a polyol with isocyanate. The isocyanate has a structure of (-N=C=O) which has an extremely conspicuous intensity around 2300 cm⁻¹. Therefore, it is very rational to monitor the decrease of
the intensity of the isocyanate as the reaction process. *Figure 11* show how the band of the isocyanate decreases.

![Figure 11 shows how the band of the isocyanate decreases.](image)

When testing, one must be able to compare the infrared spectra of a fully cured paint coating to one that has not fully cured. The knowledge of the reaction the paint coating undergoes is also crucial in making a conclusive decision about whether the paint coating has failed because it has not fully cured.

### 3.4 Inductively Coupled Plasma (ICP)

Inductively coupled plasma (ICP) is a very powerful tool in detecting metals at a concentration as low as one part per quadrillion depending on the type of the metal. This tool is widely used in analytical chemistry as well as the fields of medicine and forensic analysis. ICP was used to determine which layer of coating within the can is responsible for the failure. It was essential to the project team to determine if the passivation membrane with the paint coatings or
just the paint coatings experience failure. If it is the membrane, the Zirconium metal within the membrane will not be detected. If it is only the paint that falls off, the membrane will be detected with the presence of zirconium metal. There are several types of ICPs, but the one that is particularly discussed here is ICP-OES, or inductively coupled plasma-optical emission spectroscopy.

Figure 12 shows a typical picture of an ICP (Boss et al., 2004).

The theory behind the working mechanism of the ICP is similar to that of the IR as both depend on the interaction of light with the atoms of different elements. At an atomic level, it is known that electrons spin around the nucleus in what is called orbitals. Electrons in orbitals that are closest to the nucleus have the lowest energy. In order for an electron to go to an orbital of a higher energy, it must absorb energy that is equal to the energy of that orbital. As a result, the absorption of the energy will either increase the kinetic energy of the atom or make excited in a process known as excitation. When this process occurs, the electron jumps to an orbital with a higher energy and enters an excited state because of its low stability when compared to the stability of the electrons at its ground state. Therefore, the electron shortly goes back to its ground state by emitting an electromagnetic radiation, known as photons. The electron might also dissociate from the atom if it absorbs energy high enough, making the atom positively charged. This process is called ionization.

Measuring the light emitted by excited atoms and ions is the key to obtaining information. The emission of the light is called polychromatic since the light emitted by the excited
atoms and ions have varying wavelengths. The polychromic radiation is then fragmented into individual wavelengths in order to identify their respective elements. The extent at which the element absorbs the wavelength emitted by the ICP provides information about the concentration of the sample. The software of the ICP automatically generates a graph of concentration against the counts of emission. A typical ICP graph is shown in Figure 13.

![Figure 13](image)

*Figure 13 shows a typical ICP plot (Boss et al., 2004) in which the emission counts is plotted as a function of concentration.*

Bordering the top end of a torch, a copper coil, known as the load coil, is connected to a radio frequency generator. Through the torch made of three concentric quartz tubes, argon gas is directed. Depending on the frequency of the generator, a discontinuous current oscillates with the different magnitudes in the coil. In turn, this creates electric and magnetic fields at the top of the torch. Next, the argon gas at the top of the coil becomes positively charged, loosing electrons, as a result of the absorption of high energy created by a spark that is applied to its excited electrons. The magnetic field already created within the coil catches the electrons and accelerates them. This process of adding high energy to already-excited electrons through the use of a coil is known as *inductive coupling*. The process is shown in Figure 14.
Samples that are applied to ICP are mostly in a liquid state. In order to test a liquid, the liquid samples are nebulized into a tiny fine vapor of sample beads, called an aerosol. Being pushed by the argon flow, the sample reaches the center of the plasma where it is exposed to an extremely high temperature. The aerosol turns into a very small salt particle by removing the solvent from it. The salt particles then undergo a process known as vaporization during which they are decomposed into a gas of separate molecules that are further broken into their respective atoms. At this point, one or two processes are left: excitation and or ionization. As previously stated, excitation takes place when electrons absorb energy and are promoted to the next orbital. However, as some elements have their electrons naturally at a high-energy orbital, the absorption of additional energy may make the electron leave the atom, or the ionization process. All the five processes, shown in Figure 14, mostly take place at different temperature zones inside the plasma. These zones are depicted in Figure 15.
3.5 Muffle Test - THICKNESS EVALUATION

Thickness is considered a vital parameter when it comes to paints and coatings, it is very possible for coatings to fail because of their respective thickness. The thickness of the coating substantially varies according to the kind of substrate they are applied to. However, measuring the thickness of a coating on aluminum can be a very difficult task, if not impossible. Nonetheless, there are some tests used in the industry that provide qualitative information about the thickness of aluminum cans. An example of such test is the muffle test, which is a very simple experiment that can provide qualitative information regarding the thickness of the membrane based on the color of the can after the end of the experiment. It is achieved by placing a can in an oven that is operating at a temperature of 500° F for five minutes. After the test, if the color of the can is dark gold, then the membrane is too thick. On the other hand, if the color of the can after the test is a light yellow, the membrane is too thin. The color of the correct thickness should be a uniform light gold. The muffle test is one of the tests recommended by Henkel, the company that supplies Pacific Can with its passivation membrane and acidic cleaners.

3.6 ADHESION TESTS – ASTM D3359, D4541

Adhesion is the primary reason why paint coatings work. As a result, there are numerous methods used by experts that aim to measure the adhesion of a coating to a substrate. A very common way to test a paint coatings level of adhesion is by ASTM D3359, known as the knife or tape test. ASTM, the American Society of Testing and Materials, provided a large amount of the testing the project team conducted in this project, including various adhesion, stress, and solvent resistant tests. ASTM D3359 provides qualitative information about the adhesion of paint to a substrate. It involves the use of a special knife to make an X cut through a paint coating to the substrate. After the cuts are made, an adhesive tape is applied to the position of the cuts and is removed quickly within one to two seconds of application.
Finally, the adhesion of the paint is evaluated on a scale from 0 to 5 (5 being the best adhesion forces with 0% area of the grid removed by the tape) according to how much paint was detached when the tape was removed. Figure 16 meticulously shows how the evaluation is done.

Another way to measure the adhesion is described in ASTM D4541, known as the pull-off test. ASTM D4541 allows an investigator to determine the pull-off strength of the any coating due to the amount of perpendicular force, in inch pounds, that the coating can withstand. Following the procedures described in ASTM D4541, one could determine the maximum tensile strength of a coating. The ASTM D4541 test begins with roughening up a dolly or stud surface using light sandpaper. To ensure that the painted test panel is completely clean, use a saturated cloth with alcohol to clean the surface. A two-part adhesive is then mixed and applied to the bottom of a dolly. The dolly is then applied to the painted test panel. The remaining epoxy surrounding the dolly on the substrate is then removed. A circular hole cutter matching the inside of the diameter of the test dolly is used to make a cut through the paint coating to the substrate surrounding the diameter of the dolly. A detaching assembly is placed over the dolly head and the adhesion tester applies force to the dolly. The amount of force required to detach the dolly from the substrate allows the tester to calculate the pull-off strength of the paint coating. The complete procedures for the test can be found in the Appendix A.
3.7 Flexibility Tests – ASTM D522, D2794

When formulating paints and coatings, one of the most critical parameters that require special attention is its flexibility. This parameter differs from one coating to another depending on the type of substrate the paint coating will be applied to. If a particular kind of coating does not have a flexibility that suits its environment, it might simply fail due to the movement of its substrate or changes in temperature.

Properties that impact flexibility are tensile strength, elongation, yield strength, hardness, and toughness. There are numerous methods to measure these parameters for metals and plastics. However, it is sometimes very challenging to measure them for paints and coatings. Nonetheless, there are some methods in the literature that have been specifically designed to measure the mechanical properties of coatings. One method suggested by ASTM that aims to measure the % elongation is ASTM D522, where a coated test panel is bent around a conical mandrel. The purpose of the conical mandrel is to create cracking on the small diameter of the mandrel. The % elongation could be calculated by measuring the cracking along the axis of the mandrel.

Figure 17 shows the apparatus that is used to test the flexibility of paints and coatings (Boxall and Fraunhofer, 1981).
Another test that provides insight regarding the flexibility of a coating is described in ASTM test D2794, more commonly recognized as the impact test. The test measures the resistance of organic coatings to the effects of rapid deformation. It is accomplished by dropping a one-kilogram weight of steel freely from different heights directly on the coated or uncoated side of a test panel. The height where evident paint failure and cracking occurs is recorded as the highest impact of the coating and is reported in inch-pound or kilogram-meter. The complete procedures for the test can be found in the *Appendix A*.

