



DEBRE BERHAN UNIVERSITY

COLLEGE OF ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

**Ultramarine Blue Inorganic Pigment Production from locally
available Raw Materials**

MSc. Thesis

By:

Getahun Yifru

April 2022 G.C

Debre Berhan, Ethiopia

DEBRE BERHAN UNIVERSITY

COLLEGE OF ENGINEERING

Ultramarine Blue Inorganic Pigment Production from locally Available Raw Materials

**A Thesis Submitted to Chemical Engineering, College of Engineering, Debre Berhan
University**

**In partial fulfillment of the requirements for the Degree of Master of Science in
Chemical Engineering (Process Engineering stream)**

By: Getahun yifru

Advisor: Amha B/Mariam (Ph.D)

April 2022 G.C

Debre berhan, Ethiopia

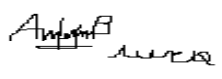
APPROVAL SHEET

DEBRE BERHAN UNIVERSITY

COLLEGE OF ENGINEERING

This is to certify that the thesis prepared by Getahun yifru, which entitled: Ultramarine Blue Inorganic Pigment Production from locally available Raw Materials and submitted in the partial fulfillment of the requirements for the Degree of Master of Science in Chemical Engineering (Process Engineering stream), compiles with the regulation of the University and meets the accepted standards concerning originality and quality and no one this thesis submitted for any other Degree or Diploma.

Approved by:

| | | |
|----------------------------|---|---------------------|
| 1. Kitaw Abirham (MSc.) | | <u>/06/2022 G.C</u> |
| Name of chairman | Signature | Date |
| 2. Amha Betemariam(Ph.D) |  | <u>/06/2022 G.C</u> |
| Name of Advisor | Signature | Date |
| 3. Felek Bayu (Ph.D) | | <u>/06/2022 G.C</u> |
| Name of Internal Examiner | Signature | Date |
| 4. Gizachew shiferaw(Eng.) | | <u>06/2022 G.C</u> |
| Name of External Examiner | Signature | Date |

DECLARATION

I declare that this thesis on ultramarine blue inorganic pigment production from locally Available Raw Materials is my original work, and all sources of material that used in this thesis have been profoundly acknowledged in the text and a list of references is given. This thesis has been submitted in partial fulfillment of the requirements for a Master of Science (MSc.) at Debre Berhan University. I declare that this thesis is not submitted to any other institution anywhere for the award of any academic degree, diploma, or certificate

Name: Getahun Yifru

Signature: -----

Place: College of Engineering, Debre Berhan University

Date of Submission: -----

ACKNOWLEDGMENT

First of all, I would like to express my gratitude to the holy God and his mother Saint Mary who helped me to conduct this study and to complete it successfully.

I would also like to thank Amha B/Mariam (Ph.D.), my teacher and advocate for bringing me here as a father, giving advice and knowledge that will benefit me in all my endeavors.

Next, I would like to thank Ato Aklilu habtehawri chemical engineering laboratory technician, at Addis Abeba institute of technology (AAU), and Ato Alebel abebaw postgraduate chemical laboratory technician at Bahir Dar institute of technology (BDU) for providing me with the resources I need and for cooperating with me. Finally, thank you to everyone who helped me with my thoughts and idea.

TABLE CONTENTS

| CONTENTS | page |
|--|------|
| CHAPTER ONE..... | 1 |
| 1. INTRODUCTION..... | 1 |
| 1.1. Background of the Study..... | 1 |
| 1.2. Statement of the Problem..... | 2 |
| 1.3. Objectives..... | 2 |
| 1.3.1. General objective..... | 2 |
| 1.3.2. Specific Objectives..... | 2 |
| 1.4. Significance of the Study..... | 3 |
| CHAPTER TWO..... | 4 |
| 2. LITERATURE REVIEW..... | 4 |
| 2.1. Pigment..... | 4 |
| 2.2. Basic color of pigment..... | 5 |
| 2.3. Inorganic pigment and their Chemical and Physical Properties..... | 5 |
| 2.4. Classification of Pigment..... | 6 |
| 2.5. Colorimetry..... | 7 |
| 2.6. Uses of Pigment..... | 8 |
| 2.7. Inorganic Blue Pigment..... | 8 |
| 2.8. Synthetic Ultramarine Pigments..... | 9 |
| 2.9. Chemical Structure..... | 9 |
| 2.10. Properties of Ultramarine Blue Pigment..... | 10 |
| 2.11. Application of ultramarine blue pigment..... | 11 |
| 2.11.1. Plastics manufacturing..... | 11 |
| 2.11.2. Paints production..... | 11 |
| 2.11.3. Printing Inks production..... | 11 |
| 2.11.4. Paper and Paper Coatings..... | 11 |
| 2.11.5. Detergents..... | 12 |
| 2.11.6. Cosmetics and Soaps..... | 12 |
| 2.11.7. Toxicology and Environmental Aspects..... | 12 |
| 2.12. Inorganic blue pigment manufacturing material deposit in Ethiopia..... | 12 |

