OPTIMIZATION OF IR REFLECTIVE AUTOMOTIVE TOPCOAT FORMULATIONS TO REDUCE VEHICLE COOLING LOAD BY USING DESIGN OF EXPERIMENT

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ABSTRACT

OPTIMIZATION OF IR REFLECTIVE AUTOMOTIVE TOPCOAT FORMULATIONS TO REDUCE VEHICLE COOLING LOAD BY USING DESIGN OF EXPERIMENT

This thesis involved creating dispersions of infrared-reflective inorganic pigments in acrylic medium. Color matching studies for RAL 9010, RAL 7021, and RAL 9011 colors were carried out using color pastes designed with IR-reflective pigments. For RAL 9010, 7021, and 9011 colors, the reflection abilities of formulas designed with traditional pigments and IR reflective innovative pigments in the infrared region were compared, and it was determined by the temperature test. Through a temperature test, it was established that the performance of the IR reflective pigments was satisfactory. Next, the discussion focused on optimization studies of the formulations that were designed using IR-reflective pigments. Preliminary studies were carried out on the designed color formulas, and pigmentation and dry film thickness were determined as parameters, and a temperature test and a rub-out test were determined as responses. Panel applications were made according to the matrices determined for each color. A temperature test apparatus was created and analysed for the panels on which paint was applied with the specified formulas. A rub-out test was performed for stability control of the formulations. The experimental design matrix was prepared to comply with the experimental design conditions. The data collected as a result of the studies was analysed using the experimental design method in Minitab 16 software. The studies examined the effects of determined parameters, such as pigmentation and dry film thickness, on the response. The performance of the established models was examined in detail and was found to be quite successful. Formulas using IR-reflective pigments, which show better reflecting performance in the infrared region compared to traditional pigments, have been optimized.

ÖZET

ARAÇLARIN SOĞUTMA YÜKÜNÜ AZALTACAK IR YANSITAN OTOMOTİV SONKAT FORMÜLASYONLARININ DENEYSEL TASARIM YÖNTEMİ İLE OPTİMİZE EDİLMESİ

Bu tez kapsamında, kızılötesi yansıtıcı inorganik pigmentlerin akrilik ortamdaki dispersiyonları oluşturulmuştur. RAL 9010, RAL 7021 ve RAL 9011 renklerine yönelik renk eşleştirme çalışmaları, IR yansıtıcı pigmentlerle tasarlanan renk pastaları kullanılarak yapıldı. RAL 9010, 7021 ve 9011 renkleri için geleneksel pigmentlerle ve IR yansıtıcı inovatif pigmentlerle tasarlanmış formüllerin kızılötesi bölgede yansıtma kabiliyetleri karşılaştırılmış ve IR yansıtıcı pigmentlerin performansının iyi olduğu sıcaklık testi ile belirlenmiştir. Daha sonra IR yansıtıcı pigmentlerle tasarlanan formüllerin optimizasyon çalışmaları ele alınmıştır. Tasarlanan renk formüllerinde ön çalışmalar yapılarak, parametre olarak pigmentasyon ve kuru film kalınlığı; response olarak ise sıcaklık testi ve rub-out testi belirlenmiştir. Her renk için belirlenen matrislere göre panel uygulamaları yapılmıştır. Belirtilen formüllerle boya uygulanan paneller için sıcaklık test düzeneği oluşturularak analizleri yapılmıştır. Formülasyonların stabilite kontrolleri için rub-out testi yapılmıştır. Deney tasarımı matrisi, deneysel tasarım koşullarına uygun olacak şekilde hazırlanmıştır. Yapılan çalışmalar sonucu toplanan veriler Minitab 16 yazılımında deneysel tasarım yöntemi ile anliz edilmiştir. Yapılan çalışmalar sonucunda pigmentasyon ve kuru film kalınlığı olarak belirlenen parametrelerin response üzerindeki etkileri incelenmiştir. Kurulan modellemelerin performansı detaylı olarak incelenmiş olup ve elde edilen modellerin başarılı olduğu görülmüştür. Geleneksel pigmentlere göre kızılötesi bölgede daha iyi yansıtma performansı gösteren IR yansıtıcı pigmentlerin kullanıldığı formüller bu tez kapsamında optimize edilmiştir.

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CHAPTER 1

INTRODUCTION

IR-reflective pigments are increasingly used for their ability to maximize reflectivity in the near-infrared region of terrestrial solar radiation, where heat is produced. Original equipment manufacturers have recently formulated them, particularly for use as automotive coatings.[1] Conventional pigments tend to absorb near-infrared radiation while maintaining appropriate absorption in the visible spectrum to impart color.[2] In conventional pigments, light colors have a somewhat high visible and near-infrared reflectance, while dark colors have a low visible and near-infrared reflectance. Total solar reflectance (TSR) is a measure of the amount of incident solar energy reflected from a surface. The mathematical expression for it is the integral of the reflectance percentage times the solar irradiance, divided by the integral of the solar irradiance when integrated over the 280 to 2500 nm range. Typical white coatings usually have a TSR of 75% or greater. This means that a white coating will absorb 25% or less of the incident radiation.[3] On the other hand, black coatings containing carbon black pigments will show a TSR as low as 3.5%, therefore absorbing 96.5% of the incident solar energy. A pigment that has a high TSR can be considered an IR-reflective pigment.[4] A variety of cool white materials are available on the market but there is a need for non-white materials to meet esthetical preferences. Over the years, many scientists have worked on replacing conventional pigments (near infrared-absorbing) with cool-color pigments (near infrared-reflective), offering similar colors but higher solar reflectance. Complex inorganic color pigments (CICPs) are synthetic crystalline metal oxides containing two or more different metals.[3] CICPs are generally inert chemically because of their synthesis and crystalline structure. Manufacturing at high temperatures ensures that they are heat-resistant. The final product locks the metal ions into its crystalline matrix, eliminating the presence of their unreacted oxides in the final pigment product.[5]

The main goal of this project was to reduce heat buildup on exterior automotive surfaces by incorporating IR-reflective pigments, resulting in fuel economy and reduced emissions.[6-7] CICPs were used for this purpose, together with coarse TiO2 and chlorinated copper phthalocyanine in the acrylic automotive topcoats, and the results were evaluated.[8-9] Subsequently, formulations designed with IR-reflective pigments were examined. Based on preliminary studies, factors and responses were identified, and these innovative formulations were optimized using the Design of Experiments method.[10]

CHAPTER 2

STATE OF THE ART

2.1. Historical Development of Paint

The history of paint is a journey that has been ongoing since the dawn of humanity. Colors have served as symbols strongly reflecting the emotional expressions of people, cultural understanding, and utilization, and most essentially, the practical needs of the species. Prehistoric humans were already painting various situations with paints from the plants, soil, and mineral matter available in nature. They practically applied their various skills in every situation, including hunting for prey and participating in religious ceremonies. The history of paint goes back before the beginning of human history. In B.C., people were known to color the walls when they painted in caves, and cultures dating back to 40000 years were filled with pigments collected from the outside world. Ancient civilizations such as Egypt, Mesopotamia, and Greece, as well as those of us who used various types of paint, made them rich by enhancing their arts with paintings, mosaics, frescoes, and other colorful art.[10]

Figure 2.1. Cave paintings of Ancient Egypt

Red paints seen in royal tombs and temple walls were commonly utilized in ancient Egypt. In ancient Greece and Rome, paint was utilized to embellish architectural structures and statues. In the Middle Ages, where the church and feudal lords ruled, artists frequently used depictions to color pictures of a sacramental or mythological kind. The pigments utilized during this phase were usually extracted from natural sources—plants and minerals. During the Renaissance, painters from Italy comprehended linear perspective and the human body much better and substantially increased the painting using the oil painting method. In the late 19th and early 19th centuries, the manufacturing of dyes experienced a historical shift owing to the chemical sector's expansion.[10] Derived synthetically from coal tar, these pigments exhibited enhanced color intensity and durability.[12] The market expanded dramatically during this period, concentrating on fresh applications such as plastic paints that were applied to automobiles and building coatings. Indeed, the 19th century has seen rapid progress in paint technology. The incorporation of synthetic resins, pigment dispersion, and other chemical components boosted paint performance and extended its use. The twentieth century's modern art movement, abstraction, and experimentation also transformed painting, as previously stated. Researchers have completed a study on environmentally efficient approaches, including the use of eco-friendly and water-based paints like 'earth-dye'. Paint continues to play an essential role in supporting more than just artistic expression. Pigments, fresh colors, and formulations are constantly expanding, and exploring new ideological concepts, particularly ecological or environmentally efficient ones, is prevalent. Paint has been an essential sign or symptom of people's never-ending ingenuity and scientific advancement since ancient times, and it will persist.[11]

2.1.1. Paint Technology and Raw Materials Used: Types and Characteristics

Paint technology involves covering surfaces with various substances to provide protection, decoration, or specific properties. Paint technology primarily extends the life of the surfaces it applies to, enhances their appearance, safeguards against destructive influences, particularly corrosion, and serves as a marking tool.[10]

2.1.2. Components of Paints

Paints primarily contain four main components: binders, pigments, solvents, and additives, based on performance and painting behaviour. The binders can also be defined as holders of the pigment particles that help the paint stick to the surface after application

2.1.2.1 Binders

Binders are polymers that create a film on the walls of a building, creating a strong and long-lasting bond. The primary categories of binders comprise alkyd resins, acrylic polymers, epoxy resins, and polyurethanes.[11]

Alkyd resins are formed by the chemical reaction between polyesters and vegetable oils. Alkyd resins are favoured, particularly for solvent-based paints, due to their cost-effectiveness. They are also utilized in the development of active components to enhance paintability and confer flexibility and impact resistance. The resins formed a rigid and strongly bonded layer on the surface. The majority of alkyd paint is commonly used for coating metal and timber surfaces.[12]

Acrylic resins are commonly utilized in the application of water- and solvent-based paints. Acrylic coatings possess indisputable benefits, including the ability to withstand ultraviolet light, maintain color integrity, and dry rapidly. Due to the little presence of volatile organic chemicals, it is accurate to describe this substance as environmentally friendly. Acrylic polymers are highly sought after for various uses, both indoors and outdoors, such as for wall and ceiling paints.[11]

Epoxy resins has remarkable attributes, including superior chemical resistance, strong adhesion, and durability. These resins are commonly found in industrial and durable paints.[12] Epoxy paint is applied by combining two components and subsequently hardens into a durable and resilient coating. Epoxy paint uses commonly include floor coatings and paints used for ships and tankers.[13]

Polyurethanes also possess the previously mentioned qualities of abrasion and chemical resistance, flexibility, and UV resistance.[14] They exist in both solvent-based and water-based forms. Polyurethane paints are widely used in the automobile industry, as well as for furniture coatings and outdoor paint applications. They produce resilient and enduring coatings.[10,13]

2.1.2.2 Pigments

Pigments are solid particles that determine paint color. Additionally, as pigments increase, their color formation can properties such as hide, corrosion resistance, and resistance to UV rays. Pigments fall into two main categories: organic pigments and inorganic pigments.[15]

Figure 2.2. A visual representation of different pigment powders

2.1.2.2.1 Organic Pigments

Organic pigments are compounds based on carbon. Such pigments have bright and saturated colors, but their color fastness to light is usually worse than that of inorganic ones. Organic pigments are used to obtain brighter colors and various tones. The main types of organic pigments are as follows.[15]

Azo pigments are compounds that contain the azo group -N=N- and generally give bright red, orange, and yellow colors. These pigments are synthesized by diazotation and are coupling reactions between aromatic amines and phenols. Phthalocyanine pigments are compounds that include phthalocyanine complexes and are always blue and green. These pigments are characterized by an excellent color retention coefficient.[16] Quinacridone pigments are quinacridone derivatives and give red, purple, and some intermediate tones. Indigoid pigments are a compound that structurally resembles indigo.[16] These pigments are mostly blue and purple. Indigoid pigments can be obtained from the leaves of the indigo plant and synthesized.

Table 2.1. Advantages and Disadvantages of Organic Pigments

Advantages	Disadvantages
Organic pigments provide a wide range of colors.	Some organic pigments can be unstable when exposed to light or chemicals.
These pigments usually have very vibrant and bright colors.	Organic pigments may not be resistant to high temperatures in some cases.
Different chemical structures allow the production of customized pigments for specific applications.	Some organic pigments may have adverse effects on the environment and human health.

2.1.2.2.2 Inorganic Pigments

Inorganic pigments are inorganic compounds used in various applications to provide color; they mainly consist of metal oxides, metal salts, and other inorganic compounds. Inorganic pigments have been used for centuries in paint, coating, and other decorative applications. The major chemical structure and color property-based classification is metal oxide pigments, metal salts, complex inorganic-colored pigments (CICPs), and natural inorganic pigments.[17] Additives are substances that alter the optimal paint's performance when a small amount of substance is added to adjust the paint's curing time, viscosity, UV exposure resistance, and surface adhesion. Metal salts are pigment obtained by various compounds of metal salts; for example, the culprit pigments' pure and bright yellow color comes from the compound $PbCrO_4$. CICPs are linked to the solid solution of more than one metal oxide by high temperature during synthesis to create a wide range of color and durability.[10] Natural inorganic pigments are pigments sourced from natural materials. For example, it contains earth pigments like umber, ocher, and sienna; mineral pigments include iron oxide. Inorganic pigments can be produced by processing natural sources or synthesizing through chemical reaction. Metal oxide pigments are produced by high-temperature calcination of metal oxides. Metal salts are obtained by the precipitation of metal salts at the right reaction conditions. CICPs are synthesized by high-temperature solid solution formation using multiple metal oxides.[18]

Table 2.2. Advantages and Disadvantges of Inorganic Pigments

Advantages	Disadvantages
Durability: Inorganic pigments generally provide high durability and longevity.	Color Limitations: Inorganic pigments generally have less bright and vibrant colors.
Opacity: These pigments have high opacity and covering properties.	Heavy Metal Contains: Some inorganic pigments may contain heavy metals that can be harmful to the environment and human health.
Heat and Chemical Resistance: Inorganic pigments are resistant to high temperatures and chemicals.	Cost: Some inorganic pigments can be costly to produce and process.

2.1.2.3 Solvents

The fluidity of the paint is ensured with liquid substances known as solvents. Solvents are used to dissolve or disperse the paint components thoroughly so that the paint can later be spread evenly over a surface. When the paint dries, the solvents evaporate, and the paint surface forms a solid film. Two types of solvents are used as thinning material in painting: Organic compounds: types, such as thinner and white spirit. These are mostly used in solvent-based paints. Water used as a solvent in water-based paints. It is environmentally friendly and has a low content of VOCs.[13]

2.1.2.4 Additives

Additives are small amounts of substances added to improve the performance and application properties of the paint. These substances are mainly used to adjust properties such as curing time, viscosity, UV resistance, and surface adhesion.

Driers are additives that are added to speed up the drying of paint. The drying process takes place when the solvent or water content of the paint is evaporated, leaving a solid film or residue. Therefore, dryers help in speeding up this process by enabling the paint to solidify. Dryers are mainly analyzed under two categories, oxidative driers and catalytic driers. Second, dispersing agents are used to ensure that pigments and other solid particles are uniformly dispersed in the liquid phase of the paint.[19] The agents help in the uniform dispersion of the paint thus increasing performance parameters such as pigment color and opacity. Dispersing agents function by preventing the combing of the pigment particles, thus ensuring the paint does not streak. In addition, UV stabilizers are used to increase the resistance of the paint against sunlight. UV rays are known to affect the color, sheen, and general structure of paint. Thus, UV stabilizers help in eliminating these effects hence preserving the life and aesthetic value of the paint. Fourth, antimicrobial agents are used to inhibit the growth of bacteria, fungi, and other microorganisms on the paint surface.[10] This implies that the agents improve the hygienic quality and prevent microbial spoilage of paint. Defoamers are also used to control or minimize foam in paint during manufacturing. For instance, foam is produced when air bubbles created during production become trapped in the liquid mixture. The foams then rise to the top, causing foaming on the mixture of the surface, which hinders spraying and increases the paint drying time.[20]

2.2 Types of Organic Coatings

Volatile organic compound (VOC) contents are used as solvents in solvent-based organic coatings. However, the use of these volatile harmful solvents is being restricted day by day for environmental health reasons. In order to minimize this interaction, different components were used instead of solvents in paint formulations and the formulas were designed accordingly.[21]

Paints that contain organic solvents are called solvent-based paints. These solvents keep the paint liquid during application and subsequently evaporate, allowing the paint to dry and harden. Common solvents used in paint include toluene, xylene, acetate, and alcohols.

Environmental and health concerns have increasingly driven the transition from solvent-based paints to more environmentally friendly alternatives. Water-based paints, which contain significantly lower levels of VOCs compared to their solvent-based counterparts, offer a reduced environmental footprint. Advances in technology have enhanced the performance and durability of water-based coatings, making them competitive with traditional solvent-based formulations. As a result, there is a growing adoption of water-based paints in both industrial applications and consumer markets, reflecting a broader commitment to sustainable practices in the coatings industry.[21]

Table 2.3. Advantages and Disadvantages of Solvent-based Paints

Advantages	Disadvantages
Durability: High durability and hardness.	Environmental Impact: Evaporation of solvents can cause air pollution and damage to the ozone layer by creating volatile organic compounds (VOCs).
Surface Compatibility: Can be applied to a wide variety of surfaces (wood, metal, plastic, concrete)	Health Risks: Solvent vapors can cause respiratory problems through inhalation and can be irritating in contact with skin.
Fast Drying: When the solvents evaporate, the paint dries quickly, shortening the work time.	Fire Hazard: Solvents are generally flammable and should be used with caution.

Water-based paints are undoubtedly the most commonly commercialized type of paint. Water-based paints are paints that often contain polymer emulsions such as acrylic or vinyl. Water is considered to be a solvent type of paint since it is used simultaneously with various polymers. Interior and exterior paint, wall paint, furniture paint,industrial coatings and automotive coatings are examples of water-based paints.[21]

Table 2. 4. Advantages and Disadvantges of Water-Based Paints

Advantages	Disadvantages
Eco-Friendly	It takes longer to dry than solvent-based paints.
Low VOC content	May be less durable than solvent-based paints in some cases
Less toxic and flammable	The surfaces may need to be prepared very well before application, otherwise adherence problems may occur.

Powder coatings are paints in fine-powder form applied to the surface typically by electrostatic application and then heating to cure. Powder coatings are used in various industrial coatings and metal-based plating. They have a wide range of applications, including cars, metal furniture, household appliances, bicycles, garden furniture, and other industrial equipment.[10]

Table 2.5. Advantages and Disadvantages of Powder Coatings

Advantages	Disadvantages
High Durability	Limited Application Areas
Scratch and abrasion resistant	It may be difficult to apply on parts with fine details or complex shapes.
Resistant to chemicals	The variation in the color matching process is more limited.
VOC free	Powder coating equipment and ovens can be expensive.