### 3.8 Reaction Titration

The reaction titration is an experimental test recommended by the supplier of the Alodine 404 passivation membrane, Henkel, whose goal is to analyze the concentration of the membrane bath used in the passivation stage of production. Using a known reaction, titration is a technique used in chemistry where a solution of a known concentration is added to a solution of an unknown concentration, until the desired reaction has fully ended. An indicator solution, normally phenolphthalein, is used to determine when the reaction is finished. Based on the amount of solution of known concentration that is used during the titration, the tester can calculate the concentration of the unknown reactant.
The results should be compared with the desired results provided by Henkel. The initial fresh bath for the sodium hydroxide titration should be 1.0 mL and .2 mL for the hydrochloric acid titration, reaching a maximum of 10 mL. The initial fresh bath levels of both titrations will increase and eventually level off and remain constant, this is the Alodine 404 bath concentration that Henkel recommends. If the initial fresh bath shows no signs of increasing or decreases at any point, the Alodine 404 application process in production will suffer and action should be made to restore the Alodine 404 bath.

### 3.9 Solvent Resistance Test – ASTM D5402

The extent to which a coating can resist a chemical attack is extremely important. There are several tests used in the analysis of paints and coatings that assess the chemical resistance of a coating. The procedures described in ASTM D5402 are widely used. It involves rubbing a panel using a cloth or Q-tip been soaked in Methyl Ethyl Ketone (MEK) on a coated substrate. After testing, the paint-coated panel should be examined for deglossing, loss of hardness, or paint failure when comparing it to the remainder of the untested coated panel.

*Figure 19 shows how the MEK test is performed: the MEK is applied to a Q-tip and then the Q-tip is used to rub the surface of the painted panel (Boxall and Fraunhofer, 1981).*

The test could provide insight about the degree of cure of a coating. Parameters including temperature, film thickness, air movement, and humidity can affect the results of the test, and thus should be recorded. The complete procedures for the test can be found in the *Appendix A*. 

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CHAPTER FOUR: RESULTS AND DISCUSSION

The intensive literature review was conducted prior to the testing and experimentation in order to shed light on the potential causes of paint coating failures. The research allowed us to develop questions regarding the aluminum can production process and how aluminum can paint coatings can fail for the engineering team at Pacific Can upon our first visit to the Pacific Can Beijing production center. After the first visit to Pacific Can Beijing, the MQP team established three hypotheses as to why the paint coatings on the aluminum can experience failure. Our hypothesis were based off the four fundamental causes of paint failure, a miss-application of a coating, a defective coating, a wrong choice of coating, and exposure to environment, and the causes of paint failure due to stress, including mechanical stress, internal stress, chemical attack, osmotic blistering, and electroendosmotic blistering. After visiting the Beijing production center and seeing their production process, it was determined that a defective coating, miss-application of a coating, mechanical stress, internal stress, and chemical attack were the only potential causes of paint failure at Pacific Can. These hypotheses were then tested during the duration of the team’s time at Beijing University of Chemical Technology using different tests commonly used in the paint industry. The following tests were eliminated from the project due to the cost of testing materials, the lack of significant data that it would bring to the project, and lack of accessibility to testing materials at the BUCT: ASTM 2370, ASTM D4541, and Fourier Transformed Infrared Spectroscopy. The elaboration and reasoning for each hypothesis developed by the MQP team are listed below along with the type of corrosion that occurs and the testing that could be used to test the hypothesis.

The First Hypotheses

Statement:

Forces experienced during the aluminum can production process cause the paint coating to fail. The parts of production that were analyzed was the necking process, the flanging process, as well as the can’s movement throughout product line.

Cause of Failure:
The mechanical stress experienced by the can are greater than the adhesion forces created between the can and its paint coatings, especially seen on cans where there was a miss-application or defective coating.

**Justification:**

Cans experience the most mechanical deformation during the necking and flanging process. Corrosion and scratching can occur on the can from rubbing against the production line conveyer belt, creating voids in the aluminum alloy substrate.

**Tests:**

- Muffle Test
- ASTM D3359 - Measuring Adhesion Tape Test
- ASTM D522 – Flexibility Test of Organic Coatings
- ASTM D4541 – Pull – Off Strength Test
- ASTM D2794 – Resistance to Rapid Deformation
- ASTM D2370 – Universal Stress/Strain Test

**The Second Hypotheses**

**Statement:**

The aluminum can undergoes three different stages of drying, once after the passivation membrane, once after the can label, and once after the interior lacquer is applied. The drying ovens do not properly cure the can’s paint coatings, not allowing for strong adhesion forces to be developed resulting in a defective exterior coating.

**Cause of Failure:**

The cause of failure could occur in one of the three different drying ovens in the can production process. Paint failure could occur from either of the first two drying ovens not properly curing either the passivation membrane or paint can label on the aluminum can, creating a defective coating. Internal stress experienced in the third drying oven could also cause paint failure, causing the exterior paint coatings to shrink, eventually resulting in paint failure.
Justification:

During the curing process the coatings experience shrinkage. The shrinkage is due to the movement of paint coating molecules. When in ovens, coatings are above the Transition Glass Temperature ($T_g$). Above this temperature, the molecules are in a rubbery state which allows them to move. Below the $T_g$, the molecules are in a hard glassy state that restricts their movement. The optimal, operating temperature of each of the drying ovens should be at or above the transition glass temperature for the minimal amount of time needed to let the paint coating cure. This way each of the aluminum can paint coatings properly establishes adhesion forces while minimizing the amount of internal stress experienced by aluminum can label.

Testing:

- Differential Scanning Calorimetry (DSC)
- ASTM D5402 – Assessing the Solvent Resistance of Organic Coatings Using Solvent Rubs (Methyl Ethyl Ketone Test)
- Fourier Transformed Infrared Spectroscopy

The Third Hypotheses

Statement:

A contaminated cleaner bath, membrane bath, or label paint may result in a defective exterior paint coating. Also, if the recommended concentration of the cleaner or membrane bath was not used during production this may result in an improper surface for the paint label to be applied, resulting in a defective exterior paint coating.

Cause of Failure: A chemical attack of the aluminum can cleaners and paint coatings could cause paint failure due to a defective coating. The use of a wrong concentration of the cleaner or membrane bath could also cause paint failure through chemical attack or the miss-application of a paint coating.

Justification:
Cans undergo a series of washing, cleaning, and drying before the printing process. If the source of the cleaner, passivation membrane, and or label paint is contaminated by other chemicals in the production plant, a defective paint coating would be applied to the can eventually resulting in paint failure. A high concentration of the Ridoline 550 or Ridoline 120 cleaner could cause the aluminum can body to erode too much resulting in an improper surface for label paint to be applied to. A low concentration of the acidic cleaner could result in the improper cleaning of all oils and lubricants used during the body forming process, resulting in a miss-application of coating. If the recommended concentration of the passivation membrane bath is not used during production, the performance of the exterior paint coating is in great jeopardy to paint failure.

Testing:

- Induced Coupled Plasma Optical Emission Spectrometer (ICP - OES)
- Light Microscopy
- Reaction Titration

The remainder of the results and discussion chapter will go into further detail about the testing that was performed for each of the project team’s three hypothesis. Using the results of each of the tests that were conducted, each hypothesis was further analyzed as to whether it was a possible cause of paint failure. The results from the project team’s testing and the conclusions drawn about each of the three hypothesis allowed the project team to make recommendations for the engineering team at Pacific Can China Holdings Limited Beijing, discussed in the chapter 5.

4.1 HYPOTHESIS #1

After conducting many ASTM stress tests and observing the parts of production that apply the most stress to the aluminum cans, the project team ruled out hypothesis #1 as a possible cause of paint failure. The aluminum can paint coatings that are produced at the Pacific Can Beijing production center received great results in terms of the strength of adhesion forces developed and the amount of stress forces the coatings can withstand. Due to the high performance of the aluminum can paint coatings in these stress tests, hypothesis #1 has been ruled out as a possible cause of paint failure during production at Pacific Can Beijing. ASTM D2370 and ASTM D4541 tests were not conducted due to the lack of accessibility to testing.
materials at the BUCT and testing materials exceeding the project budget for a specific test. The following portion of the results and discussion section will go into detail about each test that was completed and the data that was collected.