| | | |
|---------------------|--|----|
| 2.13. | Soda ash deposit in Ethiopia..... | 12 |
| 2.14. | Sulfur deposit in Ethiopia | 13 |
| 2.15. | Clay deposit in Ethiopia | 13 |
| 2.16. | General manufacture methods of inorganic pigment | 13 |
| 2.16.1. | Mechanical preparation processes..... | 14 |
| 2.17. | Precipitation reactions | 14 |
| 2.18. | Calcination processes | 15 |
| 2.19. | Other methods..... | 15 |
| 2.20. | Ultramarine blue pigment production process..... | 16 |
| 2.20.1. | Clay activation..... | 16 |
| 2.20.2. | Blending and Heating Raw Materials | 17 |
| 2.20.3. | Calcination of the prepared sample..... | 17 |
| 2.20.4. | Oxidation..... | 17 |
| 2.20.5. | Purification and Refinement..... | 17 |
| CHAPTER THREE | | 18 |
| 3. | METHODS AND MATERIALS | 18 |
| 3.1. | Materials and Equipment | 18 |
| 3.1.1. | Materials | 18 |
| 3.1.2. | Equipment's | 18 |
| 3.2. | Source of Raw Material..... | 18 |
| 3.3. | Experimental Location | 18 |
| 3.4. | Experimental Methodology..... | 19 |
| 3.4.1. | Raw materials preparation and characterization | 19 |
| 3.5. | Production of synthetic blue pigment..... | 20 |
| 3.5.1. | Blending and milling..... | 20 |
| 3.5.2. | Sintering (reaction) of the raw materials | 21 |
| 3.5.3. | Cooling..... | 21 |
| 3.5.4. | Purification of raw ultramarine blue pigment..... | 21 |
| 3.6. | Product Characterization | 22 |
| 3.6.1. | Moisture content | 22 |
| 3.6.2. | Resistance to heat..... | 22 |

| | | |
|-------------------|---|----|
| 3.6.3. | Light resistance studies | 23 |
| 3.6.4. | Density determination | 23 |
| 3.6.5. | Chemical resistance test | 24 |
| 3.6.6. | X-ray diffraction (XRD) | 24 |
| 3.6.7. | Fourier transform infrared Spectroscopy | 24 |
| 3.6.8. | Color values | 24 |
| 3.6.9. | Parameters effect on blue color..... | 25 |
| 3.7. | Statistical Design of Experiment..... | 25 |
| 3.7.1. | Response surface method of analysis (RSM) | 25 |
| CHAPTER FOUR..... | | 27 |
| 4. | RESULT AND DISCUSSION | 27 |
| 4.1. | Raw Material Characterization Result | 27 |
| 4.1.1. | Sulfur composition..... | 27 |
| 4.1.2. | Clay composition | 27 |
| 4.2. | Product Characterization Result..... | 27 |
| 4.2.1. | Moisture content | 27 |
| 4.2.2. | Heat, light, and chemical stability testing..... | 27 |
| 4.2.3. | Density | 30 |
| 4.2.4. | X-ray diffraction result | 31 |
| 4.2.5. | Fourier transform infrared spectroscopy..... | 31 |
| 4.3. | The influence of parameters on pigment coloring value..... | 32 |
| 4.3.1. | Time influence on pigment blue coloring value (b*)..... | 32 |
| 4.3.2. | Sulfur amount influences pigment blue coloring value (b*) | 33 |
| 4.3.3. | Temperature influence on pigment blue coloring value (b*)..... | 34 |
| 4.4. | Statistical Design of Experiments (DOE) Result | 34 |
| 4.4.1. | Response surface method of analysis (RSM) | 34 |
| 4.4.2. | Analysis of variance (ANOVA)..... | 35 |
| 4.4.3. | Development of regression equation | 37 |
| 4.4.4. | Model diagnoses | 37 |
| 4.4.5. | Interaction effect of the process variables | 40 |