2.3 Types of Organic Coating Layers

Primer is the first layer applied to the surface bottom paint. The primer is typically used to enhance the bonding power of the underlying color coat, remove rough surface characteristics, and lessen porosity. It is best used to cover melt areas and other blemishes on the surface, so the underlying color has an even appearance. Primers are made up of polymer resins, pigments, fillers, solvents, and extra additives. The properties such as adhesion, coverage, and efficient results are determined by these materials. The substance is commonly applied to a tool using a brush, roller, or spraying device. The adherent is subdivided into a single layer after the surface has been thoroughly clean and sand and dried. After drying, the primed surface is washed, and a coating is applied if the texture is rough or uneven sanded primers are sanded.[22]

The main color layer is the basecoat, painted over the layer of primer. This paint layer is frequently referred to as the underlay or the base color to be applied. In practice, it gives the first essential impermeable coating of color that is applied above the primer. It can, depending on its ingredients, also have comparable or same components as the primers in the primer layer.[10] It can have pigment, resin, solvent, and some other additives. Basecoats, however, normally have more pronounced pigments and better resins. The basecoat is then brushed, roller or sprayed above the primer. As the portrayed layer, color and an image are applied as needed.[23]

The topcoat is a final layer or a protecting coat that is painted over the basecoat. It is used mainly to safeguard surface colours from dust, weather, mechanical impact, and other conditions. The topcoat provides a gloss, semi-mat, and mat finish level. The commonly found high resins quality in pigments, coatings paint, solvents, and additives. All these materials have different properties that determine adhesion, coverage, gloss, and durability.[23] Topcoats are applied on the basecoat by brush, roller, and vacuum. One should ensure the topcoat has been applied homogenously on the base and it has the required mat or gloss level.[14]

Clearcoat is the final protective coating that is applied over the topcoat. Clearcoat is mainly used to protect the surface from scratches, abrasion, sunlight, and chemicals. It imparts shine and depth to the surface and helps the paint last longer. Clearcoats generally contains top-quality resins such as polyurethane, acrylic or epoxy. The resins stick to the surface and form a protective layer that lasts long and maintains the color and texture as before. It is applied to the topcoat by using a brush, roller or spraying. The clearcoat must spread homogeneously throughout the surface completion, the desired level gloss and it should be allowed to dry and harden completely. If required, the second coating can also be applied.[22]

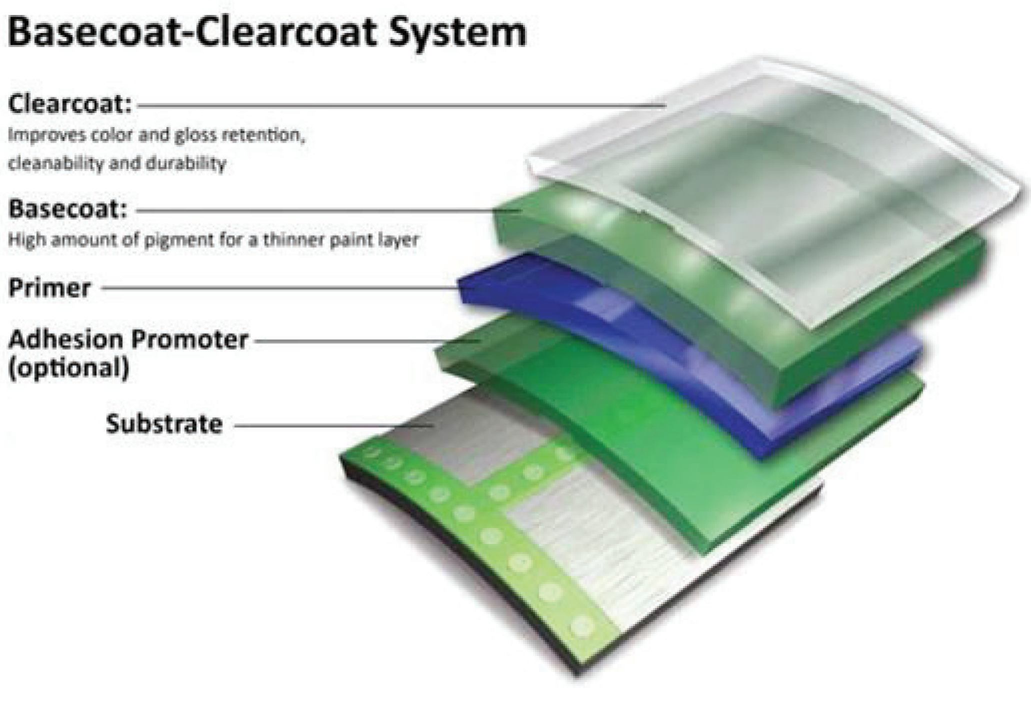

Figure 2.3. Layers of a Typical Basecoat Clearcoat Application

2.4 Paint Production Process

The pre-mixing process, the first stage of paint production, is a critical process for the sample's structure to be homogeneous. It combines the main components of the paint formulation and transfers them to the mixture through the mix. Several technical and chemical processes directly related to the quality of paint take place in the first stage. The key stages of this process include: the mixing of pigments and binders with solvents; water and other liquids; grinding of pigments; and breaking down substances.[14]

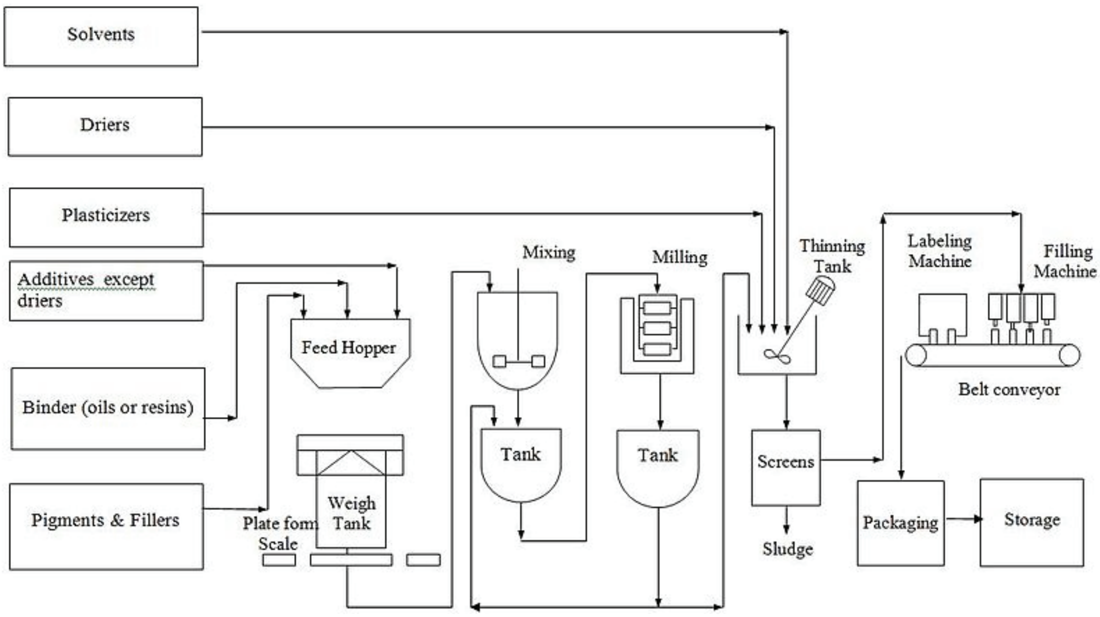

Figure 2.4. Schematic Summary of the Paint Production Prosess

The initial mixing process generally takes place in large mixing tanks, the inner surface of which is equipped with a coating resistant to chemical action. The internal auxiliary coatings are protected from chemical interaction. The mixing tanks are provided with special mixing and motor systems to obtain a uniform product. Resins and solvents are added to the mixing tank. Depending on the viscosity of the resins, it is possible to premix solvents and resins to make the dissolution process easier. The resins are completely dissolved at this stage, and a homogeneous mixture is obtained. Pigments are carefully added to the mixing tank.[10] Since pigments are in the form of a powder, the drawing freezes the powder. Therefore, it is mixed slowly and continuously. High speed mixing is applied to distribute the pigments in the mixture. Dispersing agents can be used at this stage. Dispersants prevent pigment particles from sticking together and provide even distribution in the mixture. Fillers can be added to the mixture after pigments. Fillers are usually in the form of larger particle sizes, and the mixing is carried out using a low mixing speed to help ensure their homogenous distribution during mixing. Fillers increase the viscosity in the mixture; hence, the fluidity of the mixture is checked continuously at this stage. Additives are added in the final stages of the mixing process.[14] These are preferred to increase the final performance of the paint and provide the desired properties. Although their entries in the formulas are relatively few, their effects are high. Additives are generally in liquid and powder form. The mixing process proceeds to completely dissolve the additives and obtain a homogeneous distribution.[13] Dangerous problems such as graininess may arise in non-homogeneous mixtures. Therefore, the additive amounts in the formulations must be optimized. Once the mixing process is done, the mixing process is carried out using a low-speed mixing for a certain period just to ensure the mixture has a homogenous structure. This ensures that the ingredients are completely mixed, and no lumps are present within the mixture. The completed mixed paint's viscosity is measured to establish its compliance with production standards. On completion of the mixing, the desired came as a result of composition is taken for laboratory tests.[10] The rest is returned back for further mixing until the desired combination is achieved. It should be noted that color, viscosity, opacity, pH plus some other chemical properties are determined in laboratory tests.[11] If the tests of the samples taken give results that are in line with the production standard, then the desired product has been attained. Finally, the mixture is allowed to pass to the next stage; otherwise, it is returned for further mixing. Mixing is the first process in the manufacture of paint. The technique and the control methods of the process form the foundation of the quality of the end product. The right selection of the components, mixture homogeneity and Viscosity control are some of the important and delicate factors that support the production of paint. Adequate management of the process is instrumental in ensuring consistency and the drive for excellence in the industry.[13]

Figure 2.5. Pre-mixing Process of Paint Production

Dispersion prosess is essential in paint production because it ensures that pigments, fillers, and other solid particles are evenly spread in the liquid medium. In addition, this stage affects the properties and performance of the paint by determining the strength and covering power of the color.[19] The main purpose of dispersion is to distribute pigments and fillers without clumping and to obtain a uniform distribution in the mixture. The various stages of the dispersion process include the following three steps:

-Wetting: Coating the surfaces of pigments and additives with resin and solvent

-Dispersion: Breaking up of the pigment agglomerates into primary particles

-Stabilization**:** The homogenized dispersion maintains its stable structure over a certain period of time.

Wetting ensures that the surfaces of pigments and fillers are coated with liquid ingredients. Preventing particles from clumping and ensuring efficient dispersion is a very important process for the dispersion of paint. First, solvent is added to the dispersion tank. The solvent wets the surfaces of the pigments and fillers under a certain shear force to prevent agglomeration. Pigments and fillers are slowly mixed in the solvent. In this mixing, the surfaces of the particles are wetted and coated with the solvent. Dispersing agents are then added to improve the wetting process by lowering the surface tension of the particles. This agent creates a layer on the surface of the pigment which means they can spread better.[19]

In the dispersion process, pigment agglomerates disintegrate into smaller particles through mechanical energy. The process helps distribute pigments evenly in the paint while increasing color intensity. Finally, the product after wetting is subjected to high-speed mixers. These break pigment agglomerates to allow individual pigments to separate into smaller particles. Bead mills, ball mills, or three-roll mills are commonly used for this purpose.[14] The mechanism separates pigments into smaller particles using mechanical energy. The mills crush pigment agglomerates through small glass, ceramic, or steel beads. The beads rotating quickly collide with the pigments and crush the agglomerates into small particles. The stabilization process uses a similar process with large metal or ceramic balls. As the balls revolve in the mill, they crush the pigments, thus stabilizing them. In this process, particle size and distribution are measured and monitored. This measure is done through laser diffraction or microscopy. The product is processed until the size of the pigments reaches the desired target. Stabilization entails using additives to ensure pigments do not re-agglomerate. This solves two essential issues. Firstly, this procedure provides an extension of the shelf life of the paint in storage and reduces the likelihood of clumping during application. Additionally, at the final stage of dispersion, “stabilizers are added to prevent the particle of pigment from agglomeration by adsorbing onto their surface”. Stabilizers commonly include surfactants, polymers, or dispersing agents. The low speed is maintained all the time while introducing stabilizers. This ensures that the stabilizers cover all the pigment particles and disperse them consistently. Once stabilization has been achieved, the dispersion obtained is monitored for its stability. This can be done by checking “long-term stability tests.[10]

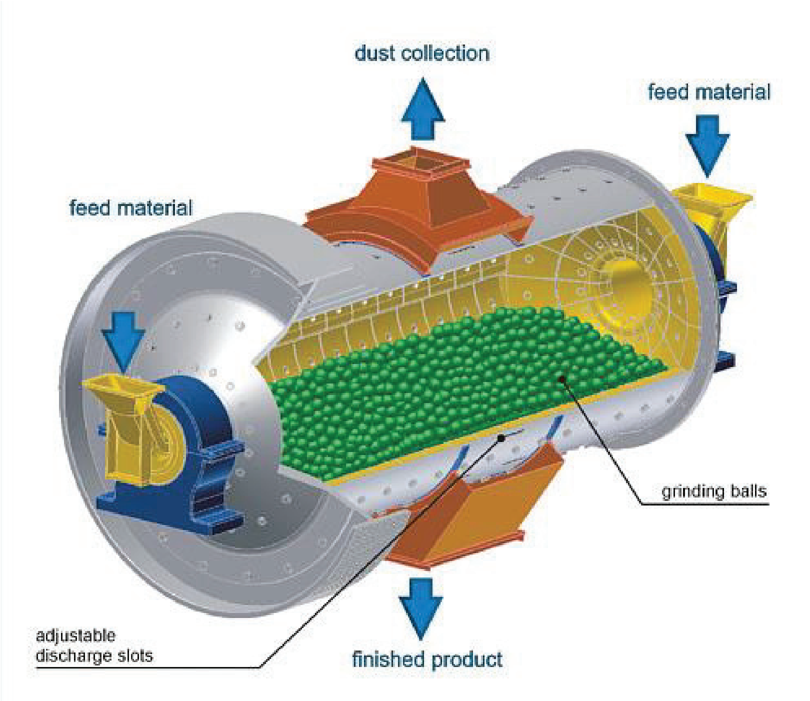

Figure 2.6. Typical Type of Ball Mill Used in Dispersion Process

The primary purpose of the intermediate addition stage is the addition of the required additives to provide the desired properties to the paint mixture and assure its stability. To be more precise, the additives are the elements that define the paint's viscosity, fluidity, drying, flicking conditions and characteristics, and adherence. In addition, various chemicals may be used to increase the longevity of the paint and harden it against exterior impact factors.[15] In most cases, the additives are supplied in a form of the liquid or powder, and before adding it, the adequate preparation is carried out. The liquid additives are usually pre-mixed or solubilized before using, and the substances in the powder state are just measured before adding. It is most important to add the additives in the correct amounts and the correct sequence to assure paint homogeny and stability. As a rule, dispersants and surfactants are added in the first place, and then the rheology control agents are added, followed by other functional agents. The additives are added to the paint mixture with the lower speed mixing. In this stage, the continuous mixing is required to assure the mixture remain homogeneous and the full dispersion of the additives.[19] Mixing time and speed are also dependent variables and are adjustable depending on the kind of additives used and the viscosity of the paint. After adding the additives, the viscosity and fluidity of the mixture are tested. These tests can be conducted using viscometers and flow tests. Viscosity regulators are added to obtain the desired fluidity when necessary. The pH and other chemical characteristics are tested after the addition of the additives. pH is a very important test to seeing the dyeing stability and performance and is maintained around neutral or slightly alkali. After adding the additives, the stability and shelf life of the let-downs are tested. This is how the paint will stand up when placed in undesired conditions like degrading, precipitating, or changing color over time.[10] Long-term storage tests, accelerated aging tests, and thermal cycle tests are carried out. Mixing tanks made of stainless steel using special mixing blades can be used. These tanks ensure that the sufficient quantity of the additives is distributed homogeneously. Mixers that rotate at a slow speed are ideal for gently distributing a sufficient quantity of the additives into the mixture. It offers the most accurate results when dealing with a viscous paint. Automated dosing systems ensure that the exact amount of each additive is obtained. The systems are equipped with the most exact measurements and will dispose or dispose of the additive when they reach the required mass.[15]

Among the final stages of the paint production process include packaging and filtration. They are crucial for storing, transporting, and presenting the paint produced to the users. Packaging entails filling and sealing the paint products in the appropriate packages. On the other hand, filtration aims at ensuring that the paint has no unwanted particles or foreign substances. The packaging materials are characterized by various types, sizes, shapes, and colors. They are made up of plastics and metal materials. The material is an essential aspect of the packaging material since it intensifies the products' portability. Second, choosing the appropriate packaging material entails the environmental safety and recyclability of the material. The packaging is often done on the automatic lines. The paint is filled into the pre-prepared packages via the filling machines. Then, the packages are sealed. The sealing is essential for the security of the product against foreign intrusions. The filtration entails removing the impurities in the paint. The strainers are important because they remove unwanted particles in the paint. The filter materials are cellulose-based, paper-based, ABS, or metal. The filters have different pores based on their purpose. The painting process is done quickly, and the outcome is determined on the laboratory analysis. The filter is an important aspect of the production process since it ensures that not all particles are removed. The packaging and filtration are the final stages of the production of paint. It is essential to ensure that the paint is produced in accordance with quality standards. Therefore, the above processes are crucial.[10]

2.5 Paint Application Methods

Paint application methods are critical in coating surfaces for aesthetic and adhesion purposes. Different surfaces require different conditions and techniques for applying paint. Paint application methods include brushing, rolling,spraying, dipping, electrostatic coating and powder coating.[10]

Figure 2.7. Brushing Application of Paint

Table 2.6. Application areas, advantages and disadvantages of Brushing Application

Application Areas	Advantages	Disadvantages
Small and detailed surfaces	Provides sensitive application	It takes longer to complete
Hard to reach areas	Minimizes material waste	Achieving a smooth surface can be difficult
Edges and corners of surfaces	The amount of paint can be easily controlled during application	May leave brush marks

Paint application by roller is an application method where the paint can be applied to any surface in a large volume quickly and efficiently. The paint is poured over a surface and distributed by the roller. In this context, the roller's feathers absorb a certain volume of paint and spread the absorbed paint to the surfaces in contact with the feathers. This method is directly connected to the paint's viscosity and the ability of the roller's material to hold this type of paint.[21] How smoothly the roller spreads the paint over the surface is determined by the balance between the pressure applied to the roller and the speed of movement.

Figure 2.8. Roller Application of Painting

Table 2.7. Application areas, advantages and disadvantages of Roller Application

Application Areas	Advantages	Disadvantages
Flat and large surfaces	Fast and effective application	Difficult to use in detailed areas
Walls and ceilings	Provides a homogeneous surface appearance	May consume more paint
Interiors	Leaves less marks than a brush	It can be difficult to ensure the surface is completely smooth

Dipping is a painting method involving complete immersion of the painted object in paint so that it is completely covered. It is used in mass production. The dip process is based on the principles of surface tension and capillarity. When dipped in paint, the paint adheres to the surface of the object due to the surface forces of tension. The thickness and evenness of the paint layer depend on the paint's viscosity and the time the object is kept in the paint.

Spraying method is applying with conventional spray guns to cover the surface with a thin layer. This is carried out by compressed air or a pump system. The spraying of primer is done by atomizing the paint and passing it out in tiny droplets. The paint is atomized by the varying viscosity of the paint and spray machine pressure thus this method the level of the surface tension and droplets size is controlled maximizing coverage uniformity.[22]

Figure 2.9. Spraying Application of Painting

Table 2.8. Application areas, advantages and disadvantages of spraying application

Application Areas	Advantages	Disadvantages
Large and flat surfaces	Fast and covers large areas	There may be high paint wastage
Vehicles and large equipment	Provides a smooth and even surface	Release into the environment may be difficult to control
Flat and smooth surfaces	Effective on objects with complex shapes	Requires equipment and experience

Figure 2.10. Dipping Application of Paintings

Table 2.9. Application areas, advantages and disadvantages of painting application

Application Areas	Advantages	Disadvantages
Small parts and equipment	Provides homogeneous and full coverage	High paint consumption
Mass production lines	It is a fast and efficient method	Requires large paint tanks
Complex shaped objects	Suitable for mass production	Paint viscosity and duration should be well controlled

The method is an electrostatic coating based on the principle that the paint can be electrically charged and attracted to the surface using an artificially created force field. The method is based on the principle of Coulomb forces.[23] The operating principle of an electrophoretic plant is also based on the principle of intercharge between the surface, the particles and the rest of the particles. The visible region of these particles can have both positive and negative charge, which is automatically distributed by the surface.