**MUFFLE TEST:**

The purpose of the muffle test was to ensure that the thickness of the membrane applied to on the can complies with the recommended membrane bath concentration provided by Henkel, the company that manufactures the membrane. A total of fifteen cans were tested using the muffle test, 5 tests were completed using a furnace at the BUCT and ten tests were completed using Pacific Can’s furnace. In the five tests that were completed at the BUCT, the can turned a combination of the following colors: dark brown, dark gold, light black, and purple. The test color indicated that the passivation membrane is too thick which, “is often detrimental to optimum adhesion and/or mobility. In order to understand whether the just the paint label or the paint label and the passivation membrane falls off the can during paint failure, the paint failure portion of the can that had experienced paint failure was tested. It was determined that just the paint label falls off the can during paint failure, due to the dark brown, gold color still remaining on the can, indicating the presence of the passivation membrane. The remaining ten tests were run at Pacific Can, where a muffle test is run every thirty minutes to ensure passivation membrane accuracy. Like at the BUCT, most of the cans exhibited dark brown, dark golf color which is an indication that the thickness of the membrane is too thick and exceeds what Henkel recommends. Following the Henkel process bulletin for a passivation membrane that is too thick, the process pH levels and temperature was analyzed. It was determined that the process pH levels of the membrane bath were 3.3-3.36 pH, very high (less acidic) compared to the Henkel recommended levels of 2.6 – 3.1. The temperature levels of the membrane bath was within the recommended values of 85° to 110° Fahrenheit. Pictures of the conducted muffle test can be found in Project Pictures section of the *Appendix B.*

**ASTM D3359:**

The purpose of the ASTM D3359 – Measuring Adhesion by Tape Test was to evaluate the adhesion of the paint coatings to the aluminum substrate. Using Pacific Can’s testing materials, a total of twenty cans were tested using Test Method B, ten with paint failure and ten painted cans. Each of the twenty cans scored a score of 5B (0% area removed from grid), ensuring that the
adhesion forces developed between the aluminum substrate and its paint coatings are very strong. ASTM D3359 was one of the many tests that the control lab at the Pacific Can Beijing production facility to ensure the paint coating quality of their aluminum cans. The test data and scoring method for the ASTM D3359 test can be found in the Testing Results Tables section of the Appendix A.

**ASTM D522:**

The goal of ASTM D522 testing was to evaluate the flexibility of the paint to the substrate when a stress is applied to it, a stress that is seen in the necking and flanging process in can production. Unfortunately, the test was unsuccessfully run due to the fact the coated testing panels made from cutting out a rectangular portion of a painted can were too small to fit in the testing apparatus and bent around the mandrel with ease. No cracking was observed during the five tests run with painted can test panels and as a result no significant data was taken from ASTM D522 testing.

**ASTM D2794:**

The ASTM D2794 – Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact) test was to assess the adhesion of paint to its substrate when deformation occurs, as seen in the necking and flanging processes of production. Painted cans that had experienced paint failure were used to create approximately 3” by 3” panels for the tests. An impact tester was purchased offline while at the BUCT and was used to test the painted can panels. Paint failure, evident cracking, occurred at stresses ranging from .12 - .15 kg*m, with an average of 0.132 kg*m. The failure occurred due to the rapid deformation and bending of the substrate. The ASTM D2794 test provided the project team with significant data as to how much stress or rapid deformation the aluminum can paint coating can undergo. Below is a bar graph of the data from the ASTM D2794 testing, where each bar graph represents an individual test and the stress that was applied to the test sample. The bar graphs are color coded in blue and red, the blue graphs experienced no cracking and the red graphs experienced evident cracking. Due to the fact that the force applied to each test sample during the ASTM D2794 test is way more stress than the aluminum can will experience during the production process, the project team ruled out hypothesis #1 as a potential cause of paint failure during production at Pacific Can Beijing.
Figure 20 shows the test results from ASTM 2794. The x axis shows the test sample number and the y axis displays the amount of stress applied to the sample. The bar graphs are color coded; the blue graphs are the test samples that experienced no evident cracking where the red graphs are the samples where evident cracking occurred.

4.2 HYPOTHESIS #2

The improper curing of paint coatings in the three, different drying ovens during production at the Pacific Can Beijing production facility could not be determined as a potential cause of paint failure with the amount of testing that was performed in regard to this hypothesis. Due to lack of accessibility to testing, the project team was not able to perform Fourier Transformed Infrared Spectroscopy, one of the more significant tests for this hypothesis. The following portion of the results and discussion section goes into detail about the testing that was conducted for hypothesis #2.

DIFFERENTIAL SCANNING CALORIMETRY

Differential Scanning Calorimetry testing gave the Paint Coatings project team insight on the temperatures at which the paint coatings undergo curing, specifically it’s glass transition temperature. The project team conducted the Differential Scanning Calorimetry testing at the BUCT. After consulting with the DSC operator, the results for the paint coating DSC tests were
inconclusive. The glass transition temperature range for a paint coating similar to those used in the aluminum can production process would show a rapid decrease in heat flux over a certain temperature range, a trend only seen in the high-quality, painted can sample from 160.72-254.87 °C. Although this could be the glass transition temperature of the paint coating, the DSC operator convinced the team that the data was faulty and could not be used. The project team believes that the test samples may have been ill-prepared by the DSC operator, despite the team telling the operator the procedure for preparing a DSC paint coating sample. Much different than preparation of a normal DSC test sample, a paint coating DSC test sample is prepared by scraping off the paint coating from its substrate and using the removed paint coating as the sample. Due to project limitations with the language barrier, the project team believes that the DSC operator didn’t understand the importance of following the procedure for preparing paint coating samples for DSC. The data received for each of the four different samples tested using DSC was very similar, the graphs were spread within 10 milliWatts, the unit used to quantify heat flow, of one another. There was such a small difference between the data graphs because the DSC testing was not analyzing the paint coatings of the aluminum can but rather the aluminum substrate. As a result, the project team could not use the data taken from the DSC testing to analyze hypothesis #2 as a potential cause of paint failure. The results from the Differential Scanning Calorimetry testing can be found under the Testing Results Tables section of Appendix B.

ASTM D5402:

ASTM D5402 test was conducted to better understand the solvent resistance that undergoes during the paint coating curing process. The chemical used in to test the paint coating panels was Methyl Ethyl Ketone (MEK). A total of twelve tests were performed using four cleaned cans with passivation membranes, four painted cans, and four painted cans with paint failure. The MEK was applied to the test sample using a Q-tip in under one minute. The MEK was applied to the test sample using 25 double rubs, a double rub consisting of rubbing the Q-tip once across the test sample to the right and back across the test sample to the left. The cans then were inspected for de-glossing and/or paint failure. Only two painted cans experienced paint failure and de-glossing where the rest of the test samples showed little to no change in appearance. The data results from the ASTM D5402 testing suggested that paint coatings may not be properly cured
during the drying processes at Pacific Can, but a conclusion in regard to whether hypothesis #2 could be a potential cause of paint failure could not be determined as a result of this test. The results from the ASTM D5402 testing can be found under the Testing Results Tables section of Appendix B.

4.3 HYPOTHESIS #3

A conclusion could not be made on whether hypothesis #3, the contamination or wrong concentration of a cleaner bath, membrane bath, or label paint used during production caused paint failure, could be a potential cause of paint failure. Due to the lack of accessibility to testing materials at the BUCT, the project team was not able to conduct many of the experiments to test this hypothesis. The testing that was completed didn’t provide the project team with enough data for the project team to confirm that paint failure at Pacific Can was due to contamination or the wrong concentration of cleaner bath, membrane bath, or label paint. The following portion of the results and discussion section will go into detail about the purpose and the attempts the Paint Coatings project team made at accessing these testing materials.

INDUCED COUPLED PLASMA – OPTICAL EMISSION SPECTROSCOPY

The purpose of ICP – OES testing was to check for any contaminants within the paint coating that could affect the wetting of the different paint coatings, ICP testing can detect metals present in a solution with a concentration of as little as $10^{-15}$. The ICP – OES could also determine whether or not the passivation membrane was present on the aluminum can that experienced paint failure. The membrane used in the pre-treatment of cans at Pacific Can is Alodine 404 developed and licensed by Henkel. The membrane contains small amounts of the metal Zirconium which could be detected by the ICP-OES. The paint coating project team conducted the ICP – OES testing at Tsinghua University where the test samples were made. Four different test samples were made by cutting cleaned cans, cleaned cans with a passivation membrane, a painted aluminum cans, and painted aluminum cans that had experienced paint failure and dissolving them in hydrochloric acid so that it can be injected into the ICP device. The ICP – OES test results are shown in Figure 20 below.
Figure 21 shows the ICP results. The y-axis represents the concentration of the metal Zr in ug/g while the x-axis represents the sample’s condition.