| | |
|---|----|
| 4.4.6. The combined effect of reaction temperature and sulfur amount on blue coloring value (-b*) | 40 |
| 4.4.7. Validation of the developed model | 42 |
| CHAPTER FIVE | 43 |
| 5. CONCLUSION AND RECOMMENDATION | 43 |
| 5.1. Conclusion..... | 43 |
| 5.2. Recommendation..... | 44 |
| 6. REFERENCES | 45 |
| 7. APPENDIX | 47 |

LIST OF TABLE

| | |
|--|----|
| Table 2.1 Classification of inorganic pigment based on optical properties | 7 |
| Table 4.1 Complete silicate analysis of local Sulfur..... | 27 |
| Table 4.2 Complete silicate analysis of Clay | 27 |
| Table 4.3 Reference sample produced ultramarine pigment CIElab value | 28 |
| Table 4.5 Lightness stability test result in CIElab and color difference value | 29 |
| Table 4.8 Detergent-resistant tests CIElab and the color difference value..... | 30 |
| Table 4.10 Experimental runs CIElab value | 35 |
| Table 4.11 ANOVA for response surface quadratic model..... | 36 |
| Table 4.12 Correlation coefficient (R^2) for blue coloring value..... | 36 |
| Table 4.13 Optimum condition and model validation | 42 |
| Table 7.2 Time influence on coloring value | 49 |
| Table 7.3 Temperature influence on coloring value | 49 |
| Table 7.4 Sequential Model Sum of Squares [Type I]..... | 50 |
| Table 7.5 Lack of Fit Tests | 50 |
| Table 7.6 Model Summary Statistics | 51 |

LIST FIGURE

Figure 2.1 Ultramarine blue production process flow diagrams..... 16

Figure 3.5 The experimental flow diagram..... 19

Figure 3.1 Blended raw material.....20

Figure 3.2 Cooling raw ultramarine blue pigment.....21

Figure 3.3 Purified ultramarine blue pigment.....21

Figure 3.4; The CIElab color space system25

Figure 4.1 XRD pattern of ultramarine blue31

Figure 4.3 Reaction time effect on coloring value (b*)33

Figure 4.4 Sulfur amount effect on coloring value (b*)33

Figure 4.6 Model diagnose plot39

Figure 4.7 The interaction effect of sulfur amount and reaction temperature40

Figure 4.8 Combined Effect of Reaction Temperature and Sulfur Amount on Blue Coloring Value (-b*).....41

Figure 7.1 Numerical optimization result49

ACRONYMS

| | |
|------------|---|
| XRD | X-ray diffraction |
| FT-IR | Fourier transform infrared Spectroscopy |
| UV CM-600d | spectrophotometer CM-600d |
| RSM | Response surface methodology |
| CCD | Central composite design |
| ASSASC | abijata-shalla Soda Ash share company |
| EMRDC | Ethiopian Mineral Resource Development Corporation |
| ASTM | American Society for Testing and Materials, |
| CIElab | Commission Internationale de l'éclairage laboratory |