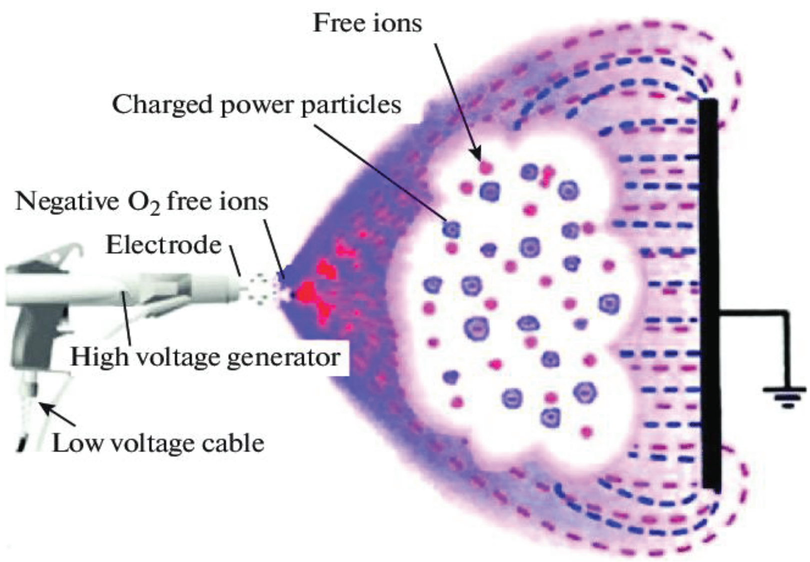

Figure 2.11. Electrostatic Spraying Application of Paint

Table 2.10. Application, advantages and disadvantages of Electrostatic spray application

Application Areas	Advantages	Disadvantages
Metal surfaces	High efficiency and low wasting	High equipment cost
Automotive industry	Provides an even and thin coating	The surface must be conductive
Industrial equipment	Effective even in complex shapes	Application environment needs to be well controlled

2.6 Basic Color Theory

Color is defined as a perception created in the human brain by the light reflected from the surface. Color perception occurs as a result of the combination of three different components: light source, object and observer.[24] We may have had difficulty describing a color we liked very much to someone else in words. Defining color has always been a difficult subject. Historically, the first focus was on determining with precise measurements which wavelengths of colored objects absorb. Color systems developed later also took into account the determinations of the light falling on the surface. As a result of all this, color systems have been developed that aim to define colors by dividing them into various components which are "Munsell Color System", "Natural Color System" and "CIELab System" should be mentioned because they are the most used systems.[25] While the Munsell color system and natural color system are used to define color, the CIELab color system is a system used in the color matching process.[25]

The name of the CIELab system is derived from the International Commission on Illumination. Its original name in French is commission international de l'eclairage. The mentioned commission created the CIE Color system, named after itself, in 1931. It is known that all colors can be obtained by mixing three-color light in different proportions.[26] Modeling of the system is based on the knowledge that there are three types of conical light-sensing cells in the human eye and that they are sensitive to blue, green and red light.[25] In the CIE system, a standard light, defined as which wavelengths of light rays it contains and in what proportion, is cast on a colored surface, and after some of it is absorbed, the remaining light beam is reflected from the surface to the observer's eye.[4] The proportions of blue, green and red lights in the reflected beam are measured instrumentally. Since these three lights stimulate three different sensory cells in the eye, their ratio is called "tristimulus". The measured tristimulus values are converted into a Cartesian system consisting of L*,a*,b* coordinates.[26]

L* (Lightness) expresses how light or dark the color is. The L value varies between 0 and 100. 0 represents completely black and 100 represents completely white. A* (Green-Red Axis) defines the balance between green and red colors. Negative a* values represent green, positive a* values represent red. b* (Blue-Yellow Axis) expresses the balance between blue and yellow colors. Negative b values represent blue, positive b* values represent yellow.[27]

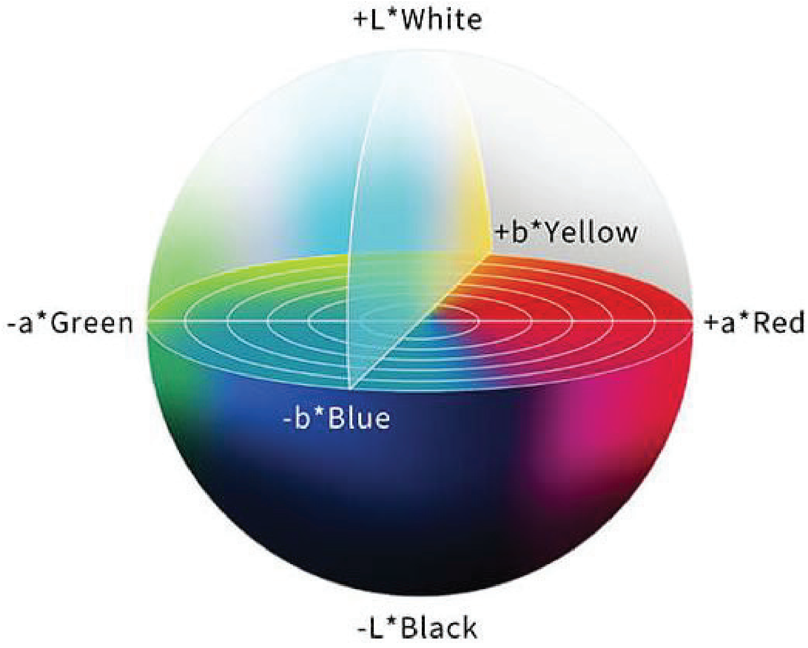

Figure 2. 12. CIE L* a* b* Color Space

On the basis of the color matching principle, delta values (ΔL*, Δa* and Δb*) are calculated for each coordinate from the L*, a* and b* values of two colors and the Euclidean distance (total color difference, ΔE) is measured according to the following equations.[24]

$$\Delta L^* = L^*_{sample} - L^*_{standard}$$
$$\Delta a^* = a^*_{sample} - a^*_{standard}$$
$$\Delta b^* = b^*_{sample} - b^*_{standard}$$
$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

2.7 Literature Survey

Ashwini K. Bendiganavale et al. calculated the total solar reflectance values of the formulations they made using IR reflective pigments. They synthesized both organic and inorganic pigments and measured the temperature values of the surface at certain intervals.

V. Landry et al conducted studies on reducing the surface temperature by adding

IR reflective pigments to water-based exterior wood coating formulations. They also aimed to eliminate the negative effects that may occur when wooden surfaces are exposed to high temperatures.

Antonio Libra and his colleagues have revealed that since traditional coating methods are used in the roof coverings of old and historical buildings in Italy, most of the rays coming from the sun are absorbed, especially in the summer months, and therefore this affects both the people living in that building and the increase in energy consumption. They analyzed the temperature behavior of surfaces using IR reflective pigments.

Thomas Sowade examined the heat-build up effect by using IR reflective pigments in many different colors in roof coatings. It has been shown that this effect can be increased by using other coating layers in the most correct way, in addition to a single coat of coating. He calculated the Total Solar Reflectance values of the formulations created using IR reflective pigments and performed surface temperature tests.

A. Synnefa et al. applied coatings formulated with 10 different IR reflective pigments to a building surface and conducted temperature tests at regular intervals. He measured the percentage of total solar reflectance values in the infrared region and examined the effect between different colors.[26]

CHAPTER 3

DESIGN OF EXPERIMENT

3.1 Overview

The design of experiments (DOE or DOX), also known as experiment design or experimental design, is the design of any task that aims to describe and explain the variation of information under conditions that are hypothesized to reflect the variation. The term is generally associated with experiments in which the design introduces conditions that directly affect the variation but may also refer to the design of quasi-experiments, in which natural conditions that influence the variation are selected for observation .[29]

In its simplest form, an experiment aims at predicting the outcome by introducing a change of the preconditions, which is represented by one or more independent variables, also referred to as "input variables" or "predictor variables." The change in one or more independent variables is generally hypothesized to result in a change in one or more dependent variables, also referred to as "output variables" or "response variables." The experimental design may also identify control variables that must be held constant to prevent external factors from affecting the results. Experimental design involves not only the selection of suitable independent, dependent, and control variables, but planning the delivery of the experiment under statistically optimal conditions given the constraints of available resources. There are multiple approaches for determining the set of design points (unique combinations of the settings of the independent variables) to be used in the experiment.[30]

Main concerns in experimental design include the establishment of validity, reliability, and replicability. For example, these concerns can be partially addressed by carefully choosing the independent variable, reducing the risk of measurement error, and ensuring that the documentation of the method is sufficiently detailed.[30,31] Related concerns include achieving appropriate levels of statistical power and sensitivity.

3.2 Basic Concepts and Terminology

In an experiment, independent variables (factors) are controlled and their effects are examined. For example, the temperature and pressure of a chemical reaction can be factors. Each factor can take specific values, known as "levels." For instance, the temperature factor may have low and high levels. The dependent variable (response) is the outcome variable that is affected by the factors and measured. For example, reaction yield or product quality can be a response. The experimental unit is the smallest unit in which the experiment is applied and can be a test tube or a production line. Blocking is done to reduce variation between experimental units, grouping them to increase the homogeneity of the experiment.[32]

3.3 Types of Design of Experiment

A factorial design is an experimental design method where multiple factors are evaluated simultaneously by arranging all possible combinations of each factor's levels with the levels of the other factors. This approach allows for the determination of the independent effects of each factor as well as the interactions between factors. It is widely used in the analysis of complex systems because it enables the observation of the effects of interactions between factors. Moreover, factorial design enhances the efficiency of experiments and provides more comprehensive information.[33] Factorial design method is examined under two subheadings: A full factorial design is an experimental design method where every possible combination of the levels of all factors is included. This approach allows for the examination of the effects of each factor independently and the interactions between factors in a comprehensive manner. By testing all possible combinations, full factorial design provides a complete and detailed understanding of how different factors and their interactions influence the outcome variable. This method is particularly useful for identifying complex interactions in a system and for optimizing processes. A fractional factorial design is an experimental design method that involves selecting a subset of the possible combinations of factor levels, rather than testing all possible combinations as in a full factorial design. This approach reduces the number of experimental runs needed, making it more efficient and cost-effective while still providing valuable information about the main effects and some interactions. Fractional factorial designs are particularly useful when the number of factors is large, and it is impractical to conduct a full factorial experiment. By carefully choosing the subset of combinations, researchers can still gain insights into the most important effects and interactions without the need for exhaustive testing.[34]

A screening design is an experimental design method used to identify the most important factors from a large number of potential variables. It is typically employed in the early stages of experimentation when the goal is to determine which factors have a significant impact on the response variable. Screening designs allow researchers to efficiently evaluate many factors with a relatively small number of experimental runs.[33] Screening design method is examined under two subheadings: A Plackett-Burman design is a type of screening design used in experiments to identify the most important factors from a large number of potential variables. This design is particularly efficient because it allows the evaluation of many factors with a minimal number of experimental runs. Plackett-Burman designs are based on a specific matrix structure that ensures orthogonality, meaning that the effects of the factors are uncorrelated. This property helps in accurately estimating the main effects of each factor while ignoring interactions. These designs are especially useful in the initial stages of experimentation when the primary goal is to determine which factors have a significant impact on the response variable, thereby guiding further, more detailed investigations.[31] Taguchi design is an experimental design method developed by Genichi Taguchi, aimed at improving the quality and performance of products and processes. This method emphasizes robustness and cost-effectiveness by focusing on making systems insensitive to variations, thus reducing variability and enhancing quality. Taguchi designs use orthogonal arrays to systematically and efficiently study the effects of multiple factors on performance. This approach helps in identifying optimal factor settings that minimize variability and improve overall performance, even in the presence of noise factors (uncontrollable variations). The Taguchi method also incorporates signal-to-noise (S/N) ratios to measure the robustness of the system, providing a quantitative measure to compare different settings and select the best combination for robustness and quality improvement.[34]

A randomized design is an experimental design method in which the assignment of treatments to experimental units is done randomly. This randomization helps to eliminate bias and ensures that the effects of uncontrolled variables are equally distributed across all treatment groups, thereby reducing the potential for confounding factors to influence the results. Randomized designs can be simple, such as completely randomized designs where treatments are randomly assigned to all units, or more complex, like randomized block designs where units are first grouped into blocks based on certain characteristics and then treatments are randomly assigned within each block. The primary advantage of randomized designs is their ability to provide unbiased estimates of treatment effects, enhancing the validity and reliability of the experimental conclusions.[34]Randomized design method is examined under three subheadings: Central Composite Design (CCD) is a widely used experimental design method in response surface methodology (RSM) for building a quadratic model of the response variable without requiring a complete three-level factorial experiment. It combines three types of points: factorial points from a factorial or fractional factorial design to provide information on linear and interaction effects, axial (or star) points located at a specific distance from the center to provide information about curvature, and replicated center points to assess experimental error and overall curvature. This combination allows for efficient estimation of second-order (quadratic) terms, enabling the development of an accurate response surface model. CCDs are particularly useful for optimizing processes with nonlinear relationships between factors and the response, helping identify optimal conditions and improve process performance.[29] Box–Behnken design is an experimental design method in response surface methodology (RSM) used to optimize processes and develop second-order (quadratic) models without requiring a full three-level factorial experiment.[29] It combines factorial points at the midpoints of the edges of the experimental space (excluding the vertices) and multiple center points to estimate experimental error and ensure robustness. Unlike central composite designs, Box–Behnken designs do not include axial points. This design is particularly efficient when the experimental region is spherical or nearly spherical, requiring fewer runs than a central composite design with the same number of factors.[31] Box–Behnken designs are widely used for process optimization, providing a good balance between the number of experiments and the quality of the resulting model.[33] D-optimal design is an experimental design method used to select a subset of possible experimental runs that maximizes the determinant of the information matrix, thereby providing the most information about the system being studied with a given number of experiments. This approach is particularly useful when the number of potential experiments is large and it is impractical to conduct all possible combinations. D-optimal designs are often used in situations where traditional factorial or response surface designs are not feasible due to constraints on resources or time. By focusing on maximizing the information obtained from the experiment, D-optimal designs provide efficient and effective estimation of the model parameters, leading to more precise and reliable conclusions about the effects of the factors under investigation.[34]

3.4 Stages of Experimental Design

Defining the Problem: Determining the research question and the purpose of the experiment. It should be defined which variables will be examined and which responses will be measured.[34]

Selection of Factors and Levels: The independent variables (factors) to be used in the experiment and the levels they will take are determined. The levels of factors can often be two or more.[34]

Creating the Experiment Plan: Taking into account the selected factors and levels, the appropriate experimental design is selected and the experiment plan is created. The experimental plan includes how and in what order the experiments will be performed.

Conduct of Experiments: Experiments are carried out according to the experimental plan and data are collected. It is important that experimental conditions are kept under control and data is recorded accurately.[30]

Analysis of Data: The collected data is analyzed using statistical methods. This analysis determines the effects and interactions of factors on the response variable.[28] Statistical software (e.g., Minitab, R, SAS) is frequently used in these analyses.

Interpretation and Reporting of Results: Analysis results are interpreted and results for the purpose of the experiment are reported. The overall validity of the findings and limitations of the experimental design are evaluated.[32]

Analysis of Variance (ANOVA): Used to determine the effects and interactions of factors on the response. ANOVA tests whether the differences between factors are significant.

Regression Analysis: It is used to model the relationship between the dependent variable and independent variables. This analysis allows the response variable to be expressed as a function of the independent variables.[31]

Analysis of Covariance (ANCOVA): Determines the effects of factors on the response by subtracting the effect of uncontrollable variables (covariates).

Response Surface Methodology (RSM): Provides optimization of the response variable using second-order polynomial models. This method helps determine optimal conditions, especially in complex systems.[34]

CHAPTER 4

MATERIALS AND METHODS

4.1. Materials

Altiris 550 was supplied as a coarse TiO_2 with augmented IR-reflectivity. $CoAl_2O_4$ pigments of 22-5600 and 22-10446 were purchased from Ferro GmbH, and $(Cr,Fe)_2O_3$ supplied from Sun Chemical. Sicopal L0095 as a Chromium iron oxide chemistry supplied from BASF. Monolite green was the only organic pigment (Cu-phthalocyanine) supplied from Heubach GmbH to give green shade to the let-down formulae shows in Figure 4.1.

The pigments mentioned above have been added to the paint formulations of RAL 9010, RAL 7021 and RAL 9011 colors in order to provide maximum reflectivity when exposed to infrared light for a certain period of time.

Figure 4.1. Pigments in powder form (left to right Altiris 550, Ferro 22-5600, Ferro 22-10446, Sicopal L0095, Monolite Green 600734).

4.2. Experimental Setup

Acrylic pigment dispersions were realized using a disperser (Das 200, Lau GmbH, Albershausen, Germany) with the presence of 1.4 - 1.6 mm zirconia grinding beads as shown ii Figure 4.2. Let-downs were formulated with certain dispersions aiming to match desired colors. Particle size distribution of CICPs was analyzed after several grinding durations using laser diffraction equipment (Malvern Mastersizer 3000, Worcestershire, UK). All let-down formulations were weighed into 1kg jars. The particle size distribution and shaker times of the pigments dispersed for a certain period of time are shown in Table 4.1.

Table 4.1. Particle size distribution of pigments after grinding at certain period of times

Pigments	Shaker Time(min)	Dx 10(μm)	Dx 50(μm)	Dx 90(μm)	Dx 99(μm)	Dx 100(μm)
Altiris 550	60	0.43	0.75	1.39	2.80	2.74
Ferro 22-5600	30	1.45	2.45	4.16	5.54	6.57
Ferro 22-10446	30	0.02	0.11	1.00	5.80	11.10
Sicopal L0095	120	0.55	1.29	2.80	4.34	5.80
Monolite Green	300	0.26	0.44	0.74	1.15	2.13

Figure 4.2. DAS 200 Pigment Disperser

Let-downs were then mixed with aliphatic polyisocyanate to give an NCO/OH molar ratio of 1.1 and applied onto steel plates, precoated with an epoxy primer via an automatic spray robot as shown in Figure 4.3. (RX20-D, Amsterdam, Netherlands). Coated color panels were finally cured at 80°C for half an hour after 15 minutes of flash-off time.

Figure 4. 3.RX20-D, Automatic Spray Robot

The cured panels were evaluated in terms of IR-reflectivity, TSR, color, gloss, haze, and distinctness of image (DoI). UV-Vis-NIR spectroscopy (Shimadzu UV-3600i Plus, Kyoto, Japan) was applied to reveal the percent reflectance of topcoats in the UV-Vis-NIR spectrum and TSR values. Color measurements were performed using visible spectroscopy (X-Rite Color i5, Regensdorf, Switzerland) together with Color iQC software. Specular gloss was measured with a glossmeter (BYK micro-TRI-gloss, Wesel, Germany), whereas haze and DoI were recorded with a goniophotometers shows in Figure 4.4 (Rhopoint IQ, East Sussex, UK).

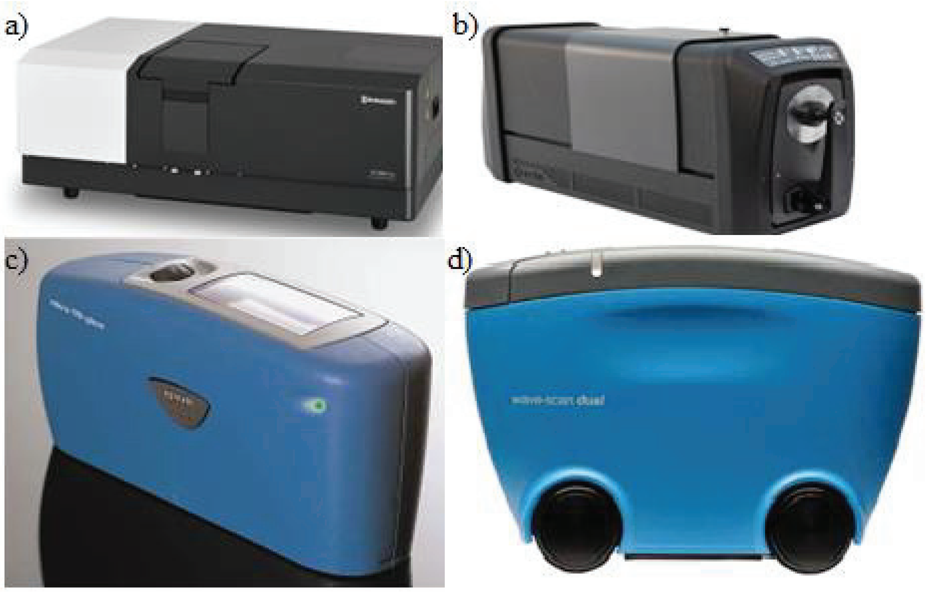

Figure 4. 4.(a) Spectrophotometer used for visible and infrared region reflectance measurement (b) X-rite ci7800 spectrophotometer with color measurement c) BYK-Mac Micro Tri Gloss, which measures the gloss value on the surface of the panels (d) Wavescan device

The temperature test setup is shown in Figure 4.5. The panels sprayed with the RX20D automatic spray robot were exposed to heat with the IRT Model 4-1 PCD brand IR Heater. Temperature measurements were taken from the surface temperatures of the panels with an IR thermometer at the specified times.

Figure 4. 5. IRT Model 4-1 PCD IR Heater

4.3. Determining the Factors and Parameters of the Experiment

Pigmentation and film thickness were determined as parameters in the thesis concept . The concept of pigmentation is a corporate culture formed at Kansai Altan Boya Sanayi. It is associated with the amount of pigment powder loaded into the formulas. Different pigmentation levels are determined for each pigment. These levels are based on the average applied film thickness of a particular resin system. For example, the system in which the work was done is a two-component acrylic system. The average application film thickness of this system is around 35-40 microns. In this film thickness, the optimum amount of pigment loaded and the desired covering levels are adjusted to be neither too much nor too little. After determining the optimum amount of loaded pigment powder for each pigment, it is simplified to a single coefficient, called the pigmentation level. The term film thickness refers to the thickness of the thin film layer formed on the panel surface and its unit is micron.

As a first response, temperature measurements were taken with an IR gun from the surfaces of the panels applied with different pigmentation level and film thicknesses, which was the main purpose of the study, once a minute for a total of 10 minutes. The difference between the measurements taken at t=0 and t=10 is presented in the table. It is aimed to minimize the temperature difference between the initial state and the final state. The rub-out test, which is one of the methods used to determine the stability of the paint formulation, was chosen as the second response. While performing the rub-out test, wet paint at certain film thicknesses was applied to a glass surface with the help of an applicator. A specific area of the surface was distorted with a hand movement in a way that did not reveal the lower layer, then the color difference between the unrubbed area and the rubbed area was measured. The color difference measurements between these two different areas taken with the same wet paint were taken.It is aimed to minimize the measured dE value. Pigmentation and film thickness levels, determined to increase linearly, were applied on the epoxy primer in fourty two different studies.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 The Comparison Between Formulas Designed with Traditional Pigments and IR Reflective Pigments

In the first step of the study, RAL 9010, 7021 and 9011 colors were matched using conventional pigments. After that, the same color matching studies were carried out using innovative IR reflective pigments. Subsequently, surface temperature values of conventional and innovative formulas were measured under a certain period of time and the difference between them is presented in the Table 5.1.