The results show that the concentration of Zr is high in the passivated sample and low in the un-passivated sample as expected. However, it also shows that the Zr concentration in the paint failure sample is lower than that of the passivated one, concluding that a portion of the passivation membrane experiences paint failure along with the organic label paint coating. The Zr concentration in the passivated sample is 58.26 ug/g, and 35.87 ug/g in the painted can that experienced paint failure. Therefore, since the difference in the concentration of Zr between the two samples is not dramatic, it is unlikely that the cause of the paint failure is due to the failure of the membrane. However, further testing may be necessary to ensure the validity of the results. As a result, the project team concluded that the cause of paint failure is not due to contamination.

LIGHT MICROSCOPY

The paint coatings project team was not able to conduct proper light microscopy testing due to the inability of the BUCT to provide us with a light microscope with a built in camera. The purpose of using a light microscope with a camera is to analyze a surplus of cans taken from different stages of the production process and take pictures of each of the samples at different angles. The pictures would later analyzed and trends amongst the samples could be developed in regard to signs of contamination, scratching, corrosion, blistering, etc. Although we were given a light microscope without a camera, a surplus of can samples could not be analyzed thoroughly
enough for trends to develop from written observations. Due to the lack of data that the testing could provide us and the lack of accessibility to the proper equipment, light microscopy was eliminated from the project testing.

**REACTION TITRATION**

Upon the project team’s first arrival to Pacific Can Beijing, it was determined that the Pacific Can engineering team conducts the Reaction Titration testing provided by Henkel, the company that supplies Pacific Can with its passivation membrane and acidic cleaner. The membrane bath concentrations along with other parts of the production process are tested using titration every two hours at Pacific Can. During one of the visits to the production facility, the project team conducted one Reaction Titration test with the Pacific Can engineering team and collected a week’s worth of testing data. After analyzing the data, it was concluded that Pacific Can follows all of the recommended values of operation temperature, pH levels, and concentration of the majority of the line washer processes. The only data that was taken from the Reaction Titration testing was that the pH levels of the passivation membrane bath were too high, ranging from 3.3 -3.36 pH, as seen in the Muffle Test results and discussion section under Hypothesis #1. The project team concluded that further Reaction Titration testing would not provide significant data to make recommendations from, due to the fact that the test is already conducted at Pacific Can. The test data from the Reaction Titration testing can be found in the Testing Results Tables section of the *Appendix B*.

**4.4 Project Limitations**

Throughout the project duration in Beijing, there were some major constraints that affected the progression and success of the project. First of all, the Improving Aluminum Can Paint Coatings project was a very complex subject and problem. With limited funds and time to complete the project, it was very difficult for the project team to complete the project with significant recommendations that could convince Pacific Can to alter their production process to increase the performance of their paint coatings. Due to the fact that the paint coatings industry is such a small sector in the chemical engineering industry, there were no BUCT professors that were willing to take on the project as an advisor to help us in developing hypothesis, conducting testing, and analyzing the problem. Constant consultation with a paint expert was needed in order to conduct a successful project with significant recommendations. Along with the
complexity of the project, Pacific Can failed to provide us with very crucial information about our project and the problem at hand. Upon our last observation visit to Pacific Can with two weeks left in the project, the paint coatings team learned that the majority of paint failure on aluminum cans occurs at beverage packaging facilities, not at Pacific Can production facilities. With this knowledge, the team would have altered the types of testing conducted as well as asked to visit and observe a beverage packaging facility. With this information, the project team determined that the cause of paint failure is due to mechanical stresses and osmotic blistering that occurs during the pasteurization process during the packaging of the Jia Duo Bao herbal tea. The hot water used to kill bacteria and cool the tea can prior to packaging at the Jia Duo Bao facility easily penetrated the minuscule cracking created in the can’s paint coating during the necking and flanging parts of production at Pacific Can. The water’s penetration through the paint coating leads to the development of osmotic cells in the paint coating at the top of can, eventually leading to paint failure. Pacific Can also failed to tell the project team that the cans that experienced paint failure, the Jia Duo Bao herbal tea can, had been discontinued. This limited the amount of testing that could be conducted due to the limited number of cans that experienced paint failure that Pacific Can had collected from their client.

As predicted, the language barrier was a constraint especially when the BUCT students acted as translators between the project team and professors, engineers at Pacific Can, and other professionals. At first, the project team underestimated the amount of English our Chinese partners and members of the engineering team at Pacific Can knew. It was crucial that the paint coatings team portrayed our questions and thoughts in the easiest, shortest way possible in order to ensure our Chinese partners understood what we were saying, especially when translating our questions to the engineering team at Pacific Can. While at the BUCT, the paint coatings project team worked without an advisor from the BUCT and as a result the project team had limited access to desired testing and appropriate lab space. During the duration of the project, the project team was given two different lab spaces, each of which had none of the desired materials and testing devices that were needed for the project. The project team’s lack of testing hindered the results and discussion and recommendations that the project team developed. Prior to the PQP preparation period of the project, the project team was told that the significance of the Paint Coatings project was of equal importance to the Chinese students as the Major Qualifying Project is to WPI students; that is, the completion of the project is needed for the completion of
their degree at the BUCT. The project team soon came to learn upon asking the BUCT students that the Paint Coatings project was a voluntary project for them, having little to no weight on their academic requirements. As a result, the Chinese students weren’t as willing to put forth as much effort as the WPI project team was willing to in order to complete the project. Despite the numerous constraints experienced during the project, working on my major qualifying project at the Beijing project center was a positive engineering and cultural experience that kick started our final year in completing our chemical engineering degree at WPI.
CHAPTER FIVE: RECOMMENDATIONS

The project team developed short term and long term recommendations for Pacific Can China Holdings Limited Beijing from the conducted research, testing, and observation at the Beijing production plant. Along with the short term and long term recommendations, we would recommend that the Pacific Can engineering team continues to research how to improve the performance of the paint coatings used on their aluminum cans. The testing that we would encourage the engineering team to perform is differential scanning calorimetry and Fourier transformed infrared spectroscopy. These types of testing will provide the Pacific Can engineering team with the most significant data in regard to optimizing their can production process. Fourier transformed infrared spectroscopy will provide data in regard to the functional groups making up the paint coatings, identify forces that attract foulants, and predict the tensile strength of the paint coatings. Further testing with differential scanning calorimetry, when using the correct sample preparation methods, will allow for Pacific Can to better understand how their paint coatings cure in each oven and as a result optimize their oven operating temperatures. If Pacific Can decides to continue their production of the Jia Duo Bao herbal tea aluminum can, the project team recommends that they conduct more testing and research including induced coupled plasma optical emission spectroscopy, ASTM D2370, and ASTM D4541. If Pacific Can continues to not produce the Jia Duo Bao aluminum can, then the project team recommends to not conduct these additional tests. Due to the small amount of cans that experience paint failure during production at Pacific Can facilities, it is not economical to conduct additional testing on paint coatings. The following are the short and long term recommendations to reduce paint failure and increase paint coating performance as well as project limitations experienced throughout the duration of the project.

5.1 SHORT TERM RECOMMENDATIONS

The MQP project team developed two short term recommendations. First, the project team recommends that the passivation membrane bath, Alodine 404, pH levels are maintained between 2.6 - 3.1 pH. While conducting the muffle test, it was determined that the thickness of the applied passivation membrane at the Pacific Can Beijing facility is too thick, the can displaying a dark brown, gold color after heating in a furnace at 1000°F Fahrenheit for five
minutes. Following the Henkel process bulletin and muffle test procedure, it was determined through the reaction titration testing and consulting with Pacific Can engineering team that the pH levels of the membrane bath were too basic at pH levels of 3.3 – 3.36 pH. As a result, the project team recommends that the Pacific Can engineering team decreases the pH levels to those recommended by Henkel, 2.6 – 3.1 pH. By reducing the membrane thickness, the membrane will not only develop the proper adhesion forces but the paint label coating will perform better. In regard to paint coatings, the thicker the paint coating is, the more susceptible the paint coatings is to paint failure.