ABSTRACT

Synthetic ultramarine inorganic blue pigment is one of common type of blue pigment which can be easily produced from locally available geomaterials. The chemical composition of these geo-materials (sulphur and clay) was investigated by the silicate analysis method and Synthetic ultramarine blue pigment was synthesized by a solid-state calcination process. A literature review was used to select and investigate the effect of reaction temperature (750, 800 and 850 °C), residence time (4, 5, and 6 hours), and sulfur weight amount (20.56, 21.34 and 22,06w %) on the blue pigment production process. The main blue coloring strength was identified by Commission Internationale de l'éclairage laboratory coordinate value (L^ , a^* , b^*) where L^* is the lightness value starting from 0 up to 100, a^* and b^* are correlation coordinates which show the coloring value between +60 and -60. The optimum process parameters for the production of blue color pigment were determined by a design expert. The optimal process parameters were a reaction time of 4.87hr. (4 hours and 52 minutes), reaction temperature (799.84°C), sulfur concentration (22.06 wt. %), and blue color value ($b^*=-13.13$). The pigment properties were characterized by density, moisture content and color value, resistance to heat, detergent, acid, alkali and light. The crystalline nature structure and the functional group were determined by X-ray diffraction and infrared spectroscope. The quality of the blue color strength was also examined by spectrophotometer CM- 600d. According to the results of the research, there's an opportunity to produced ultramarine pigment material by using local geo-minerals.*

Keywords: *Geominerals, Color Value, Microstructure, Ultramarine, Pigment*

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the Study

The word "pigment" comes from the Latin word "pigmentum," which was originally known as "color". Pigments can be also defined as substances consisting of small particles that are practically insoluble in an application system (Gerhard 2017). The most common blue earth pigment is ultramarine. It is an aluminous silicate sulfur compound with a crystal structure. As a result, it has a very bright light and pure color. The advantages of ultramarine blue pigment are very good heat resistance, excellent light fastness, no migratory safety and innocuousness are easily dispersed (Buxbaum and Pfaff 2005). Ultramarine Blue occupies a unique position in the blue color space that no other pigment or pigment blend can reach. It is used, in plastics, paints and powder coatings, printing inks, paper and paper coatings, rubber and thermoplastic elastomers, latex products, detergents, cosmetics and soaps, artists' colors, toys and educational equipment, leather finishes, powder markets, roofing granules, Synthetic fibers (Gerhard 2017).

Ultramarine is commonly used to whiten raw materials. The micro ultramarine pigment can be used to remove the yellow color from the material, making it whiter. Ultramarine powdered coating is the best choice as a result of weather ability tests in a variety of applications showing that ultramarine performs exceptionally well in powdered coatings (O'Brien 2005).

Ultramarine Blue pigment is an inorganic pigment whose color has been classified as pigment blue 29/C.I. 77007 by the Color Index System. Inorganic pigments are made using a variety of mechanical and physical-chemical techniques the procedures are designed to produce pigments with the right composition, crystal structure, and particle size (Gerhard 2017). In this study, the synthetic ultramarine blue pigment was produced using a solid-state calcination method, with raw materials sourced locally from minerals such as Soda ash, kaolin, Sulfur, and Activated carbon (reducing agent). It's a sodium aluminum sulphosilicate chain member.

1.2. Statement of the Problem

Today, due to the fast expansion of cities, construction, paints, printing ink and other industries in the country, there is a high demand for ultramarine blue and other types of colored pigments. To fulfill this demand, the country is importing more than one hundred thousand tons per year of blue pigment by spending a huge amount of hard currency. Due to hard currency shortage as well as because of alarmingly increasing demand, the price of the pigment is exponentially increasing. However, blue pigment can be easily produced from locally available geomaterials such as clay (kaolin), sulfur, and soda ash which are widely available in different parts of the country. Therefore, this research is aimed to produce blue pigment from locally available raw materials, particularly clay (Ankober), Soda ash (Lake Abyata) and sulfur (Afar).

1.3. Objectives

1.3.1. General objective

The main objective of this study is the production of synthetic inorganic ultramarine blue pigment from locally available raw materials such as Soda, Clay, and Sulfur.

1.3.2. Specific Objectives

The specific objectives of the study are:-

1. To analyze the chemical composition of the local geo-materials (Sulfur and Clay).
2. To prepare ultramarine blue pigment and examine the effect of process parameters (reaction temperature, residence time, and amount of Sulfur) on the coloring properties of pigment.
3. To study the chemical, physical, microstructure, and particular color properties of the inorganic ultramarine blue pigment.
4. To optimize process parameters such as reaction temperature, residence time, and Sulfur amount for ultramarine blue color.