Table 5.1. The measurement results obtained from painted panel surfaces subjected to temperature testing.

Time, (minute)	**Conventional RAL 9011(C°)**	**IR Reflective RAL 9011(C°)**	**Conventional RAL 7021(C°)**	**IR Reflective RAL 7021(C°)**	**Conventional RAL 9010(C°)**	**IR Reflective RAL 9010(C°)**
0	25.00	25.00	25.00	25.00	25.00	25.00
2	53.46	43.10	46.44	37.06	35.76	31.99
4	68.60	52.87	56.72	42,75	41.09	35.54
6	75.41	56.23	62.94	47.55	43.55	37.84
8	78.96	57.76	64.03	49.12	45.18	38.89
10	79.57	59.48	64.13	49.90	45.39	39.56

According to Table 5.1, especially for RAL 9011 and RAL 7021, serious differences in reducing the surface temperature were observed compared to formulas designed with conventional pigments. Due to the RAL 9010 formula structure, white pigment is used as the main component. White conventional pigments are naturally very high in IR reflectance, but when designed with IR reflective white pigment, the results are improved.

The percent reflectance values in the infrared region of the panels applied with the traditional and innovative topcoat are illustrated in Figure 5.1.

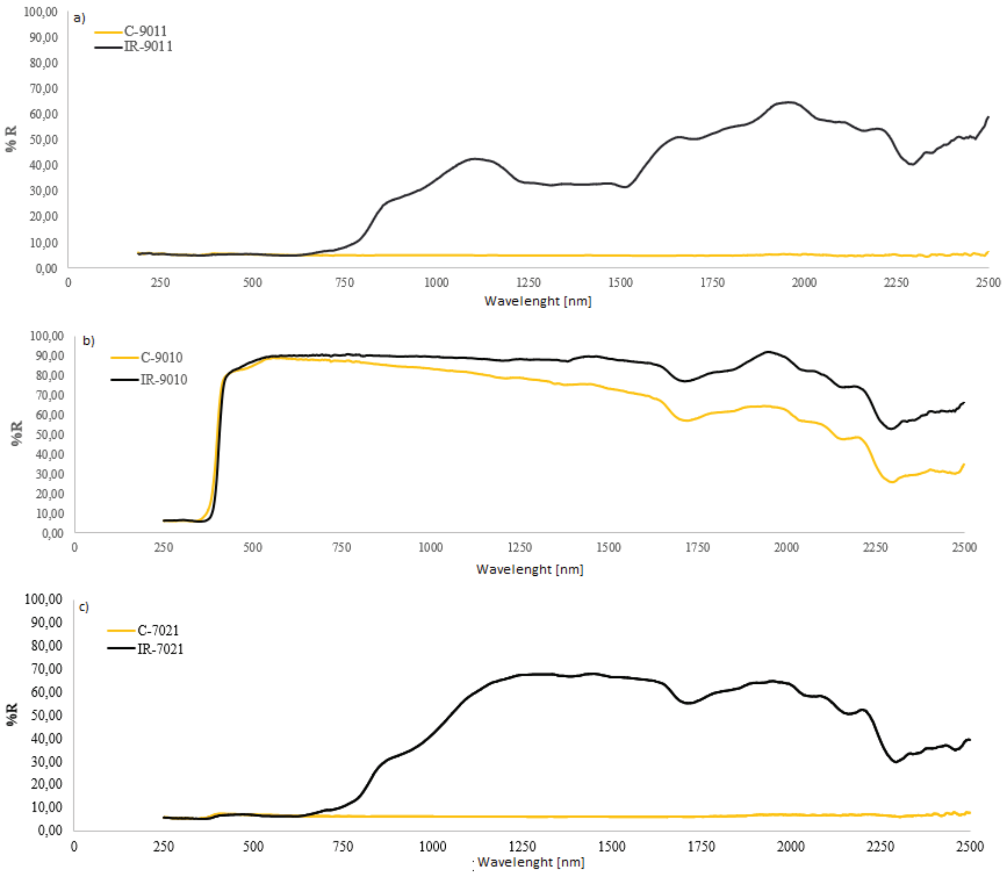

Figure 5.1.Percent Reflection Values in the Infrared Region of Topcoats Formulated with Conventional and Traditional Pigments

Table 5.2 shows the color differences of the traditional (shown with the prefix C-) and innovative (shown with the prefix I-) coatings.

Table 5.2. Surface and Color Properties of Topcoats Formulated with Traditional and Innovative Pigments

Color Formulations	**RGB Images**	**L***	**a***	**b***	**dL***	**da***	**db***	**dE**	**Dry Film Thickness (µm)**
C- 9011		27.61	-0.09	-0.99					30-35
I-9011		27.17	-0.13	-0.89	0.08	-0.06	0.05	0.11	30-35
C-9010		93.97	-1.06	6.67					55-60
I-9010		94.34	-1.09	6.52	0.36	-0.03	-0.15	0.39	55-60
C-7021		31.29	-0.41	-1.64					40-45
I-7021		30.78	-0.12	-1.44	-0.51	0.29	0.2	0.48	40-45

The results obtained from the formulas designed with IR reflective pigments have been found to be quite promising. After this stage, formulation parameters were examined and studies were carried out to optimize them. Altiris 550, 22-5600, 22-10446, Sicopal L0095, Monolite green pigments dispersed in the binder-solvent environment with a shaker were added to the paint formulations at certain concentrations after the grinding process, particle size of pigments were found to be appropriate. The formulation of each fourty-two applied panels was designed to be dE<0.50 for the RAL colors.

Experimental results obtained for RAL 9010, 7021 and 9011 were analyzed as three different data sets. This is because the pigment types used in the three different colors differ from each other. For example, as mentioned before, the IR reflectance of conventional white pigments is good under normal conditions, while black pigments tend to absorb almost all of the light. Therefore, comparing different colors did not reveal any meaningful results. It can only be revealed which one gives better results in terms of IR reflective feature.

5.2. Analysis of Experimental Result of RAL Colors by Design of Experiment

5.2.1 Color Matching Study and Experimental Results for RAL 9010

Color matching study for RAL 9010 was done with dE<0.50, all work was done in a two-component acrylic system. The amounts of pigment powder and Color Index numbers used for color matching study are listed in Table 5.3. Visual evaluation of the study was done in the Byk Spectra Light Booth in Figure 5.2.

Table 5.3. Color Index and Pigment Chemistry for RAL 9010

Color Index (CI)	Pigment Chemistry
Pigment White 6- Altris 550	Titanium Dioxide
Pigment Yellow 42	Iron Oxide
Pigment Yellow 184	Bismuth Vanadate

The results of the studies carried out according to the design matrix created with the parameters and responses determined for the RAL 9010 color are shown in Table 5.4. In the study, a significant relationship was tried to be established and modelled between the parameters determined as pigmentation and film thickness and the temperature test and rub-out results. MS Excel was used to create regression graphs. Following this, Minitab statistical software (Minitab 16 Statistical Software. Minitab, Inc., State College, PA) was used for the Design of Experiment method used in the data analysis obtained from the experimental result.

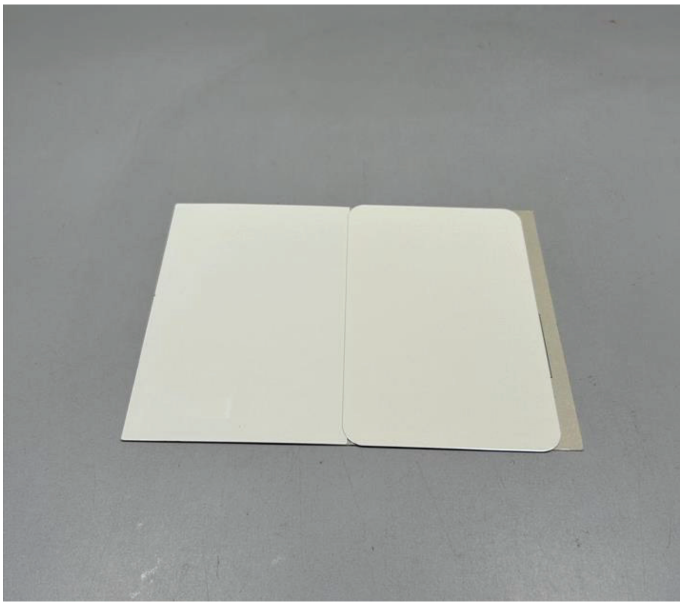

Figure 5.2. Color matching study of RAL 9010 (Left one is conventional RAL 9010, right one is color matching study with IR reflective pigments)

Table 5.4. Experimental Design for RAL 9010

Sample	**Pigmentation**	**Dry film thickness, [µm]**	**ΔTemperature, [°C]**	**Rub-Out[ΔE]**
RAL 9010	0.80	40.00	29.90	0.48
	0.80	50.00	29.00	0.47
	0.80	60.00	28.20	0.44
	1.00	40.00	26.70	0.38
	1.00	50.00	22.70	0.42
	1.00	50.00	22.80	0.43
	1.00	50.00	22.80	0.45
	1.00	50.00	22.70	0.44
	1.00	50.00	22.90	0.43
	1.00	50.00	23.10	0.42
	1.00	60.00	20.40	0.47
	1.20	40.00	30.90	0.52
	1.20	50.00	28.10	0.53
	1.20	60.00	24.50	0.50

After determining the parameter selections according to the preliminary study results, three different levels were determined for pigmentation and dry film thickness. nine studies were planned with three levels and two factors. The midpoint of the experimental design matrix was 1.00 pigmentation and 50.00 micron dry film thickness degrees of freedom and was repeated 6 times to increase the repeatability of the experiment. Therefore, fourteen studies were performed. Equation 1 represents a second-order (quadratic) regression model, which is used to describe the relationship between a dependent variable (y) and one or more independent variables (x_1 and x_2) through both linear and quadratic terms. Such models extend beyond linear regression by capturing more complex relationships for three RAL colors which are the RAL 9010, RAL 7021 and RAL 9011.

- $y = b_0 + b_1 \cdot x_1 + b_2 \cdot x^2 + b_{11} \cdot x_{12} + b_{22} \cdot x_2^2 + b_{12} \cdot x1 \cdot x2$ (1)

  - y is the dependent variable
  - b_0 is the intercept of the model
  - b_1 and b_2 are the linear coefficients for the independent variables x_1 and x_2, respectively.
  - b_{11} and b_{22} are the quadratic coefficients for x_1 and x_2
  - b_{12} is the coefficient for the interaction term between x_1 and x_2

Figure 5.3. represents the regression graph showing actual vs predicted Δtemperature values. The R^2 value is 0.9768, which means that approximately 97.68% of the variability in predicted Δtemperature can be explained by actual Δtemperature. This high R^2 value indicates that the model fits the data very well. The scatter plot shows that most data points are close to the regression line, indicating that the model predictions are generally accurate. However, there are a few points that deviate slightly from the line and indicate minor prediction errors. One of the main reasons for these errors may be that the surface Δtemperature test is a non-standardized and error-prone method.

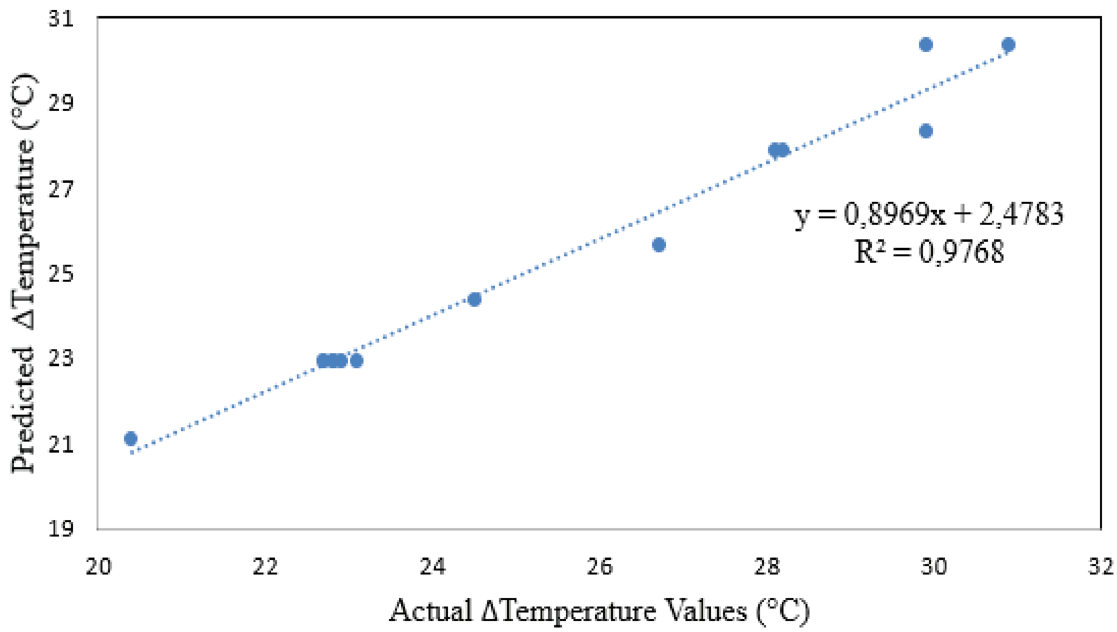

Figure 5.3. Regression Plot of ΔTemperature (°C) for RAL 9010

Figure 5.4. represents the regression graph showing actual vs predicted Rub-out values. The R^2 value is 0.8117, which means that approximately 81.17% of the variability in the predicted rub-out value can be explained by the actual rub-out value. This relatively high R^2 value indicates a good fit of the model to the data, though it is not as strong as the previous Δtemperature prediction model. The scatter plot shows that while many data points lie close to the regression line, there is more scatter compared to the Δtemperature prediction graph. This indicates that there are some prediction errors, and the model may not be as accurate for some data points. One of the main reasons for this can be explained by the margin of error between measurements of spectrophotometry, which measures the color difference between the rubbed and non-rubbed area.

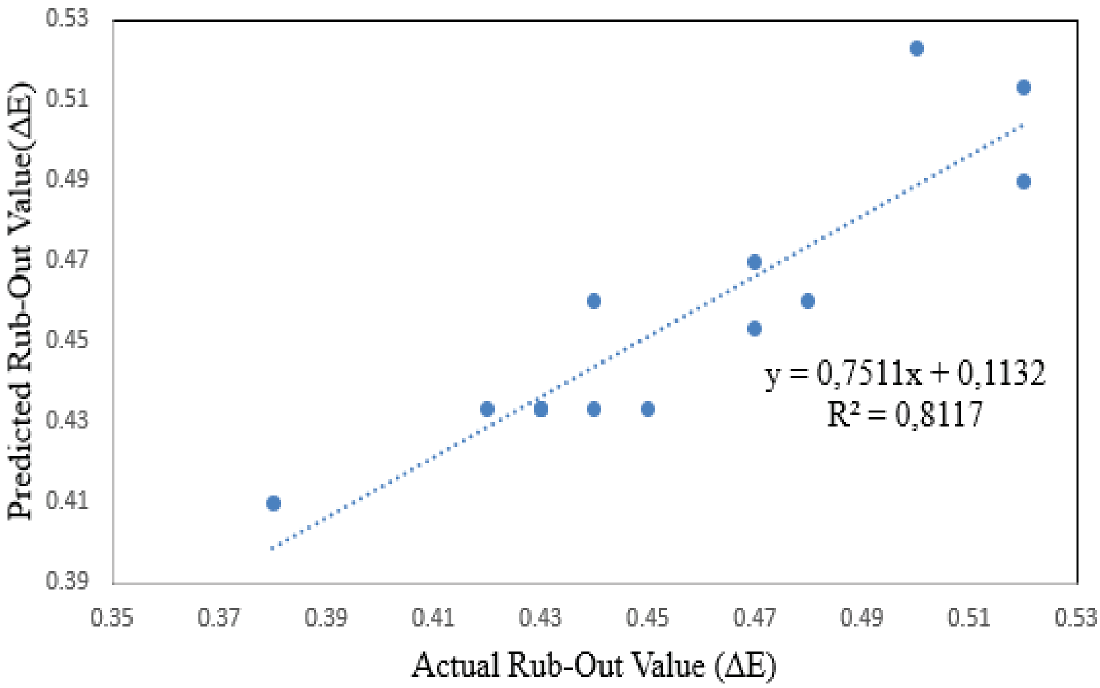

Figure 5.4. Regression Plot of Rub-Out (ΔE) for RAL 9010

Table 5.5. shows that analysis of variance results of ΔTemperature for RAL 9010. All factors and their interaction was determined in %95 confidence level which means that if the p value<=0,05, the factors are significant on dependent variable. . Based on the table 5.5, the model is highly significant overall, indicating that the independent variables collectively explain a significant portion of the variance in the dependent variable. Pigmentation has a significant effect on the dependent variable. This indicates that the effect of pigmentation on the response variable is statistically significant. Dry film thickness has a very strong and significant effect on the dependent variable, explaining a large portion of the variance. The quadratic term for pigmentation has a very strong and significant effect on the dependent variable. This indicates that the quadratic effect of pigmentation is important in explaining changes in the response variable. The quadratic term for dry film thickness does not have a significant effect on the dependent variable. This suggests that the linear effect of dry film thickness is sufficient, and the quadratic term does not provide additional explanatory power. The interaction between pigmentation and dry film thickness has a significant effect on the dependent variable. This indicates that these two variables work together to have a significant impact on the response variable.

Table 5.5. Analysis of Variance Results of ΔTemperature for RAL 9010

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	143.243	143.243	286.485	94.33	<0.001
Linear	2	36.72	36.72	183.6	60.46	<0.001
Pigmentation	1	2.16	2.16	21.6	7.11	0.028
Dry film thickness, μm	1	34.56	34.56	345.6	113	<0.001
Square	2	101	101	505	166.29	<0.001
Pigmentation*Pigmentation	1	100.75	79.5	795	261.78	<0.001
Dry film thickness, μm*Dry film thickness, μm	1	0.25	0.5	0.5	1.64	0.391
Interaction	1	5.522	5.522	55.225	18.18	0.003
Pigmentation*Dry film thickness, μm	1	5.522	5.522	55.225	18.18	0.003
Residual Error	8	2.43	2.43	0.3037		
Lack-of-Fit	3	2.316	2.316	0.7721	34.06	<0.001
Pure Error	5	0.113	0.113	0.0227		
Total	13	145.672				

Table 5.6 shows Analysis of Variance Result of Rub-Out (ΔE) for RAL 9010. The model is highly significant overall, indicating that the independent variables collectively explain a significant portion of the variance in the dependent variable. Pigmentation has a significant effect on the dependent variable. This indicates that the effect of pigmentation on the response variable is statistically significant. Dry film thickness has a very strong and significant effect on the dependent variable, explaining a large portion of the variance. The quadratic term for pigmentation has a very strong and significant effect on the dependent variable. This indicates that the quadratic effect of pigmentation is important in explaining changes in the response variable. The quadratic term for dry film thickness does not have a significant effect on the dependent variable. This suggests that the linear effect of dry film thickness is sufficient, and the quadratic term does not provide

additional explanatory power. The interaction between pigmentation and dry film thickness has a significant effect on the dependent variable. This indicates that these two variables work together to have a significant impact on the response variable.

Table 5.6. Analysis of Variance Result of Rub-Out (ΔE) for RAL 9010

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	25.0718	25.0719	5.0144	7.71	0.006
Linear	2	22.9417	22.9417	11.4708	17.64	< 0.001
Pigmentation	1	7.26	7.26	7.26	11.16	< 0.001
Dry film thickness, µm	1	15.6817	15.6817	15.6817	24.11	< 0.001
Square	2	2.1202	2.1202	1.0601	1.63	0.255
Pigmentation*Pigmentation	1	0.801	1.6696	1.6696	2.57	0.148
Dry film thickness, µm*Dry film thickness, µm	1	1.3192	1.3192	1.3192	2.03	0.192
Interaction	1	0.01	0.01	0.01	0.02	0.904
Pigmentation*Dry film thickness, µm	1	0.01	0.01	0.01	0.02	0.904
Residual Error	8	5.2025	5.2025	0.6503		
Lack-of-Fit	3	5.1341	5.1341	1.7114	125.22	0
Pure Error	5	0.0683	0.0683	0.0137		
Total	13	30.2743				

Figure 5.5. shows the residual analysis graphs created for Δtemperature (°C). The purpose of residual analysis is to check the accuracy of the model and the validity of its assumptions. In this analysis, normal probability plot, residual versus fits, histogram and residual versus order plots were used. When the normal probability plot is examined, it is observed that the standardized residuals follow a normal distribution. Most of the points are aligned at a 45-degree angle, close to the curve, but some points fall outside this trend line. This shows that some observations are valid from the model. Residual vs. Looking

at the fits graph, it shows that the residuals are normally distributed and that the residuals are homogeneous and independent. However, some points are found to be extremely deviated. It has been commented that this may reduce the predictive performance of the model. According to the histogram chart, most of the residuals are close to the average and extreme values are very rare. In this context, the comment that it is suitable for normal distribution is made very clearly. According to the residual vs order plot, it is observed that there is no independence and autocorrelation for time in the model. The absence of a specific trend or pattern is an indicator of the performance of the model and its suitability for normal distribution.