The paint coatings team also recommend that Pacific Can purchases mixers for the barrels of Alodine 404 to ensure that the concentration of the passivation membrane among the entire barrel is the same. Without the mixer, the Alodine 404 may vary in concentration as the barrel enters the end of its “barrel life,” which may lead to an improper membrane application which could lead to paint failure. Limit the exposure of the label paint to the environment to avoid contamination with dust, different paint, etc. If the paint has become contaminated with another paint, that portion of the bucket should be scooped out and the remaining paint should be well mixed before it is applied to the roller paint tray. The lid of the label paint should stay on top of the paint tub until it is time to refill the paint tray. A basic, low powered microscope should be purchased by the control lab at the Pacific Can factory. With the microscope, the engineering team will be able to pick up on minor flaws in the aluminum can and can alter their production process accordingly to allow for a better surface preparation, paint application, and final product. The short term recommendations developed by the paint coatings project team are low-cost, uncomplicated adjustments made to the production parameters and facility equipment that will ensure the proper concentration and operating conditions of the application of the acidic wash and passivation membrane.

5.2 LONG TERM RECOMMENDATIONS

The MQP team developed two long term recommendations for Pacific Can in regard to alternatives to passivating the aluminum can substrate and surface preparation. The paint coatings project team recommends that further research is conducted into eliminating the passivation membrane from the production process through either applying a varnish to the bottom of the can using a roller or purchase anodized aluminum. During consultation with the
Pacific Can engineering team, it was determined that one of the main reasons for the passivation membrane is a protective layer for the bottom of the can, a part of the can that experiences a lot of stress and contact moving along the production line. Without the passivation membrane, the engineers stated that the bottom of the aluminum can would turn black after moving through the entirety of the production process. By eliminating the expensive passivation membrane, Pacific Can would reduce production cost while maintaining a proper surface for paint label application. The corrosion experienced during the acidic wash creates crevices in the surface of the aluminum can that allow for the proper surface for paint application, allowing for hydrogen bonding to occur between the can and its paint coatings. Applied to the bottom of the can using a paint roller after exiting the washer process drying oven, the varnish would allow for the can to move freely among the production conveyer belt while not experiencing discoloration.

The paint coatings project team also recommends that further research is conducted into purchasing anodized aluminum from their aluminum supplier. As described in the Literature Review, anodizing is a process of metal passivation by submerging the metal in an acid electrolyte bath and passing a current through it, resulting in a metal oxide passivation layer. Reducing the thickness of the overall exterior paint coating, the anodized aluminum will provide the proper, passivated surface for the organic label paint to create adhesion forces, especially hydrogen bonding. As stated before, reducing the thickness of the exterior paint coating will increase the overall performance of the paint coating and increase the amount of stress the coating can withstand. The cost of purchasing anodized aluminum for can production should be compared to the cost of applying the Alodine 404 passivation membrane to the aluminum can to ensure that the alternative is economically sound. Further research and testing should be conducted by the Pacific Can engineering team before adapting the paint coating project team’s recommendations to the can production process at Pacific Can Beijing.
CHAPTER SIX: CONCLUSION

The goal of the Improving Aluminum Can Paint Coatings project was to investigate paint coating failure experienced during production at Pacific Can Beijing. The project team conducted in-depth research pertaining to the composition of paint coatings, how paint coatings work, how paint coatings fail, laboratory testing techniques used in industry, and common equipment used for testing. As a result, three hypotheses were formulated as to why aluminum can paint coatings experience paint failure: failure due to the mechanical stresses experienced during production, failure due to the improper curing of paint coatings after application, and failure due to the presence of chemical contaminants. The project team concluded that the adhesion forces developed by the can’s paint coatings can withstand the mechanical forces experienced during Pacific Can production, receiving great results in the conducted stress tests. Unfortunately, not enough testing related to the other two hypotheses were performed due to the lack of accessibility to testing materials at the BUCT, the short duration of the project, and testing materials exceeding the project budget. These project limitations hindered the project outcomes substantially and the project team’s ability to determine whether or not hypotheses #2 and #3 could be potential causes of paint failure. Short and long term recommendations were developed by the project team based on the observations made at the Pacific Can Beijing production facility, the conducted research, and the test data. The short term recommendations include decreasing the pH level range of the membrane bath from 3.3 – 3.36 to 2.6 – 3.1 pH and purchasing mixers for the passivation membrane and acidic cleaner barrels feeding the line washer. The long term recommendations developed by the paint coatings team were to conduct research into replacing the passivation membrane and applying the label paint coating directly to the aluminum substrate by applying a varnish on the bottom of the can or purchasing anodized aluminum. The project team also recommends that the Pacific Can Beijing engineering team continues to conduct testing using Fourier transformed infrared spectroscopy and differential scanning calorimetry to better understand how their aluminum can paint coatings work. The goal of the Improving Aluminum Can Paint Coatings project was to develop recommendations for Pacific Can Beijing that would alter the production process and operation parameters to strengthen the adhesion forces created between the paint coatings and the aluminum substrate.
The desired results from the project would increase the aluminum can paint coating performance and reduce the amount of cans that experience paint failure at Pacific Can.
WORKS CITED


A. TESTING PROCEDURES

The testing procedures portion of the appendix contains the testing procedures used for the conducted testing during the Improving Aluminum Paint Coatings project. The following are the materials and procedures for paint coating industry laboratory techniques to test paint coatings.

A.1 REACTION TITRATION

Materials: 250mL glass beaker, plastic 25 mL automatic burette, stirring rods, phenolphthalein, sodium fluoride, 2 quarts of .1 N sodium hydroxide, 2 quarts of .1 N hydrochloric acid.

Procedure:

1. Collect the necessary test materials to perform the Alodine 404 reaction titration test.
2. 10 mL of Alodine 404 bath is placed in a 250 mL glass beaker.
3. 10 drops of phenolphthalein is added to the beaker.
4. 25 mL of .1N Sodium hydroxide is added to automatic burette, reaching the zero line.
5. .1N Sodium hydroxide is added to the Alodine 404 bath in the beaker using the automatic burette while constantly stirring the beaker solution with a stirring rod.
6. Sodium hydroxide is slowly added to the Alodine 404 solution beaker until it turns a dim purple.
7. Record the amount of Sodium hydroxide needed to turn the beaker solution a dim purple.
8. 25 mL of .1N Hydrochloric acid is added to a different, clean automatic burette to the zero line.
9. 1 gram (1/2 teaspoon) of sodium fluoride is added to the Alodine 404 beaker solution and mixed using a stirring rod. Once fully dissolved, the beaker solution will turn a deep pink color.
10. .1N Hydrochloric acid is slowly added to the beaker solution while stirring with a stirring rod. Hydrochloric acid is added to the beaker solution until the solution turns clear.
11. Record the amount of hydrochloric acid added to the beaker solution.
A.2 ASTM D2794

Materials: impact tester, aluminum can test panels, magnifier, microscope.

Procedure:

1. Prior to testing, the ambient temperature and pressure of the laboratory space was recorded along with the thickness of the aluminum can test panel used.
2. An aluminum can test panel is placed in the impact tester with the beverage label paint coating facing upward (facing the weight).
3. The weight is lifted up to the desired height in the impact tester and then dropped.
4. The test panel is removed from the impact tester and inspected for cracking or paint failure.
5. The test panel was placed in the impact tester and the weight’s height was increased by one inch until failure was observed.
6. Once paint failure had occurred, fifteen tests were run, five at the desired height, five at a height slightly above the desired height, and five at slightly below the desired height.
7. A microscope was then used to examine the area for cracking.
8. The following information was recorded after each test: inch pounds at impact, intrusion or extrusion, and diameter of the punch.

A.3 ASTM D5402

Materials: Methyl ethyl ketone, Q-tips, safety glasses, safety gloves, ventilation hood, aluminum can test panels.

Procedure:

1. The methyl ethyl ketone safety data material sheet was read prior to testing to understand the proper safety equipment that would be needed to complete a safe, professional test.
2. Proper safety equipment was gathered prior to testing, safety glasses, safety gloves, and a ventilation hood were used to ensure the project team’s safety. Safety goggles and gloves were put on and ventilation hood was turned on prior to testing.
3. The temperature, pressure, and humidity of the lab space was recorded prior to testing.
4. A 330 mL, passivized aluminum can without the top piece was cut at a 90° angle from the top of the can down to the bottom of the sidewall. A cut was then made around the
bottom circumference of the can to make a rectangular test panel. The test panel was flattened to ensure for a proper application of the methyl ethyl ketone.

5. 6” portion of the can was selected for the application of the methyl ethyl ketone.

6. Methyl ethyl ketone sample top was unscrewed. Cotton swab was dipped into the sample of the methyl ethyl ketone.

7. Cotton swab was held at a 180° angle with the aluminum can, parallel with the substrate surface. The cotton swab was run along the substrate a total of 50 times, the motion of the running the cotton swab from the left to the right of the desired test portion of the aluminum counted as one “time”.

8. Cotton swab with methyl ethyl ketone was then properly discarded.

9. The inner 5” of the desired test portion, giving a ½” margin of the test portion of the can, was examined for results. Hardness, visual changes, and gloss of the test portion of the aluminum can was compared with untested portions of the aluminum can for any changes.

10. The change in gloss was measured using the procedure from ASTM D523 while the change in pencil hardness was measured using ASTM D3363 method.

11. The “Solvent Double Rub Test” form in Appendix IX of the ASTM D5402 testing procedure was used in writing down the observations of the test.

12. The methyl ethyl ketone test was run a total of five times to ensure proper results were examined by the project team.

A.4 ASTM D3359

Materials: cutting tool, cutting guide, 1 inch tape, aluminum can test panels, rubber eraser.

Procedure:

1. An area free of blemishes and minor surface imperfections was chosen on the aluminum can to make the cut.

2. A 1 inch “X” cut was made through the exterior paint coating on the test panel to the aluminum substrate. The cut was examined to ensure that the “X” cut was made through the paint coating to the surface of the substrate.

3. A piece of the tape was placed over the “X” cut and applied using the rubber eraser of the pencil.
4. The tape was removed rapidly at an angle as close to 180° from the substrate as possible in under two seconds from application of the eraser.

5. The grid area of the “X” cut was examined with a magnifying glass and compared to the “Classification of Adhesion Test Results” supplied in the ASTM D3359 Standard Test Method. Based on the amount of the paint coating that was removed from the grid area, the test sample was given a rating of 0B – 5B, where 5B showed no removal of the paint coating from the grid area.
### B. TESTING RESULTS TABLES

#### B.1 ASTM D2794 TESTING RESULTS

<table>
<thead>
<tr>
<th>Test #</th>
<th>Force Applied to Panel Kg*m</th>
<th>Cracking or No Cracking</th>
<th>Intrusion or Extrusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>0.08 Kg<em>m (90 g</em>m)</td>
<td>No Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 2</td>
<td>0.08 Kg<em>m (90 g</em>m)</td>
<td>No Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 3</td>
<td>0.11Kg<em>m (110g</em>m)</td>
<td>No Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 4</td>
<td>0.11Kg<em>m (110g</em>m)</td>
<td>No Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 5</td>
<td>0.11Kg<em>m (110g</em>m)</td>
<td>No Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 6</td>
<td>0.12 Kg<em>m(120g</em>m)</td>
<td>Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 7</td>
<td>0.12 Kg<em>m (100 g</em>m)</td>
<td>Cracking is not evident</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 8</td>
<td>0.12Kg<em>m (120g</em>m)</td>
<td>Cracking is not evident</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 9</td>
<td>0.13Kg<em>m (130 g</em>m)</td>
<td>Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 10</td>
<td>0.13Kg<em>m (130 g</em>m)</td>
<td>Cracking</td>
<td>Intrusion</td>
</tr>
<tr>
<td>Test 11</td>
<td>0.11 Kg<em>m (110 g</em>m)</td>
<td>No cracking</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Test 12</td>
<td>0.11 Kg<em>m (110 g</em>m)</td>
<td>No cracking</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Test 13</td>
<td>0.13 Kg<em>m (130 g</em>m)</td>
<td>Paint failure observed from rapid bending of test panel</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Test 14</td>
<td>0.13 Kg<em>m (130 g</em>m)</td>
<td>Paint failure observed from rapid bending of test panel</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Test 15</td>
<td>0.15 Kg<em>m (150 g</em>m)</td>
<td>Paint failure observed from rapid bending of test panel</td>
<td>Extrusion</td>
</tr>
</tbody>
</table>
## B.2 ASTM D3359 Testing Results

<table>
<thead>
<tr>
<th>Test #</th>
<th>Painted Can - Too</th>
<th>Painted Can - Side</th>
<th>Paint Can w/ Paint Failure - Too</th>
<th>Tape Used</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td>Scotch Premium Grade Transparent Cellophane E10-1PM 1&quot; x 2552&quot;</td>
<td>Tape applied for 1.5 seconds prior to being removed. Pen cap was used to apply tape.</td>
</tr>
<tr>
<td>Test 2</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td>Tape was removed at a 180 degree angle from the substrate.</td>
</tr>
<tr>
<td>Test 3</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td>Cut made was 3/8&quot; at a 30-45 degree angle to the substrate.</td>
</tr>
<tr>
<td>Test 4</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td>Cut was examined for penetration to the substrate prior to tape application.</td>
</tr>
<tr>
<td>Test 5</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td>If this occurred, one would be able to see the shine/reflect from the aluminum.</td>
</tr>
<tr>
<td>Test 6</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td>Test score was determined -&gt; SB.</td>
</tr>
<tr>
<td>Test 7</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 8</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 9</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 10</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 11</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 12</td>
<td>SB</td>
<td>SB</td>
<td>SB</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Classification of Adhesion Test Results

<table>
<thead>
<tr>
<th>Classification</th>
<th>Surface Outline</th>
<th>Flaking due to Thinning of the Paint Parallel to Cuts and Adhesion Issue by Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0%</td>
<td>None</td>
</tr>
<tr>
<td>45</td>
<td>Less than 5%</td>
<td>Flaking due to Thinning of the Paint Parallel to Cuts and Adhesion Issue by Percentage</td>
</tr>
<tr>
<td>30</td>
<td>5% - 25%</td>
<td>Flaking due to Thinning of the Paint Parallel to Cuts and Adhesion Issue by Percentage</td>
</tr>
<tr>
<td>25</td>
<td>15% - 30%</td>
<td>Flaking due to Thinning of the Paint Parallel to Cuts and Adhesion Issue by Percentage</td>
</tr>
<tr>
<td>14</td>
<td>20% - 65%</td>
<td>Flaking due to Thinning of the Paint Parallel to Cuts and Adhesion Issue by Percentage</td>
</tr>
<tr>
<td>10</td>
<td>Greater than 65%</td>
<td>Flaking due to Thinning of the Paint Parallel to Cuts and Adhesion Issue by Percentage</td>
</tr>
</tbody>
</table>

**FIG. 1 Classification of Adhesion Test Results**
### B.3 ASTM D5402 Testing Results

<table>
<thead>
<tr>
<th>ASTM D5402 - MEK Test</th>
<th>BUCT</th>
<th>8/6/2015</th>
<th>Solvent: Methyl Ethyl Ketone</th>
<th>Double Rubs: 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test #</td>
<td>Test 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>12:30 pm - 40 seconds</td>
<td>12:40 pm - 41 seconds</td>
<td>1:07 pm - 41 seconds</td>
<td>1:24 pm - 45 seconds</td>
</tr>
<tr>
<td>Observations</td>
<td>No change, Minor gloss changes</td>
<td>No change</td>
<td>No change</td>
<td>No change, Paint observed on Q-tip</td>
</tr>
<tr>
<td>Test 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>12:36 PM - 70 seconds</td>
<td>12:55 pm - 58 seconds</td>
<td>1:21 pm - 39 seconds</td>
<td>1:27 pm - 40 seconds</td>
</tr>
<tr>
<td>Observations</td>
<td>No change, Minor gloss changes</td>
<td>Paint failure, Horizontal corrosion streaks</td>
<td>No change, Paint observed on Q-tip</td>
<td>No change</td>
</tr>
<tr>
<td>Test 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>1:05 pm - 60 seconds</td>
<td>1:10 pm - 42 seconds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>No change, Minor gloss changes</td>
<td>No change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>1:00 pm - 55 seconds</td>
<td>1:13 pm - 48 seconds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>No change, Minor gloss changes</td>
<td>Paint failure, Horizontal corrosion streaks</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### B.4 ASTM D2794 Testing Results