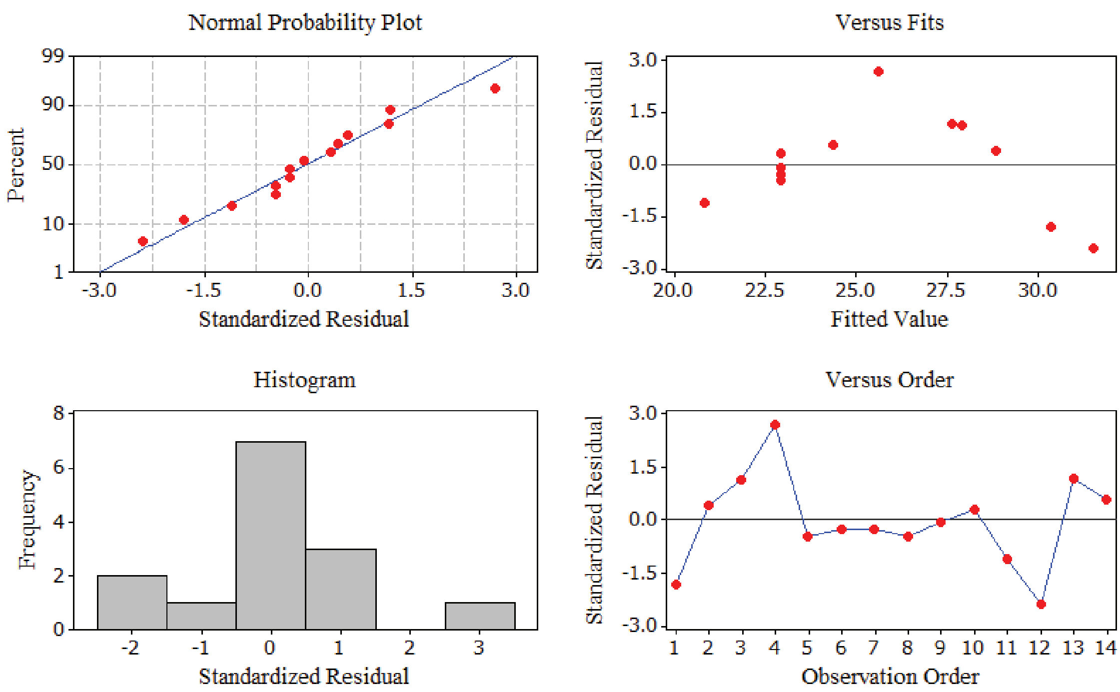

Figure 5.5. .Residual Plots for ΔTemperature °C

In Figure 5.6, residual analysis was performed for the Rub-Out parameter. Model assumptions were verified, and its performance was analyzed. Since similar behaviors are exhibited with the Figure 5.5, detailed explanation is not given. Briefly, when four different graphs were examined, some points deviating from the model were detected, but when evaluated in general, it was determined that the normal distribution was appropriate.

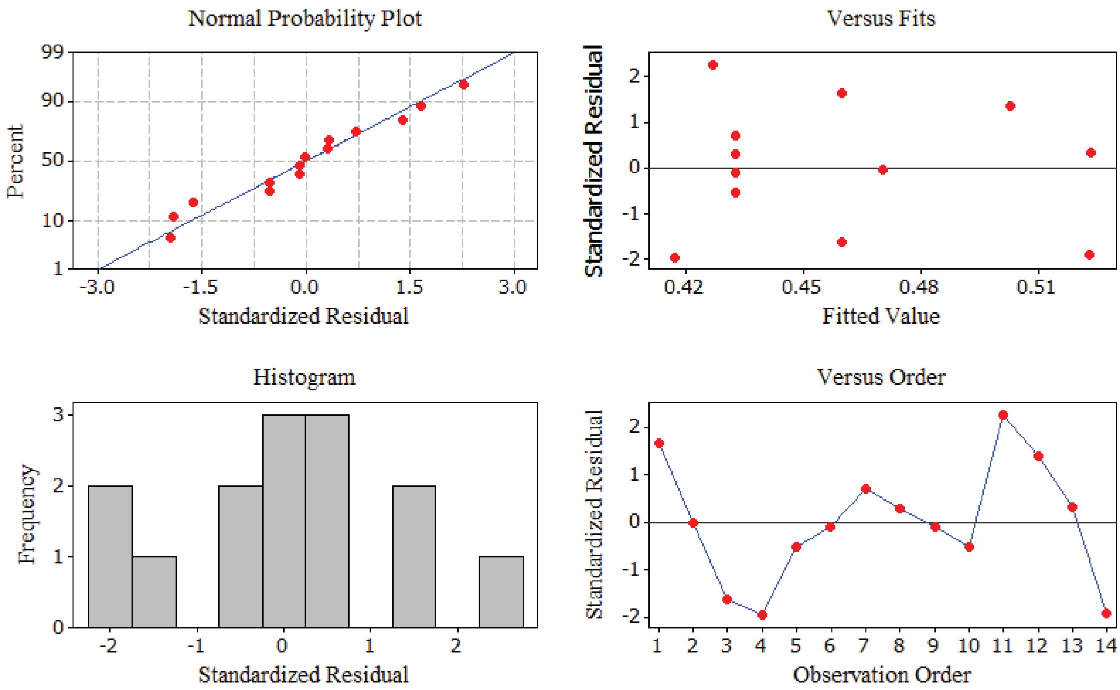

Figure 5.6. Residual Plots for Rub-Out

In Figure 5.7. the relationship between Δtemperature, dry film thickness and pigmentation is examined. The slope and shape of the graph surface reveal the interaction between the three different variables mentioned. To comprehend and interpret the Δtemperature change with dry film thickness and pigmentation, it is necessary to examine the surface of the graph. The Δtemperature reaches its maximum at low pigmentation and low dry film thickness levels. It is observed that the increase in pigmentation level causes a decrease in Δtemperature value. Likewise, it is interpreted that the increase in dry film thickness is a Δtemperature-lowering factor. In general, the increase in pigmentation and dry film thickness plays an important role in the change in Δtemperature.

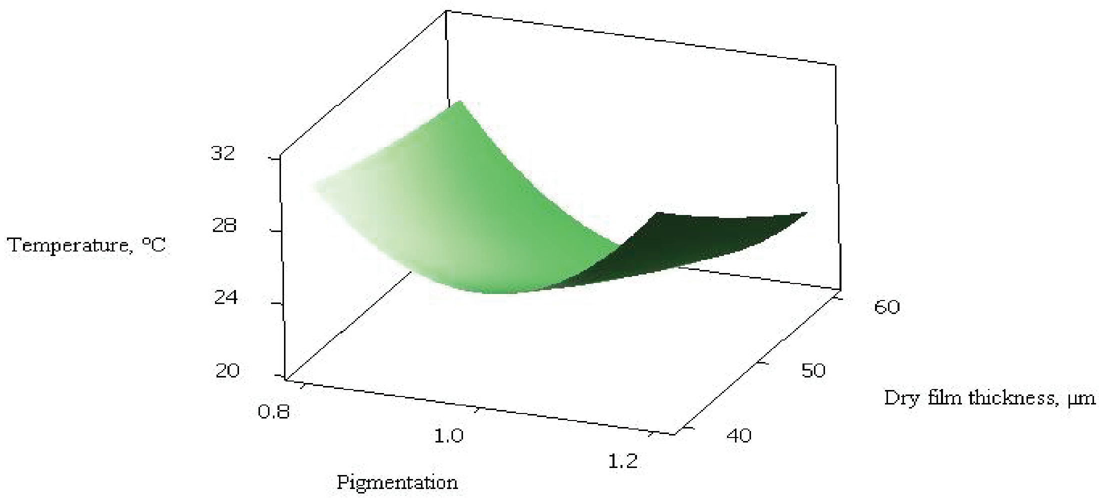

Figure 5.7. 3D Surface Plot of ΔTemperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

Figure 5.8 shows the interaction between rub-out, dry film thickness, and pigmentation and its results with a three-dimensional surface graphic. According to the chart, rub-out values vary between 0.40 and 0.52. The surface's slope indicates the variation in rub-out value at specific levels of pigmentation and dry film thickness. As the level of pigmentation increases, there is a corresponding drop in the rub-out value. It is interpreted that the increase in dry film thickness is directly related to the rub-out result. Especially at low pigmentation levels, increasing dry film thickness increases the rub-out value. In summary, when a low rub-out value is expected, film thickness should be kept low and pigmentation should be kept high.

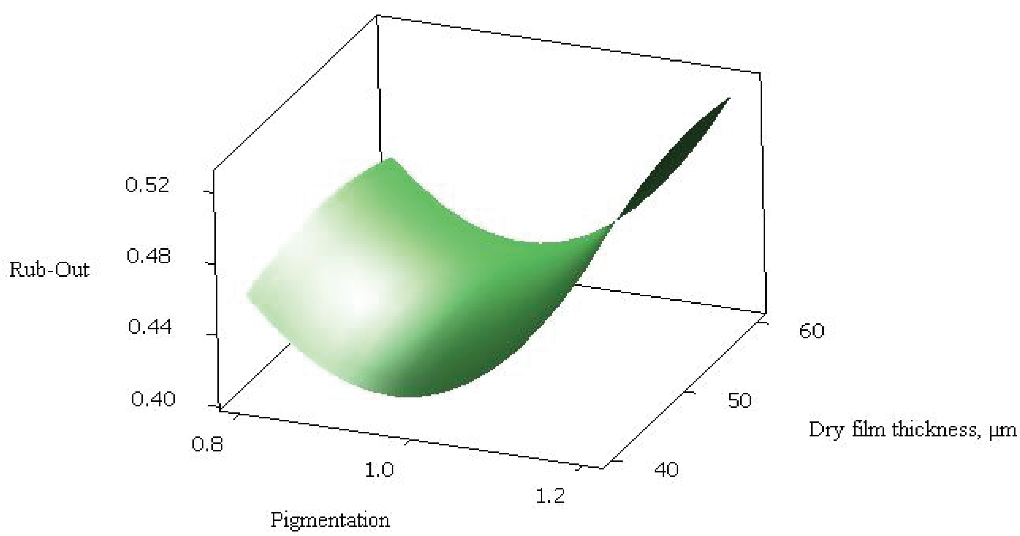

Figure 5.8. 3D Surface Plot of Rub-Out vs. Dry Film Thickness (µm) and Pigmentation

Figure 5.9 examines the relationships between Δtemperature, pigmentation, and dry film thickness using a two-dimensional counter plot. ΔTemperature levels are indicated by contour lines of different colors. The Δtemperature value varies between 21 and 31 degrees. The lowest Δtemperature value is expressed in dark blue, and the highest Δtemperature value is expressed in dark green. A decrease in Δtemperature value was observed with an increase in pigmentation. It was inferred that the increase in dry film thickness caused a significant decrease in the Δtemperature value. Especially when the pigmentation is 0.80, a decrease in Δtemperature value is observed with increasing film thickness. When the Δtemperature is at the minimum level, pigmentation is 1.00, and the dry film thickness is 60 microns.

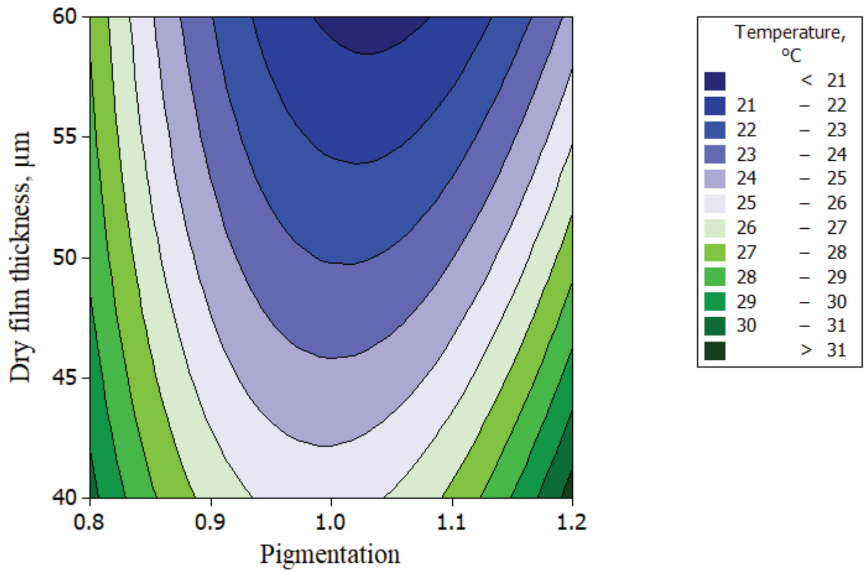

Figure 5.9. Contour Plot of ΔTemperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

Figure 5.10 presents an analysis of the relationship between Rub-Out, dry film thickness, and pigmentation using a two-dimensional counter plot. The chart uses several colors to denote rub-out values. The range of rub-out values is from 0.42 to 0.52. Dark blue represents the minimum value, while green represents the maximum value. An evident reduction in the erasure value was noted as the pigmentation level increased. Particularly when the pigmentation is at level 1, the rub-out value has reached its minimum threshold. The relationship between an increase in dry film thickness and an increase in rub-out value is implied. Nevertheless, the extent of this rise fluctuates according to the level of pigmentation. When the pigmentation is set to 1 and the dry film thickness is 40 microns, the rub-out value reaches its minimum.

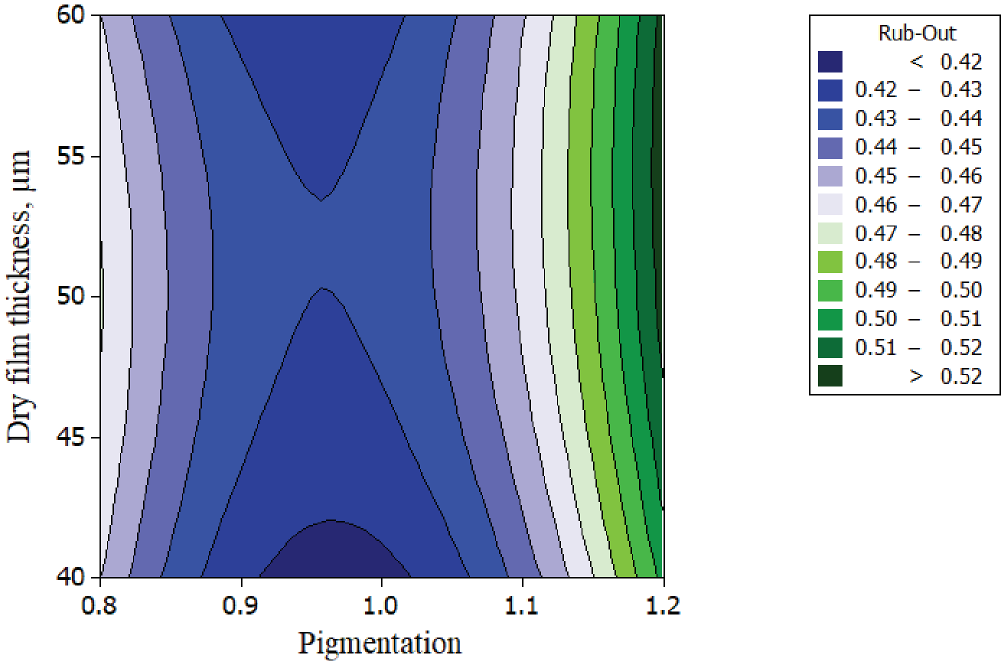

Figure 5.10. Contour Plot of Rub-Out vs. Dry Film Thickness (µm) and Pigmentation

Figure 5.11 presents a graph that requires the simultaneous examination of two distinct sets of variables: Δtemperature and rub-out. The statement illustrates the variations in Δtemperature and rub-out outcomes based on pigmentation and film thickness. Examining Δtemperature and rub-out values simultaneously is crucial as they provide significant indications. The grey portions in the graph indicate areas that lie outside specific combinations. The Δtemperature contours were primarily found in areas with little pigmentation and low film thickness. In contrast, the Rub-out contours were identified as locations where pigmentation and dry film thickness were concentrated.

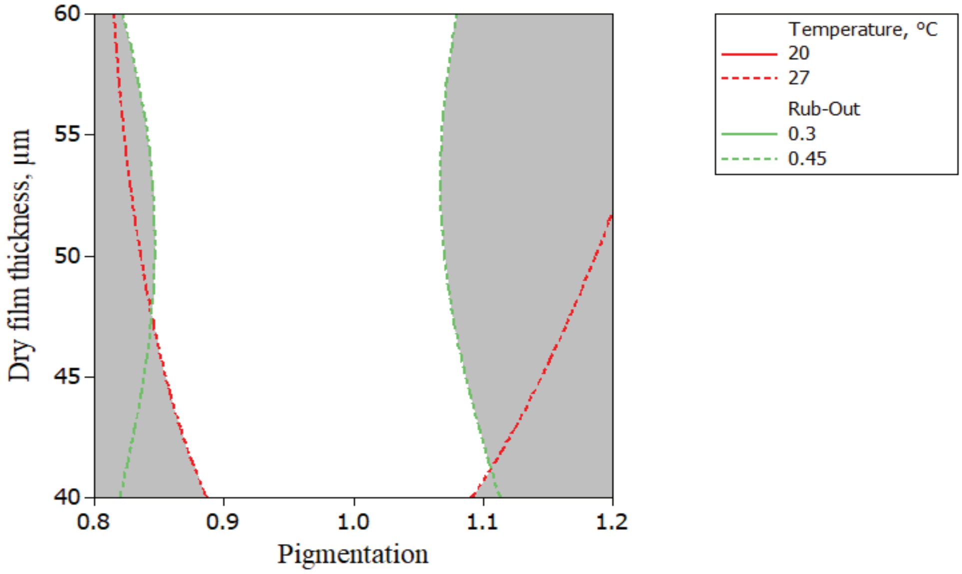

Figure 5.11. Contour Plot of Temperature, °C and Rub-Out

The optimization plot shown in Figure 5.12 is utilized to ascertain the most favourable conditions by examining the impacts of pigmentation and dry film thickness parameters on Δtemperature and rub-out. The optimal conditions are identified and achieved at a pigmentation level of 1.03 and a thickness of 59.72 microns.

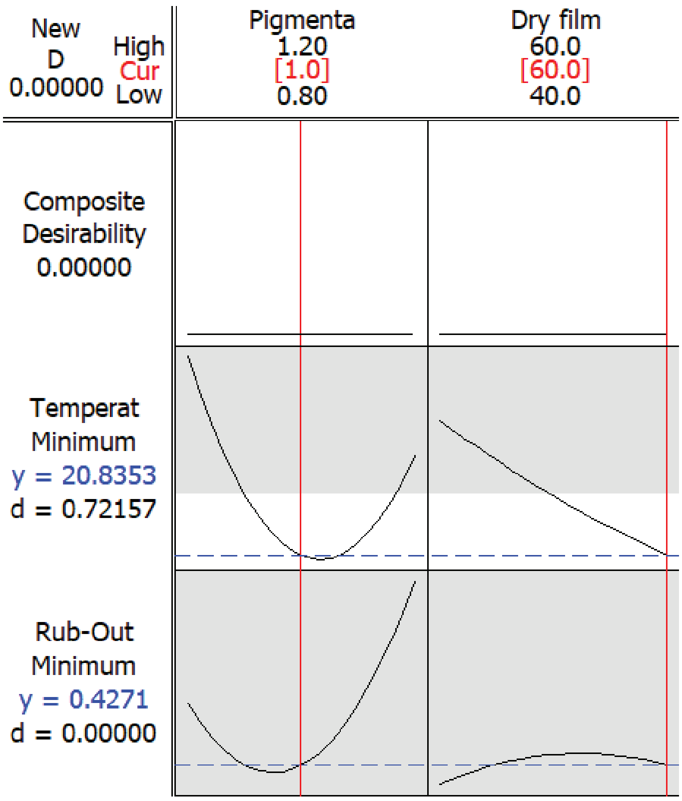

Figure 5.12. Pigmentation and dry film thickness optimization plot of RAL 9010

5.2.2 Color Matching Study and Experimental Results for RAL 7021

Color matching study for RAL 7021 was done with dE<0.50, all work was done in a two-component acrylic system. The amounts of pigment powder and Color Index numbers used for color matching study are listed in Table 5.7. Visual evaluation of the study was done in the Byk Spectra Light Booth in Figure 5.13.

Table 5.7. Color Index and Pigment Chemistry for RAL 7021

Color Index (CI)	Pigment Chemistry
Pigment Brown 29- Sicopal Black L 0095	Chromium[III] and Iron Oxide
Pigment White 6- Altris 550	Titanium Dioxide
Pigment Violet 23	Dioxazine
Pigment Yellow 184	Bismuth Vanadate

The results of the studies carried out according to the design matrix created with the parameters and responses determined for the RAL 7021 color are shown in table 5.8. In the study, a significant relationship was tried to be established and modeled between the parameters determined as pigmentation and film thickness and the temperature test and rub-out results. MS Excel was used to create regression graphs. Following this, Minitab statistical software (Minitab 16 Statistical Software. Minitab, Inc., State College, PA) was used for the Design of Experiment method used in the data analysis obtained from the experimental result.

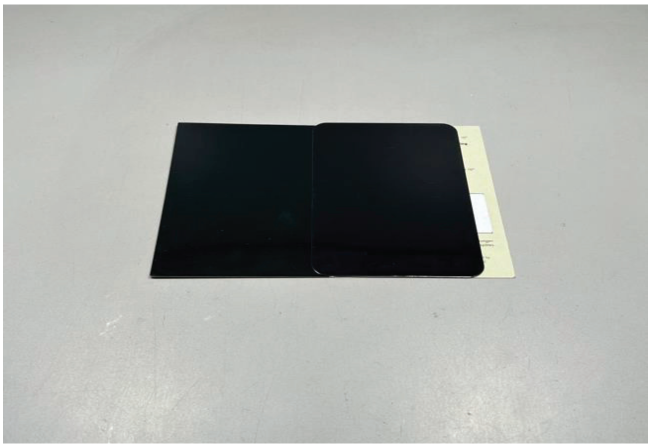

Figure 5. 13. Color matching study of RAL 7021 (Left one is conventional RAL 7021, right one is color matching study with IR reflective pigments)

Table 5.8. Experimental Design for RAL 7021

Sample	Pigmentation	Dry film thickness, [µm]	ΔTemperature, [°C]	Rub-Out[ΔE]
RAL 7021	0.80	40.00	37.30	0.44
	0.80	50.00	35.30	0.45
	0.80	60.00	33.10	0.44
	1.00	40.00	34.30	0.43
	1.00	50.00	33.80	0.45
	1.00	50.00	33.70	0.42
	1.00	50.00	33.70	0.38
	1.00	50.00	33.50	0.37
	1.00	50.00	33.80	0.39
	1.00	50.00	33.60	0.40
	1.00	60.00	32.80	0.41
	1.20	40.00	34.20	0.55
	1.20	50.00	34.70	0.60
	1.20	60.00	30.20	0.58

After determining the parameter selections according to the preliminary study results, three different levels were determined for pigmentation and dry film thickness. nine studies were planned with three levels and two factors. The midpoint of the experimental design matrix was 1.00 pigmentation and 50.00 micron dry film thickness degrees of freedom and was repeated six times to increase the repeatability of the experiment. Therefore, fourteen studies were performed as shown in Table 5.8.

Figure 5.14 represents the regression graph showing actual vs predicted Δtemperature values. the graph demonstrates that the model used to predict Δtemperature is quite accurate, with a strong correlation between the actual and predicted values. The R^2 value of 0.9208 indicates that the model explains a significant portion of the variability in the Δtemperature data, though there is still some room for improvement in prediction accuracy as RAL 9010.

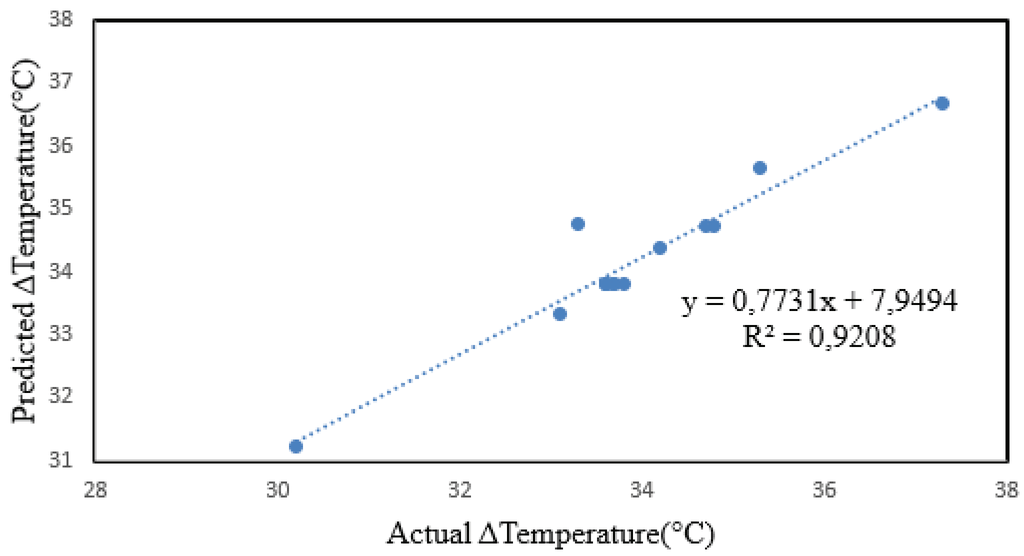

Figure 5.14. Regression Plot of ΔTemperature (°C) for RAL 7021

Figure 5.15. shows that the R^2 value is 0.9408, which means that approximately 94.08% of the variability in the predicted rub-out value can be explained by the actual rub-out value. This high R^2 value indicates a very good fit of the model to the data.The scatter plot shows that most data points lie close to the regression line, suggesting that the model predictions are generally accurate. However, there are a few points that deviate from the line, indicating some prediction errors as RAL 9010.

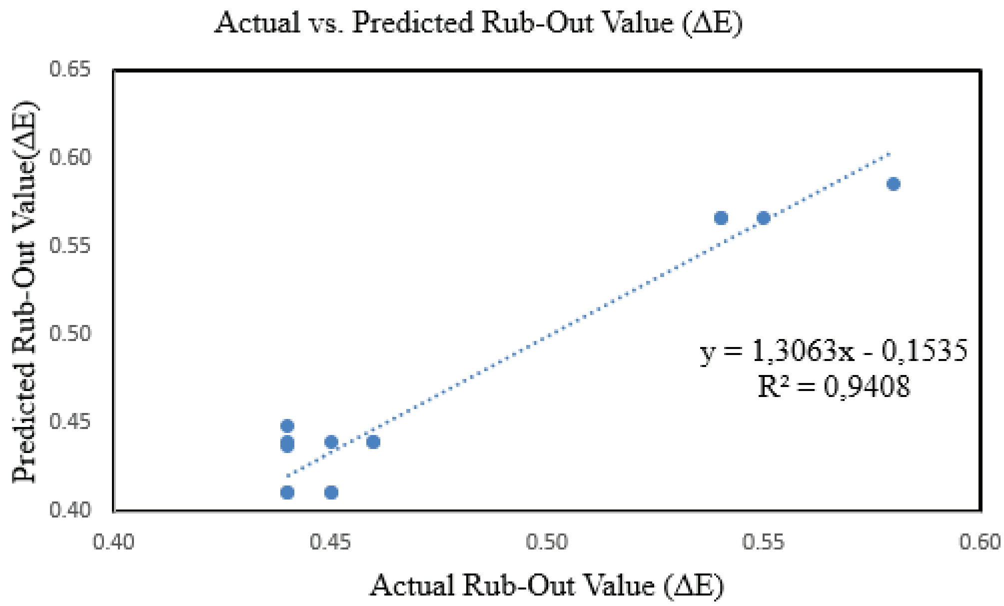

Figure 5.15. Regression Plot of Rub-Out (ΔE) for RAL 7021

In according to Table 5.9., the overall model is highly significant, indicating that the independent variables collectively explain a significant portion of the variance in the dependent variable.Pigmentation has a significant effect on the dependent variable. This indicates that the effect of pigmentation on the response variable is statistically significant.Dry film thickness has a very strong and significant effect on the dependent variable, explaining a large portion of the variance.The quadratic term for pigmentation does not have a significant effect on the dependent variable. This suggests that the quadratic effect of pigmentation is not important in explaining changes in the response variable.The quadratic term for dry film thickness does not have a significant effect on the dependent variable. This indicates that the quadratic term does not provide additional explanatory power beyond the linear effect.The interaction between pigmentation and dry film thickness does not have a significant effect on the dependent variable. This indicates that these two variables do not work together to significantly impact the response variable.

Table 5.9. Analysis of Variance Results of ΔTemperature for RAL 7021

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	25.0718	25.0719	5.0144	7.71	0.006
Linear	2	22.9417	22.9417	11.4708	17.64	< 0.001
Pigmentation	1	7.26	7.26	7.26	11.16	< 0.001
Dry film thickness, µm	1	15.6817	15.6817	15.6817	24.11	< 0.001
Square	2	2.1202	2.1202	1.0601	1.63	0.255
Pigmentation*Pigmentation	1	0.801	1.6696	1.6696	2.57	0.148
Dry film thickness, µm*Dry film thickness, µm	1	1.3192	1.3192	1.3192	2.03	0.192
Interaction	1	0.01	0.01	0.01	0.02	0.904
Pigmentation*Dry film thickness, µm	1	0.01	0.01	0.01	0.02	0.904
Residual Error	8	5.2025	5.2025	0.6503		
Lack-of-Fit	3	5.1341	5.1341	1.7114	125.22	0
Pure Error	5	0.0683	0.0683	0.0137		
Total	13	30.2743				

In Table 5.10, the overall model is highly significant, indicating that the independent variables collectively explain a significant portion of the variance in the dependent variable.Pigmentation has a significant effect on the dependent variable. This indicates that the effect of pigmentation on the response variable is statistically significant.Dry film thickness does not have a significant linear effect on the dependent variable. This suggests that the linear effect of dry film thickness is not sufficient to explain changes in the response variable.The quadratic term for pigmentation has a very strong and significant effect on the dependent variable. This indicates that the quadratic effect of pigmentation is important in explaining changes in the response variable.The quadratic term for dry film thickness does not have a significant effect on the dependent variable. This indicates that the quadratic term does not provide additional explanatory power beyond the linear effect.The interaction between pigmentation and dry film thickness does not have a significant effect on the dependent variable. This indicates that these two variables do not work together to significantly impact the response variable.

Table 5.10. Analysis of Variance Result of Rub-Out (ΔE) for RAL 7021

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	0.06382	0.06382	0.01276	16.8	< 0.001
Linear	2	0.02668	0.02668	0.01334	17.56	< 0.001
Pigmentation	1	0.02667	0.02667	0.02667	35.11	< 0.001
Dry film thickness, µm	1	1.7E-05	1.7E-05	1.7E-05	0.02	0.886
Square	2	0.03691	0.03691	0.01845	24.29	< 0.001
Pigmentation*Pigmentation	1	0.03691	0.03691	0.03691	40.43	< 0.001
Dry film thickness, µm*Dry film thickness, µm	1	2E-06	2E-06	2E-06	0	0.958
Interaction	1	0.00023	0.00023	0.00023	0.3	0.601
Pigmentation*Dry film thickness, µm	1	0.00023	0.00023	0.00023	0.3	0.601
Residual Error	8	0.00608	0.00608	0.00076		
Lack-of-Fit	3	0.00179	0.00179	0.0006	0.7	0.592
Pure Error	5	0.00428	0.00428	0.00086		
Total	13	0.06989				

Figure 5.16 shows the residual analysis graphs for Δtemperature (°C). The purpose of residual analysis is to check the accuracy of the model and the validity of its assumptions. In this analysis, normal probability plot, residual versus fits, histogram and residual versus order plots were used. Similar observations can be made as in Figure 5.5. When four different graphs are examined, it is interpreted that the data sets have a normal distribution. The only difference is that the prediction performance is lower than RAL 9010. The data set can be reviewed, or studies can be repeated on this issue.

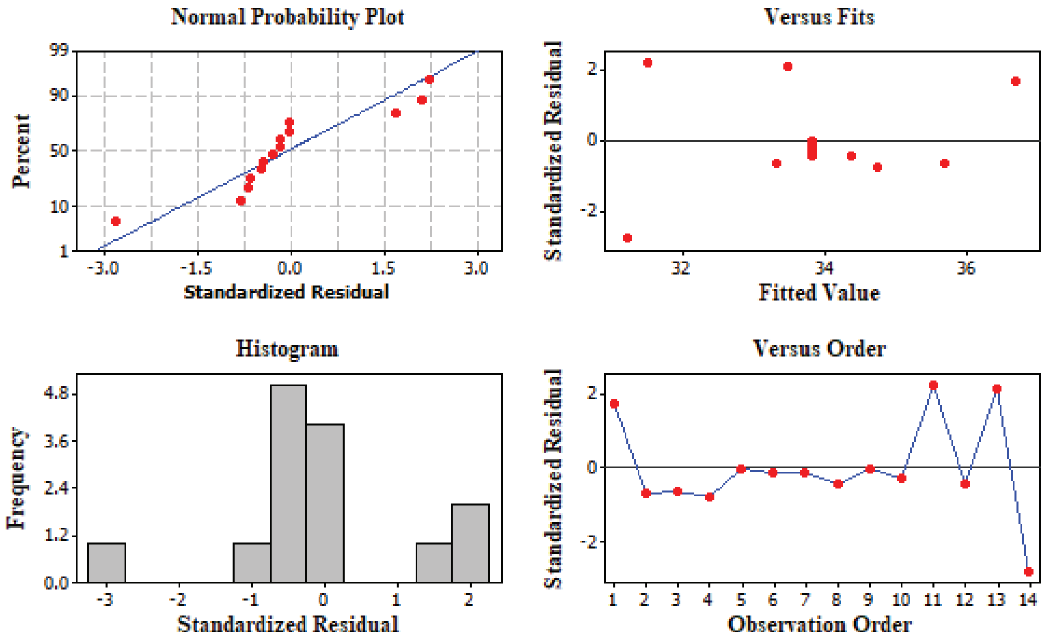

Figure 5.16. Residual Plots for ΔTemperature °C

In Figure 5.16, similar observations can be made as in Figure 5.5. When four different graphs are examined, it is interpreted that the data sets have a normal distribution.

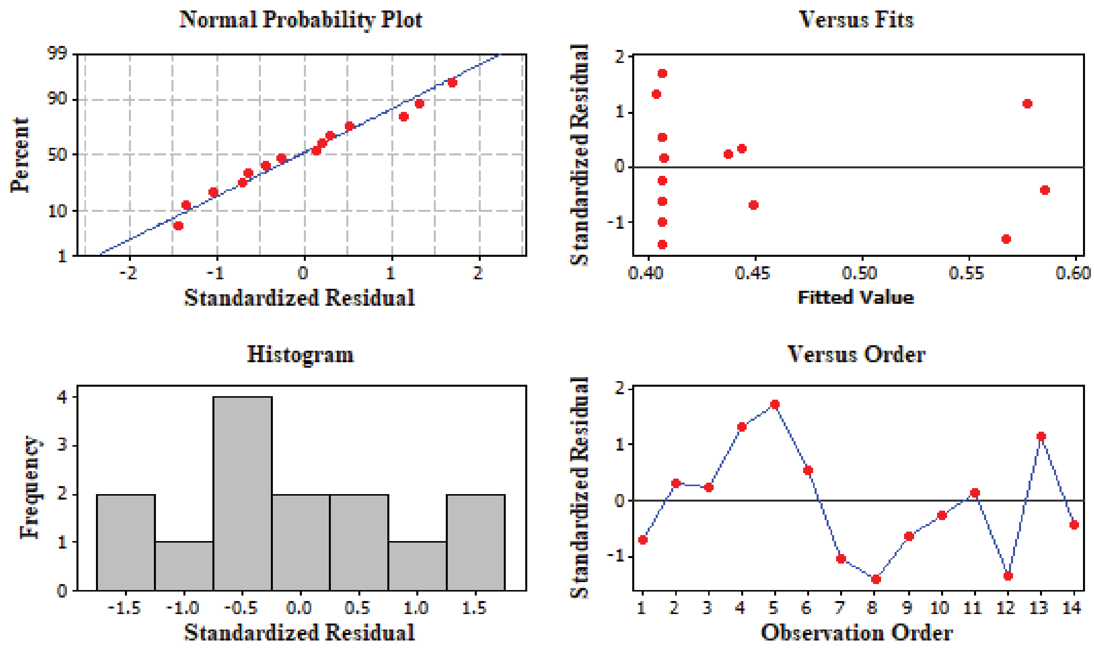

Figure 5.17. Residual Plots for Rub-Out (ΔE)

In Figure 5.18, the relationship between Δtemperature, dry film thickness and pigmentation is visualized with a 3D surface graph. As a result of the resulting graph, it was seen that the dry film thickness was stable at low pigmentation and Δtemperature. When high pigmentation and high Δtemperature levels are reached, dry film thickness tends to decrease. When the curvature of the surface in the graph is examined, it is interpreted that the relationship between Δtemperature, dry film thickness and pigmentation is not linear.

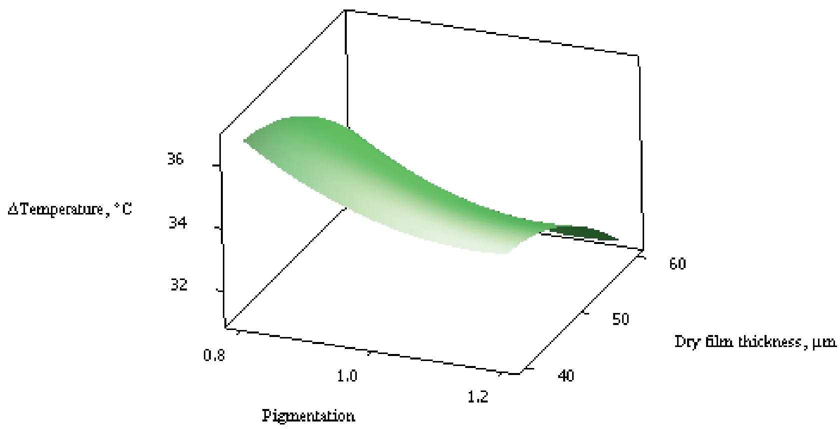

Figure 5. 18. 3D Surface Plot of ΔTemperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

In Figure 5.19, the interaction between Rub-out, pigmentation and dry film thickness is visualized with a 3D surface plot. Dry film thickness tends to decrease at low and high pigmentation levels. Based on this, it is interpreted that rub-out has a significant effect on dry film thickness. It is commented that the rub-out value is lowest at the point where the pigmentation level is approximately 1.0.

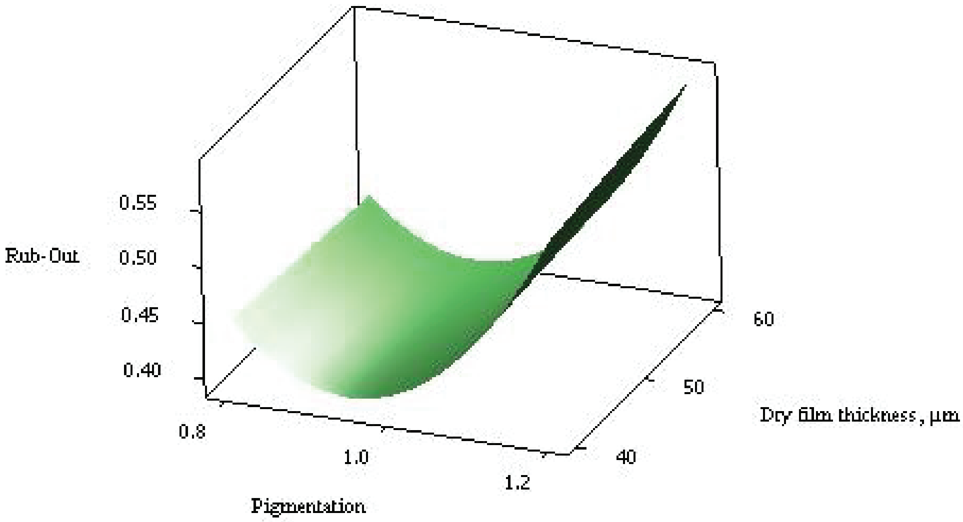

Figure 5.19. 3D Surface Plot of Rub-Out vs. Dry Film Thickness (µm) and Pigmentation

In Figure 5.20, Δtemperature values also decrease because of increasing film thickness at low and high pigmentation levels. At the points where the Δtemperature value drops to a minimum, pigmentation is at 1.20 and dry film thickness is at 60 microns. It is commented that increasing levels of pigmentation and dry film thickness have a significant impact on Δtemperature.