<table>
<thead>
<tr>
<th># of Sample</th>
<th>Force</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 Kg<em>m (50g</em>m)</td>
<td>No cracking</td>
</tr>
<tr>
<td>2</td>
<td>0.08 Kg<em>m (80 g</em>m)</td>
<td>No Cracking</td>
</tr>
<tr>
<td>3</td>
<td>0.11Kg<em>m (110g</em>m)</td>
<td>No Cracking</td>
</tr>
<tr>
<td>4</td>
<td>0.11Kg<em>m (110g</em>m)</td>
<td>No Cracking</td>
</tr>
<tr>
<td>5</td>
<td>0.11Kg<em>m (110g</em>m)</td>
<td>No Cracking</td>
</tr>
<tr>
<td>6</td>
<td>0.12 Kg<em>m(120g</em>m)</td>
<td>Cracking is evident</td>
</tr>
<tr>
<td>7</td>
<td>0.10 Kg<em>m (100 g</em>m)</td>
<td>Cracking is not evident</td>
</tr>
<tr>
<td>8</td>
<td>0.12Kg<em>m (120g</em>m)</td>
<td>Cracking is not evident</td>
</tr>
<tr>
<td>Stage</td>
<td>Force (Kg(\cdot)m)</td>
<td>Result</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>9</td>
<td>0.13 Kg(\cdot)m (130 g(\cdot)m)</td>
<td>Cracking</td>
</tr>
<tr>
<td>10</td>
<td>0.13 Kg(\cdot)m (130g(\cdot)m)</td>
<td>Cracking</td>
</tr>
<tr>
<td>11</td>
<td>0.13 Kg(\cdot)m (130 g(\cdot)m)</td>
<td>Cracking</td>
</tr>
<tr>
<td>12</td>
<td>0.13 Kg(\cdot)m (130 g(\cdot)m)</td>
<td>No cracking (extrusion test) ( A total of three tests at this force)</td>
</tr>
<tr>
<td>13</td>
<td>0.15 Kg(\cdot)m (150g(\cdot)m)</td>
<td>Cracking (extrusion test)</td>
</tr>
</tbody>
</table>

**B.5 Reaction Titration Test Results**

<table>
<thead>
<tr>
<th>Stage</th>
<th>PH</th>
<th>1.40</th>
<th>1.44</th>
<th>1.42</th>
<th>1.40</th>
<th>1.45</th>
<th>1.47</th>
<th>1.45</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEMP (°C - °F)</td>
<td>59.8</td>
<td>59.9</td>
<td>58.6</td>
<td>58.8</td>
<td>59.3</td>
<td>59.7</td>
<td>59.8</td>
</tr>
<tr>
<td>Stage 2</td>
<td>Filtrate (P)</td>
<td>40.2 - 38.5</td>
<td>39.7 - 40.1</td>
<td>39.4 - 39.8</td>
<td>42.3 - 39.7</td>
<td>39.6 - 39.8</td>
<td>42.4 - 29.6</td>
<td>39.2 - 39.8</td>
</tr>
<tr>
<td>Free Acid (FA)</td>
<td>9.0 - 9.6</td>
<td>9.5 - 9.5</td>
<td>9.5 - 9.5</td>
<td>9.1 - 9.1</td>
<td>9.5 - 9.5</td>
<td>9.5 - 9.5</td>
<td>9.5 - 9.5</td>
<td></td>
</tr>
<tr>
<td>Total Acid (TA)</td>
<td>26.6</td>
<td>27.3</td>
<td>27.6</td>
<td>27.3</td>
<td>26.8</td>
<td>27.2</td>
<td>26.6</td>
<td></td>
</tr>
<tr>
<td>PH</td>
<td>1.24</td>
<td>1.32</td>
<td>1.2</td>
<td>1.35</td>
<td>1.24</td>
<td>1.21</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>TEMP (°C - °F)</td>
<td>59.1</td>
<td>57.9</td>
<td>57.6</td>
<td>57.7</td>
<td>56.9</td>
<td>57.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 3</td>
<td>(COND)</td>
<td>600</td>
<td>440</td>
<td>320</td>
<td>410</td>
<td>410</td>
<td>430</td>
<td>450</td>
</tr>
<tr>
<td>PH</td>
<td>7.12</td>
<td>7.3</td>
<td>7.28</td>
<td>7.29</td>
<td>7.51</td>
<td>7.28</td>
<td>7.28</td>
<td></td>
</tr>
<tr>
<td>TEMP (°C - °F)</td>
<td>59.5</td>
<td>57.9</td>
<td>57.6</td>
<td>57.7</td>
<td>56.9</td>
<td>57.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 4</td>
<td>Free Acid (FA)</td>
<td>5 - 5 - 5</td>
<td>5 - 5</td>
<td>5 - 5</td>
<td>5 - 5</td>
<td>5 - 5</td>
<td>5 - 5</td>
<td>5 - 5</td>
</tr>
<tr>
<td>PH</td>
<td>3.33</td>
<td>3.34</td>
<td>3.34</td>
<td>3.34</td>
<td>3.32</td>
<td>3.31</td>
<td>3.31</td>
<td></td>
</tr>
<tr>
<td>Reaction Product</td>
<td>4.8</td>
<td>4.6</td>
<td>4.5</td>
<td>4.7</td>
<td>4.2</td>
<td>4.3</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Filtrate (P)</td>
<td>-72</td>
<td>-72</td>
<td>-72</td>
<td>-72</td>
<td>-72</td>
<td>-72</td>
<td>-72</td>
<td></td>
</tr>
<tr>
<td>TEMP (°C - °F)</td>
<td>56.5</td>
<td>37.9</td>
<td>36.6</td>
<td>37.3</td>
<td>37.4</td>
<td>37.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 5</td>
<td>(COND)</td>
<td>450</td>
<td>430</td>
<td>410</td>
<td>440</td>
<td>410</td>
<td>430</td>
<td>410</td>
</tr>
<tr>
<td>PH</td>
<td>7.21</td>
<td>7.28</td>
<td>7.28</td>
<td>7.3</td>
<td>7.27</td>
<td>7.28</td>
<td>7.28</td>
<td></td>
</tr>
<tr>
<td>TEMP (°C - °F)</td>
<td>51.5</td>
<td>37.9</td>
<td>36.6</td>
<td>37.3</td>
<td>37.4</td>
<td>37.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 6</td>
<td>Fg - COND</td>
<td>20 - 16 - 17 - 18</td>
<td>18 - 17</td>
<td>18 - 19</td>
<td>18 - 17</td>
<td>19 - 18</td>
<td>17 - 18</td>
<td></td>
</tr>
<tr>
<td>DI - COND</td>
<td>1.9</td>
<td>1.8</td>
<td>1.6</td>
<td>1.5</td>
<td>1.7</td>
<td>1.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>PH</td>
<td>6.81</td>
<td>6.88</td>
<td>6.88</td>
<td>6.88</td>
<td>6.84</td>
<td>6.81</td>
<td>6.81</td>
<td>6.70</td>
</tr>
</tbody>
</table>
B.6 DIFFERENTIAL SCANNING CALORIMETRY TEST RESULTS

C. PROJECT PICTURES

C.1 EXAMPLES OF ALUMINUM CAN PAINT COATING FAILURE

An example of paint coating failure on an aluminum can. This can is produced for the Chinese herbal tea company Jia Duo Bao, the company whose paint label experiences paint failure the most. The paint failure is due to the company’s pasteurization process after the can has been filled, putting the entire can in a 120° C bath prior to be putting into cardboard packaging. This process is conducted so that the cold tea can doesn’t condensate in the cardboard packaging causing the cardboard to become saturated and break.
Paint coating failure on an aluminum can normally occurs at the top part of the can, where the can undergoes a lot of stress during the necking, flanging, and the application of the top of the can. The project team has determined that during these processes miniscule cracks are formed in the paint coating layer. The pasteurization process, the application of hot water to the exterior of the can to warm the can before packaging, then causes osmotic blistering to occur resulting in exterior paint coating failure.
C.2 MUFFLE TEST