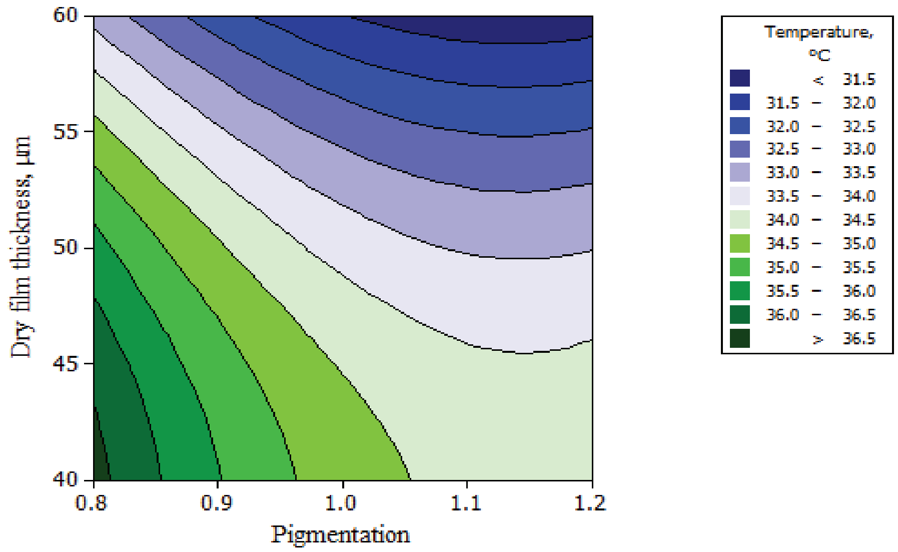

Figure 5.20. Contour Plot of ΔTemperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

Figure 5.21 shows that the rub-out value also increases with the increasing pigmentation level. It is observed that the contour levels in the graph are parallel. It is commented that the effect of pigmentation on rub-out is more pronounced than the effect of dry film thickness on the rub-out result.

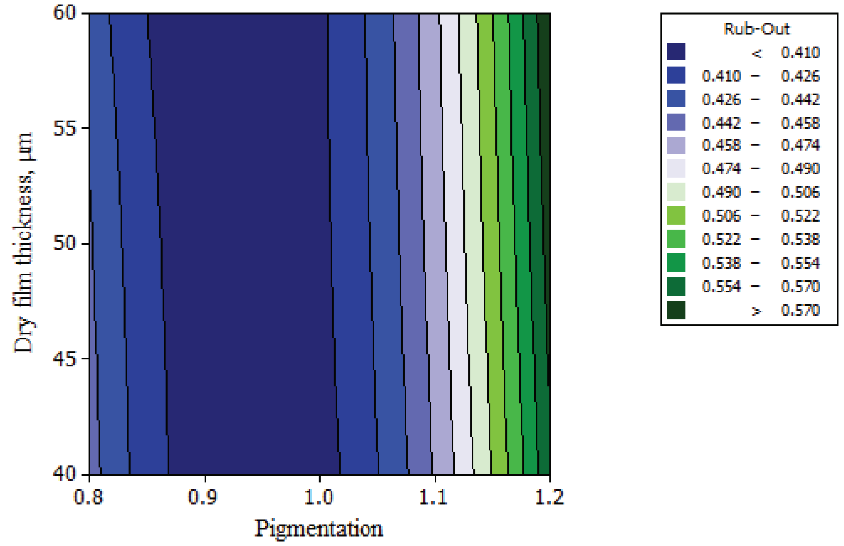

Figure 5.21. Contour Plot of Temperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

In Figure 5.22, x-axis represents pigmentation and y-axis represents dry film thickness value. The shaded gray area in the graph represents low points for rub-out value and acceptable points for Δtemperature value. It is interpreted that the rub-out value is low between approximately 0.9 and 1.0 pigmentation levels.

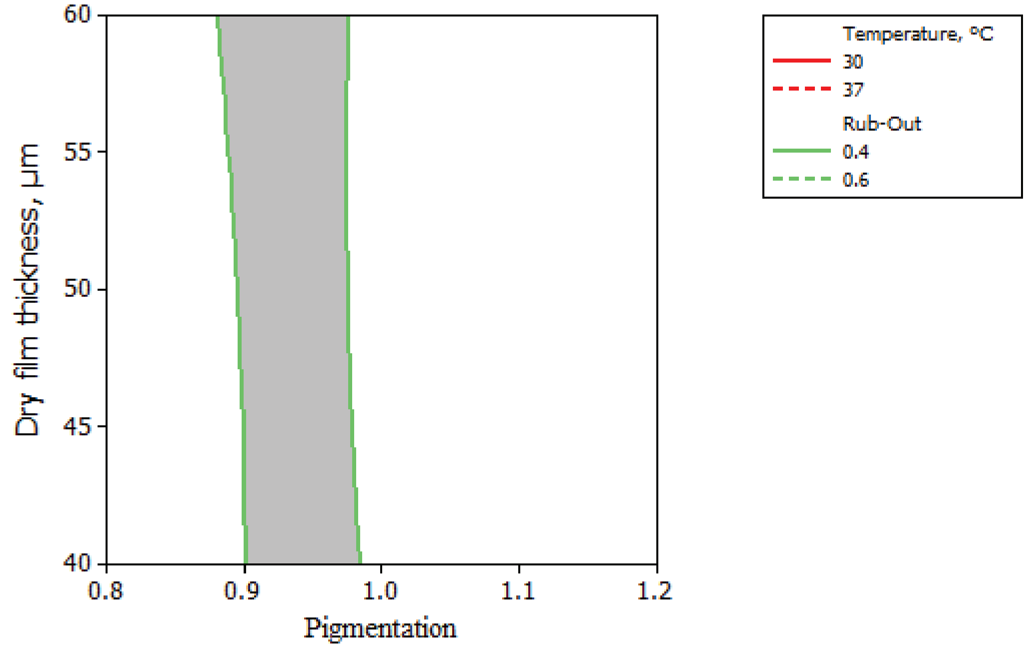

Figure 5.22. Contour Plot of Temperature and Rub-Out

Figure 5.23. is used to determine the optimum points of Δtemperature and rub-out values with varying pigmentation and dry film thickness. It is commented that optimum results are obtained with 1.01 pigmentation and 60 micron dry film thickness. In addition, the d value shown as optimal desirability was determined as 0.66. According to the literature, it is concluded that modeling has medium-high performance.

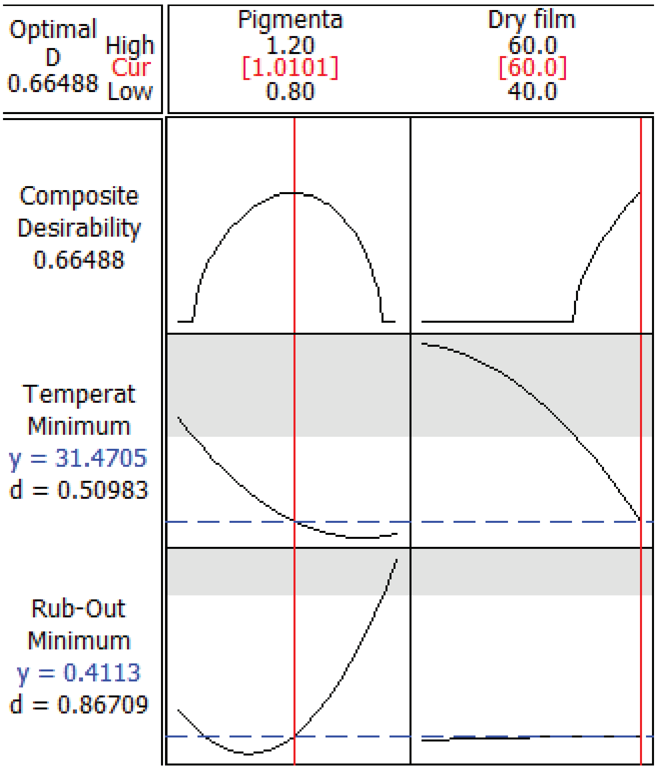

Figure 5.23. Pigmentation and dry film thickness optimization plot of RAL 7021

5.2.3 Color Matching Study and Experimental Results for RAL 9011

Color matching study for RAL 9011 was done with dE<0.50, all work was done in a two-component acrylic system. The amounts of pigment powder and Color Index numbers used for color matching study are listed in table 5.11. Visual evaluation of the study was done in the Byk Spectra Light Booth in Figure 5.24.

Table 5.11. Color Index and Pigment Chemistry for RAL 9011

Color Index (CI)	Pigment Chemistry
Pigment Brown 29- Sicopal Black L 0095	Chromium[III] and Iron Oxide
Pigment White 6- Altris 550	Titanium Dioxide
Pigment Blue 28	Cobalt Aluminate
Pigment Green 7	Chlorinated Copper Phtalocyanine

The results of the studies carried out according to the design matrix created with the parameters and responses determined for the RAL 9011 color are shown in table 5.12. In the study, a significant relationship was tried to be established and modeled between the parameters determined as pigmentation and film thickness and the temperature test and rub-out results by Minitab 16 Software.

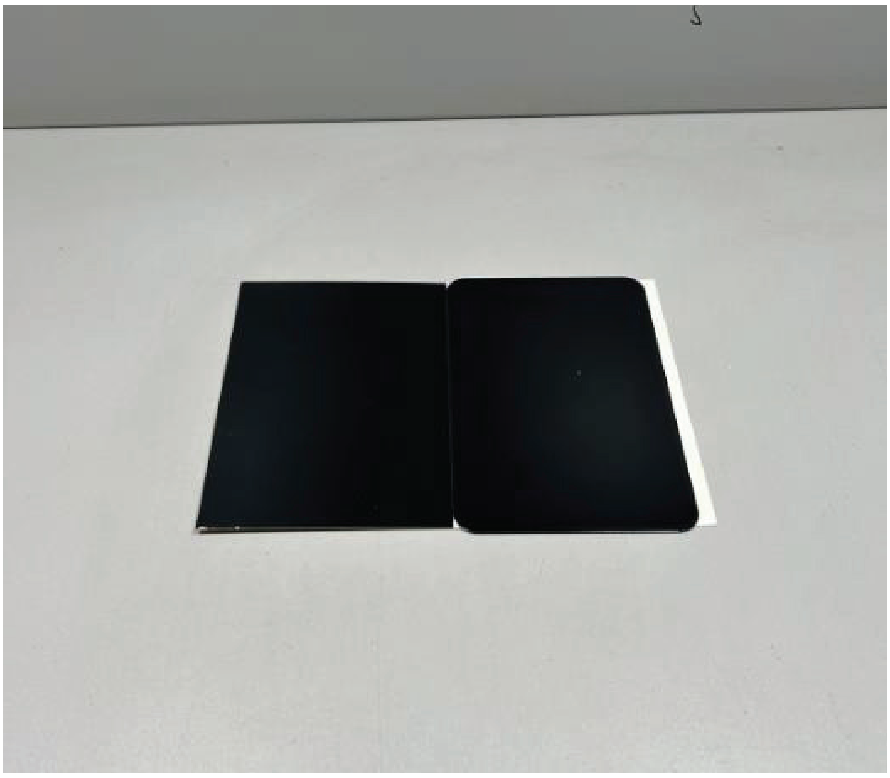

Figure 5.24. Color matching study of RAL 9011 (Left one is conventional RAL 9011, right one is color matching study with IR reflective pigments)

The results of the studies carried out according to the design matrix created with the parameters and responses determined for the RAL 9011 color are shown in table 5.12. In the study, a significant relationship was tried to be established and modeled between the parameters determined as pigmentation and film thickness,responses as a Δtemperature test and rub-out test. MS Excel was used to create regression graphs. Following this, Minitab statistical software (Minitab 16 Statistical Software. Minitab, Inc., State College, PA) was used for the Design of Experiment method used in the data analysis obtained from the experimental result.

Table 5.12. Experimental Design for RAL 9011

Sample	Pigmentation	Dry film thickness, µm	ΔTemperature, [°C]	Rub-Out[ΔE]
RAL 9011	0.80	40.00	39.00	0.35
	0.80	50.00	38.30	0.36
	0.80	60.00	34.10	0.35
	1.00	40.00	38.50	0.33
	1.00	50.00	37.10	0.33
	1.00	50.00	37.00	0.32
	1.00	50.00	36.90	0.34
	1.00	50.00	37.20	0.35
	1.00	50.00	37.10	0.33
	1.00	50.00	37.10	0.32
	1.00	60.00	33.40	0.38
	1.20	40.00	36.98	0.38
	1.20	50.00	36.80	0.40
	1.20	60.00	31.80	0.44

After determining the parameter selections according to the preliminary study results, three different levels were determined for pigmentation and dry film thickness. nine studies were planned with three levels and two factors. The midpoint of the experimental design matrix was 1.00 pigmentation and 50.00 micron dry film thickness degrees of freedom and was repeated six times to increase the repeatability of the experiment. Therefore, fourteen studies were performed as shown in Table 5.12.

Based on Figure 5.25., The R^2 value is 0.9897, which means that approximately 98.97% of the variability in the predicted Δtemperature can be explained by the actual Δtemperature. This very high R^2 value indicates an excellent fit of the model to the data.The regression plot shows that most data points lie very close to the regression line, suggesting that the model predictions are highly accurate with minimal prediction errors.

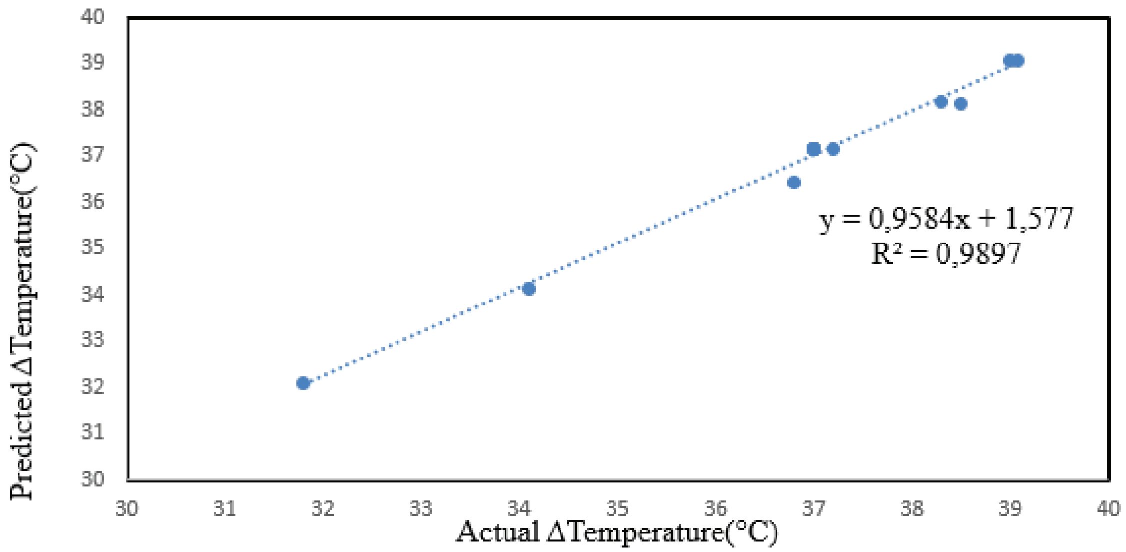

Figure 5.25. Regression Plot of ΔTemperature (°C) for RAL 9011

Figure 5.26 demonstrates that the model used to predict the rub-out value is fairly accurate, with a strong correlation between the actual and predicted values. The R^2 value of 0.8076 indicates that the model explains a significant portion of the variability in the rub-out values, though there is still room for improvement in prediction accuracy as RAL 9010.

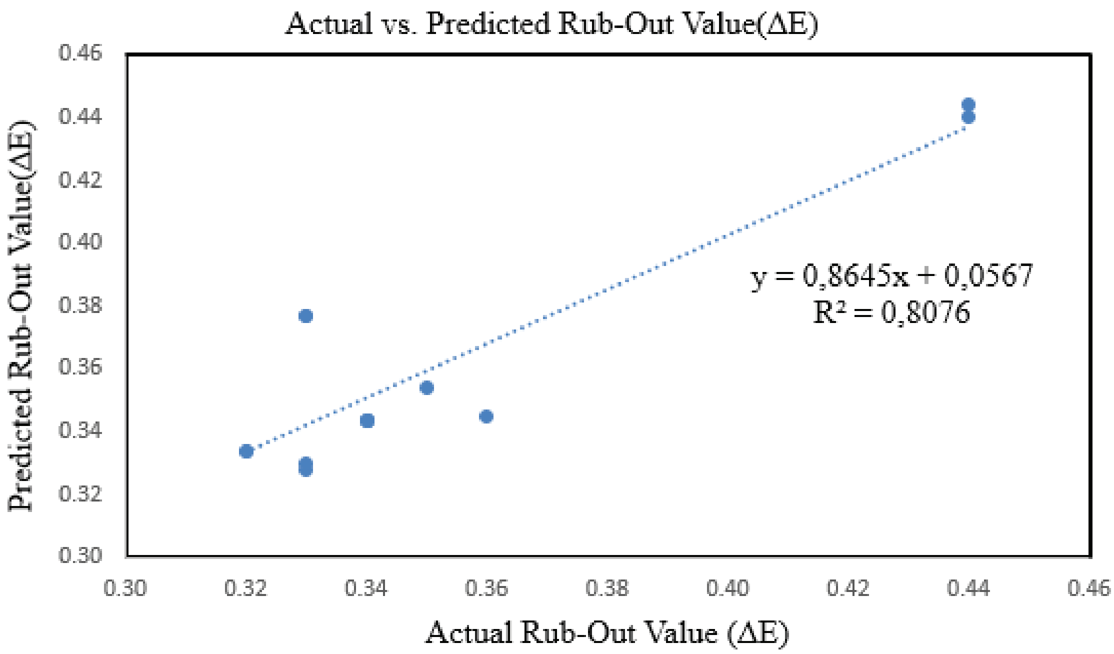

Figure 5.26. Regression Plot of Rub-Out (ΔE) for RAL 9011

In according to Table 5.13., the overall model is highly significant, indicating that the independent variables collectively explain a significant portion of the variance in the dependent variable. Pigmentation has a significant effect on the dependent variable. This indicates that the effect of pigmentation on the response variable is statistically significant. Dry film thickness has a very strong and significant effect on the dependent variable, explaining a large portion of the variance. The quadratic term for pigmentation does not have a significant effect on the dependent variable. This suggests that the quadratic effect of pigmentation is not important in explaining changes in the response variable. The quadratic term for dry film thickness has a very strong and significant effect on the dependent variable. This indicates that the quadratic effect of dry film thickness is important in explaining changes in the response variable. The interaction between pigmentation and dry film thickness does not have a significant effect on the dependent variable. This indicates that these two variables do not work together to significantly impact the response variable.

Table 5.13. Analysis of Variance Results of ΔTemperature for RAL 9011

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	523.9	523.9	104.78	98.06	<0.001
Linear	2	440.508	440.508	220.254	206.13	<0.001
Pigmentation	1	56.454	56.454	56.454	52.63	<0.001
Dry film thickness, µm	1	384.054	384.054	384.054	359.43	<0.001
Square	2	83.196	83.196	41.598	39.03	<0.001
Pigmentation*Pigmentation	1	13.357	0.0025	0.0025	0.02	0.881
Dry film thickness, µm*Dry film thickness, µm	1	69.839	69.839	69.839	65.36	<0.001
Interaction	1	0.0196	0.0196	0.0196	0.18	0.68
Pigmentation*Dry film thickness, µm	1	0.0196	0.0196	0.0196	0.18	0.68
Residual Error	8	0.8548	0.8548	0.1068		
Lack-of-Fit	3	0.8015	0.8015	0.2672	25.05	<0.001
Pure Error	5	0.0533	0.0533	0.0107		
Total	13	532.448				

Based on Table 5.14., the overall model is highly significant, indicating that the independent variables collectively explain a significant portion of the variance in the dependent variable. Pigmentation has a significant effect on the dependent variable. This indicates that the effect of pigmentation on the response variable is statistically significant. Dry film thickness has a strong and significant effect on the dependent variable, explaining a portion of the variance. The quadratic term for pigmentation has a very strong and significant effect on the dependent variable. This indicates that the quadratic effect of pigmentation is important in explaining changes in the response variable. The quadratic term for dry film thickness does not have a significant effect on the dependent variable. This suggests that the quadratic term does not provide additional explanatory power beyond the linear effect. The interaction between pigmentation and dry film thickness has a significant effect on the dependent variable. This indicates that these two variables work together to have a significant impact on the response variable.

Table 5.14. Analysis of Variance Result of Rub-Out (ΔE) for RAL 9011

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	0.01381	0.01381	0.00276	16.56	< 0.001
Linear	2	0.00628	0.00628	0.00314	18.84	< 0.001
Pigmentation	1	0.00427	0.00427	0.00427	25.58	< 0.001
Dry film thickness, mm	1	0.00202	0.00202	0.00202	12.09	< 0.001
Square	2	0.00663	0.00663	0.00331	19.86	< 0.001
Pigmentation*Pigmentation	1	0.00663	0.00395	0.00395	23.7	< 0.001
Dry film thickness, µm*Dry film thickness, µm	1	2E-06	0.00043	0.00043	2.59	0.146
Interaction	1	0.0009	0.0009	0.0009	5.4	0.049
Pigmentation*Dry film thickness, µm	1	0.0009	0.0009	0.0009	5.4	0.049
Residual Error	8	0.00133	0.00133	0.00017		
Lack-of-Fit	3	0.00065	0.00065	0.00022	1.59	0.303
Pure Error	5	0.00068	0.00068	0.00014		
Total	13	0.01514				

Almost the same comments are made in Figure 5.27 as in Figure 5.5. in section 5.2.1. When the normal probability plot is examined, almost all of the points are arranged around the 45-degree line. This indicates compliance with normal distribution. The absence of a specific pattern in the residual versus fits graph reveals that the data is in compliance with the modelling. The presence of a bell curve in the histogram reveals the interpretation that the residuals have a normal distribution. In general, there are very few outlier points, but the modelling performance has been found to be quite successful.

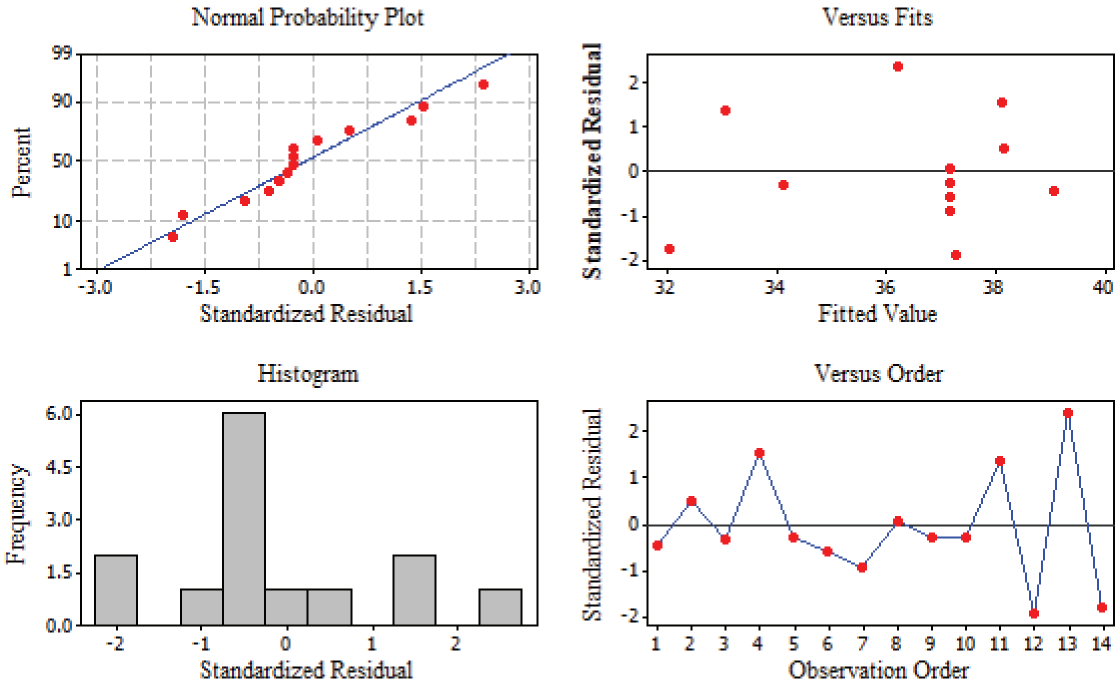

Figure 5.27. Residual Plots for ΔTemperature °C

Similar observations can be made in Figure 5.28. as well as in Figure 5.5.. In a normal probability plot, almost all of the points are aligned around the 45-degree line, so it fits the normal distribution. Since the outlier points do not have a specific pattern, the residuals are interpreted as randomly distributed. In the residual versus fit plot, it was observed that the residuals were not distributed randomly but within a certain range. In the histogram, the data are generally collected at the middle point and slightly spread to the outer points. In the residual versus order graph, it was determined that the residuals did not form a specific pattern. In general, when the 4 graphs were examined, it was concluded that they were suitable for normal distribution and the modelling performance was quite valid.

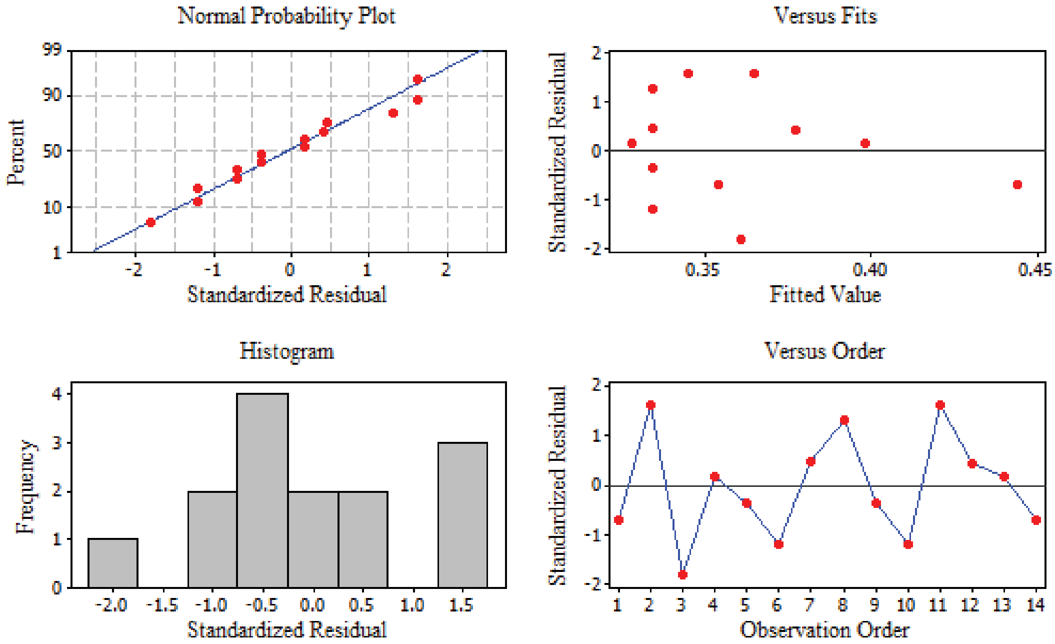

Figure 5.28. Residual Plots for Rub-Out

According to Figure 5.29, it was determined from the slope of the surface graph that the Δtemperature decreased with the increase in dry film thickness and pigmentation level. It was observed that after a certain point, the Δtemperature change remained constant with an increase in dry film thickness and pigmentation level.

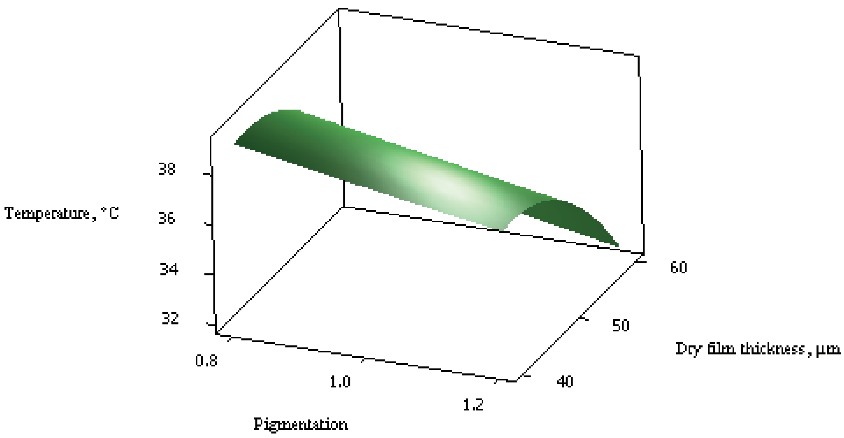

Figure 5.29. 3D Surface Plot of ΔTemperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

According to the surface plot in Figure 5.30, the rub-out value reaches its maximum value at 0.45 with increasing dry film thickness and pigmentation level. It has a minimum value of approximately 0.35 with decreasing dry film thickness and pigmentation levels. As a result, pigmentation and dry film thickness have a significant effect on the rub-out value.

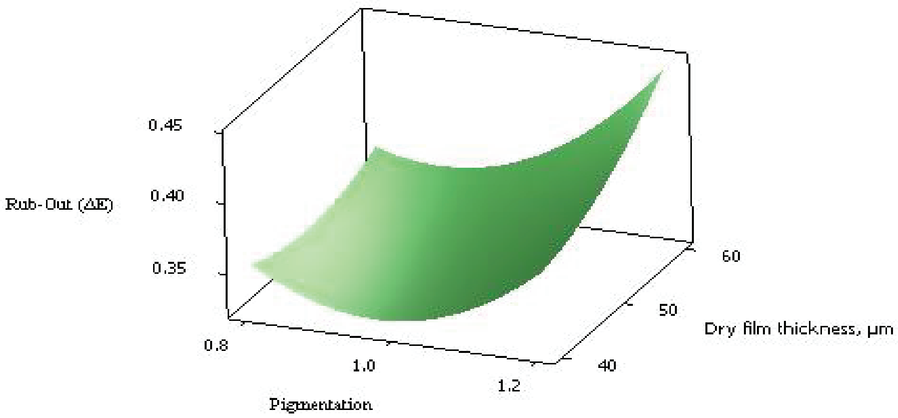

Figure 5.30. 3D Surface Plot of Rub-Out vs. Dry Film Thickness (µm) and Pigmentation

In Figure 5.31, the scale ranging from 0.8 to 1.20 represents pigmentation, and the scale ranging from 40 to 60 represents dry film thickness. The color scale is indicated in the chart; Δtemperature values decrease as you move from green to blue. The minimum Δtemperature was reached at 1.2 pigmentation level and 60 micron dry film thickness

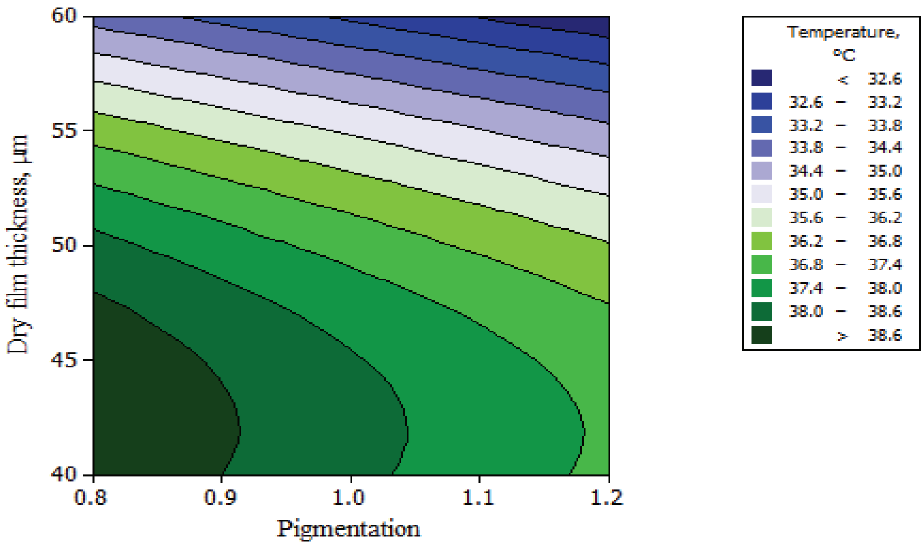

Figure 5.31. Contour Plot of ΔTemperature (°C) vs. Dry Film Thickness (µm) and Pigmentation

In Figure 5.32, the effect of varying dry film thickness and pigmentation levels on the rub-out value is examined. Minimum rub-out values were found to be between approximately 0.9 and 1.1 pigmentation and a dry film thickness of 40-50 microns. An increase in rub-out value is observed with increasing film thickness and pigmentation.

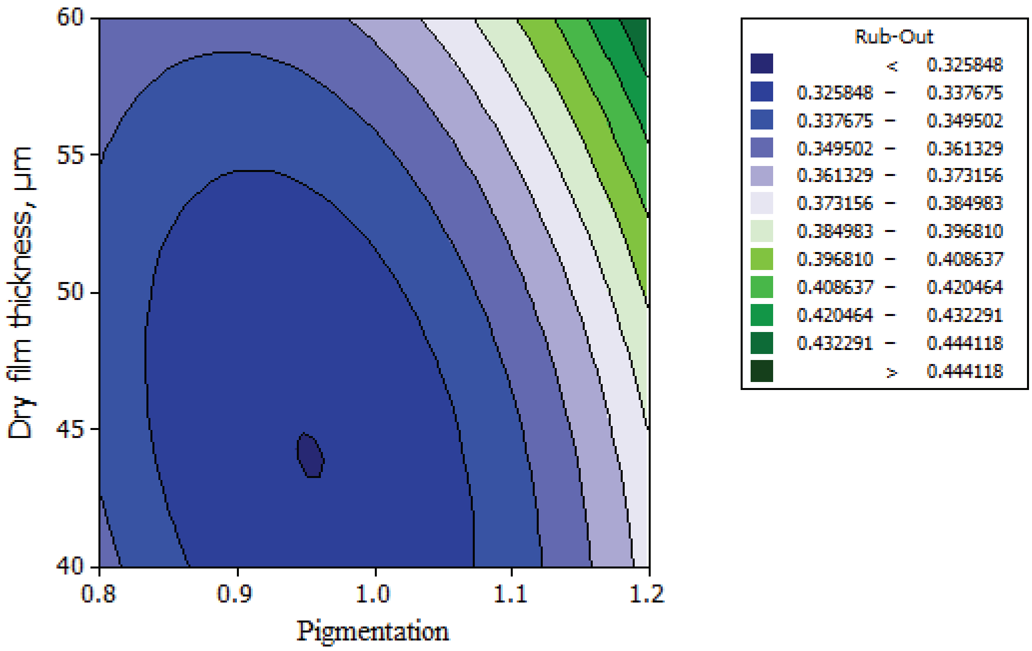

Figure 5.32. Contour Plot of Rub-Out (°C) vs. Dry Film Thickness (µm) and Pigmentation

In Figure 5.33, the points with the highest Δtemperature value (39°C) are between 0.8 pigmentation and 45-micron dry film thickness. Acceptable results were obtained in combinations between 0.8 and 1.1 pigmentation and 45-55-micron dry film thickness. In the combination of 1.2 pigmentation and 60-micron dry film thickness, the rub-out value reached its maximum point (0.40).

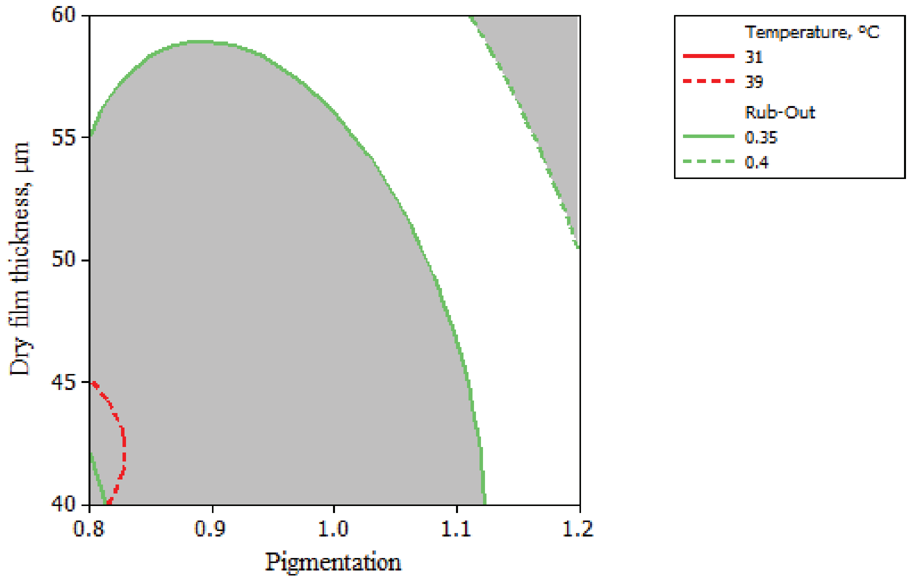

Figure 5.33. Contour Plot of ΔTemperature and Rub-Out vs Dry Film Thickness and Pigmentation

In Figure 5.34., the values at which points the pigmentation and dry film thickness variables give optimum Δtemperature and rub-out values are determined. It was determined that optimum values were reached when pigmentation was 0.93 and dry film thickness was 60 microns. Optimal desirability was determined as 0.80, which is a very suitable value. While the composite desirability value decreases as the pigment increases, the composite desirability value increases with the increase in dry film thickness.

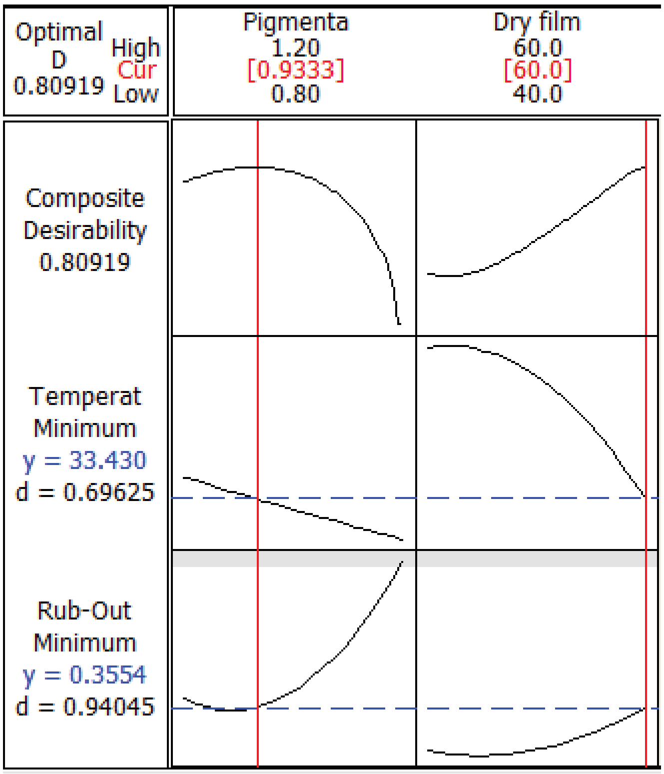

Figure 5.34. Pigmentation and dry film thickness optimization plot of RAL 9011

CHAPTER 6

CONCLUSION

Dispersions of infrared reflective inorganic pigments were prepared in 2K acrylic medium. Color matching studies for RAL 9010, RAL 7021 and RAL 9011 colors were carried out using color pastes designed with IR reflective pigments. Based on preliminary studies, pigmentation and dry film thickness were determined as parameters, surface temperature test and rub-out test were determined as responses. Accordingly, an experimental matrix was created for all three RAL colors. The results obtained were analyzed by designing the experimental method using Minitab 16 software. It was determined that IR reflective coatings for RAL 9010 color had 5.83°C less surface temperature accumulation than the conventional coatings. Then, an optimization study was carried out for RAL 9010. According to the results obtained, the formula applied with 1.03 pigmentation and 59.72 micron dry film thickness was determined to be the optimum point as a result of the temperature test and rub-out test. Modeling performance was found to be successful with R^2=0.9768 and R^2=0.8117 for both Δtemperature and rub-out. It was determined that the formula designed with IR reflective pigments for RAL 7021 color had 14.23°C less surface temperature accumulation than the conventional coatings. Then, an optimization study was carried out for the RAL 7021 formulation. According to the results obtained, the formula applied with 1.01 pigmentation and 60 micron dry film thickness was determined to be the optimum point as a result of the temperature test and rub-out test. Modeling performance was found to be quite successful with R^2= 0.9208 and R^2= 0.9408 for both Δtemperature and rub-out. It was determined that the formula designed with IR reflective pigments for RAL 9011 color had 20.09 °C less surface temperature accumulation than the conventional RAL 9011 coatings. Then, an optimization study was carried out for the RAL 9011 formulation. According to the results obtained, the formula applied with 0.93 pigmentation and 60 micron dry film thickness was determined to be the optimum point as a result of the temperature test and rub-out test. Modeling performance was found to be promising with R^2 = 0.9897 and R^2 = 0.8076 for both Δtemperature and rub-out testing. The innovative coatings designed with IR pigments are expected to reduce thermal buildup in vehicles, thereby decreasing the energy and effort required for cooling, and subsequently lowering associated costs.

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