The first test that the project team was able to conduct at the BUCT was the muffle test, a test where a passivated aluminum can is placed in a muffle furnace for 5 minutes at 500°F to determine the thickness of the applied membrane based on the color of the can after heating. These two pictures depict the project limitations the project team experienced at the BUCT in regard to accessing testing materials. The muffle furnace used during testing was found in a closet and was relatively dirty, not the appropriate laboratory environment to conduct testing.
Despite conducting the experiment in a closet, the muffle test left the project team with good results. When taken out of the muffle furnace, the color of the passivated can was a dark brown, dark gold, light black, and purple color. The color of the can indicated that the passivation membrane applied to the aluminum can at the Beijing production site was too thick, a potential cause of paint failure. The thinner a paint coating is, the better it will perform and withstand to stress. Also, a can that had experienced paint failure was tested using the muffle furnace to see whether the passivation membrane remained on the can or it fell off with the failed paint coating. As you can see, the gold color of the aluminum where the paint coating has fallen off indicates that the membrane is still on the exterior of the can.
In order to ensure that we were properly conducting the muffle test, the project team conducted 10 separate muffle tests using Pacific Can Beijing’s muffle furnace. The muffle test is conducted every thirty minutes at the Beijing production facility and the test results are stored on this board next to the muffle furnace. The engineering team at Pacific Can varies the thickness of the passivation membrane applied to aluminum can depending on the complexity of a beverage company’s label. The project team recommends that Pacific Can engineering team reduces the thickness of the passivation membrane being applied to their cans by reducing the pH levels of the membrane bath. A thinner membrane will allow the organic beverage label paint coating to perform better and withstand to higher stress levels during production and packaging.
C.3 ASTM D3359 – Measuring Adhesion By Tape Test

The ASTM D3359 test was conducted twenty times in Pacific Can Beijing’s control lab using their cutting tool and tape. Just like the muffle test, ASTM D3359 is conducted on a daily basis on the control lab at Pacific Can to ensure the performance of their can’s paint coatings. During this test, the cutting tool seen in the second image was used to make an “X” cut in the exterior paint coating, cutting through the aluminum substrate. Scotch Premium Grade Transparent Cellophane tape was then applied to the cut and ripped off the substrate within 1-2 seconds of application. Using a scoring system provided by ASTM, each test sample was given a score based on the total area for the “X” cut that was removed from the substrate. All 20 test samples scored a rating of 5B, 0% of the area removed from the can. The project team determined that the paint coating develops the proper adhesion forces onto the aluminum can substrate, exceeding all our expectations.
C.4 Differential Scanning Calorimetry (DSC)

Above, is the differential scanning calorimeter that was used to test a clean can, a passivated can, a high-quality can, and a can that had experienced paint failure at the BUCT. The differential scanning calorimeter allowed the project team to analyze the glass transition temperature $T_G$, changes in heat flow, and the changes in heat capacity of the thermosetting paint coatings used at Pacific Can. The samples of a paint coating are prepared differently than other types of DSC samples, a knife is scraped across a painted substrate and parts of the scraped off paint coating is used for the sample. Due to very insignificant data received after performing the DSC, we believe that the DSC samples were improperly prepared by our Chinese partners while the project team attended a conference at Beihang University. The glass transition temperature was not able to be determined from the data received from the conducted test. The project team recommends that Pacific Can continues DSC testing to better understand how their thermosetting paint coatings cure during the three drying processes during production.
A total of twelve ASTM D2794 tests were run in a BUCT laboratory that was given as project space to the project team, 4 passivated can test samples, 4 high-quality cans, and 4 cans that had experienced paint failure. The ASTM D2794 test allowed the project team to analyze the solvent resistance of the organic, exterior label paint coating on the aluminum can. Thermosetting paint coatings become more and more resistant to solvents during their curing process and should develop a high resistance prior to the final exterior paint coating is applied to a substrate. As a result, the ASTM D2794 test analyzed whether the solvent resistance of the passivation membrane was high enough, developing high adhesion forces between the exterior paint coating and the passivation membrane during curing, and was able to withstand chemical attack. Square test samples were cut from the three different types of cans and a line was made across the center of the sample, the bottom half of the test sample acted as the control in order to properly compare the area of the sample that was rubbed (as seen in the first picture “C1”). Methyl ethyl ketone was applied with a Q-tip to the top half of the test sample in under one minute with twenty five double rubs, one swipe across the substrate to the right and one swipe back across the substrate to the left. After the methyl ethyl ketone was applied to the test sample, the sample was inspected for de-glossing or loss of hardness. Two of the high-quality cans experienced minor de-glossing, as seen in the second picture, the remaining samples showing no sign of de-glossing or loss of hardness. As a result, the project team determined that a proper solvent resistance was developed during the curing process of the passivation membrane.
After the aluminum has been molded into the shape of a can, it must undergo a series of washes and passivation before the beverage label paint can be applied to the exterior of the can. The top left picture depicts Line Washer #1 at the Pacific Can Beijing production facility, one of the three major parts of production observed and analyzed by the project team. In the Line Washer, a conveyor belt full of aluminum cans (seen entering the Line Washer in the top right photo) undergo seven processes including a prewash, cleaning, water rinsing, passivation, water rinsing, and a deionized water rinsing followed by the first drying process. The prewash and cleaning stages can be seen in the bottom left picture where Ridoline 120 W and Ridoline 550, an aqueous solution containing hydrogen fluoride, is sprayed over the cans to wash off any contaminants, oils, or lubricants left on the cans. The bottom right picture depicts the process of applying the passivation membrane, Alodine 404, to the can during stage four of the line washer. The membrane properly prepares the aluminum substrate for the application of the exterior paint label, creating hydrogen bonding between the organic paint coating and the substrate.
The Line Washer was one of the three potential causes of paint failure during the production process of Pacific Can because the surface of the aluminum can must be properly cleaned and free of all contaminants before the passivation membrane is applied. Also, if the passivation membrane is not properly applied to the aluminum substrate it would result in a defective paint coating due to the improper preparation of the aluminum substrate. The Alodine 404 (passivation membrane) Process Bulletin by Henkel states that if problems regarding the adhesion of paint coatings occur that the Ridoline and Alodine stages should be analyzed. The above pictures depict the supply of the chemicals used in the Line Washer and the type of spray nozzles that are used in the line washer to properly wet the aluminum cans with each stage of the line washer. The project team recommended that Pacific Can buys mixers for each of the blue barrels in order to ensure that the concentration of the cleaners and membrane bath used in the Line Washer is consistent throughout the barrel life of each chemical. The project team determined that the sprayers not properly wetting the aluminum cans or having a clog was not a cause of paint failure due to monthly maintenance that Pacific Can conducts in order to ensure the proper performance of the line washer.
The can undergoes three different drying processes during production, once after the Line Washer (top left picture), once after the exterior paint label is applied, and once after the interior lacquer is applied to the can (bottom right picture). The three different drying ovens was the second part of the production process that was heavily observed and analyzed as a potential cause of paint failure on aluminum cans, due to internal stress experienced by paint coatings. The operating temperature of each drying oven was analyzed to ensure that the can’s thermosetting paint coatings underwent a proper curing process. Differential scanning calorimetry and the ASTM D5402 tests were conducted to better analyze how the aluminum can paint coatings cured during each drying process.
The four pictures above is where the aluminum can beverage label is applied to the exterior of the can, after the can has been properly passivated (top left). The application of the exterior paint label to the aluminum can was not analyzed extensively by the project team because the rapid pace at which the paint application occurs, around 1800 cans per minute, allowing for the mass production of aluminum cans. As you can see in the top right, each roller contains one color that is to be applied to the can and the label paint is added to each tray as needed. As you can see in the bottom right picture, there is contamination of the red paint with yellow and blue paint. The project team recommended that contamination of paint should be avoided and the paint should be properly mixed prior to being added to each paint tray.
The third and final part of production that was heavily observed and analyzed by the project team was the necking and flanging process that the can undergoes before it is checked for quality by X-ray and sent to packaging. The project team originally hypothesized that the stresses occurred during these processes and the movement along the conveyer belt caused paint failure due to mechanical stress. The project team determined this hypothesis was false due the fact that paint failure doesn’t occur at the Pacific Can production facility and the can is carefully bent and stretched through a seventeen stage process, only creating miniscule cracking in the exterior paint coating. The project team did determine that paint failure occurs due to the combination of this miniscule cracking and osmotic blistering from rigorous pasteurization processes at the Jia Duo Bao Herbal Tea Company. Prior to packaging, the herbal tea can undergoes a hot water bath at 120º Celsius to destroy pathogens in the tea and to prepare the can for packaging. The hot water easily seeps into the cracks created during production and create an osmotic cell, eventually leading to the paint failure of the exterior coating.