1.4. Significance of the Study

The importance of this research work is given as follows:

1. Local geo-minerals utilization for the production of ultramarine blue pigment.
2. Substitution of imported pigment by locally prepared pigment.
3. The findings of this study will serve as a foundation for future research.
4. If the study further strengthened and made industrially applicable, it do creates job opportunities for local people.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Pigment

The word "pigment" comes from the Latin word "pigmentum," which was originally known as "color". The term was also employed in the late Middle Ages to refer to a variety of plant and vegetable extracts, particularly those used for coloring. The term pigment is still used in biological language to refer to dyestuffs produced by plant or animal species and found as extremely minute grains inside cells or cell membranes, as deposits in tissues, or suspended in body fluids (Buxbaum and Pfaff 2005).

The Pigments are expressed as "black, white, colored, particulate, and organic or inorganic solids which are essentially, physically and chemically are not affected by the substrate in which they are incorporated". They may alter the appearance by selective absorption and scattering of light. Pigments can be classified by their chemical composition, and optical or technical properties(Sandhya Kumari L. 2012).

The Ultramarine blue and artificial lapis lazuli (Egyptian blue and cobalt aluminum spinel) was the first blue pigments. Malachite, Terraverte, and a synthetically prepared copper hydroxyl chloride were the first green pigments. Ceramic pigments were widely used by the Chaldeans. Calcite, some phases of calcium sulphate, and kaolinite were the white pigments used at that time (Gerhard 2017,O'Brien 2005).

The pigment industry was started in the 18th century with end products such as cobalt blue (1777), Berlin blue (1704), chrome yellow (1778), and Scheele's green. In the 19th century, ultramarine, cobalt pigments, iron oxide pigments, cadmium, and Guignet's green pigments were developed in quick succession. In the 20th century, pigments became the subject of scientific investigation. In the past few decades, the synthetic colored pigments cadmium red, manganese blue, molybdenum red and mixed oxides with bismuth came onto the market. Titanium dioxide with anatine or rutile structures and acicular zinc oxide were introduced as new synthetic white pigments and extenders, respectively. Luster pigments (metal effect, pearl, and interference pigments) have assumed increasing importance(Buxbaum and Pfaff 2005).

The availability of more and more synthetic pigments was accompanied by the development of suitable application systems. Paints, printing inks, coatings, and cosmetic formulations, with the introduction of the car, the revolutionary development of automotive coating systems began. Printing inks were adapted according to the requirements of the different printing substrates and processes used. The development of plastics and other polymer materials in the nineteenth, but especially in the twentieth century opened a new wide application spectrum for inorganic and organic pigments (Gerhard 2017).

2.2. Basic color of pigment

The primary pigment color is red, yellow, and blue but the colour of a pigment is mainly dependent on its chemical structure. The selective absorption and reflection of various wavelengths of light that impinge on the pigmented surface determines its hue (whether it is red or yellow, etc.)(Müller and Poth 2007). A blue pigment appears so because it reflects the blue wavelengths of the incident white light that falls upon it and absorbs all of the other wavelengths. Hence, a blue car in orange sodium light looks black, because sodium light contains virtually no blue component. Black pigments absorb almost all the light falling upon them, whereas white pigments scatter and reflect virtually all the visible light falling on their surfaces. Fluorescent pigments have an interesting characteristic. As well as having high reflection in specific areas of the visible spectrum, they also absorb light in areas outside the visible spectrum (the ultraviolet part where our eyes are unable to detect), splitting the energy up, and re-emitting it in the visible spectrum. Hence, they appear to emit more light than actually falls upon them, producing their brilliant colour(Shinohara 2017).

2.3. Inorganic pigment and their Chemical and Physical Properties

Most of the time inorganic pigments consist of single particles of uniform chemical composition and crystal structure. Exceptions are pigment mixtures (blended pigments) and layer substrate pigments (typical for special effect pigments), which consist of chemically and crystallographically nonuniform or multicomponent particles (Buxbaum and Pfaff 2005).

2.4. Classification of Pigment

Pigments can be classified from different points of view. Those are based on chemical structure, optical properties, or technological properties of pigment. According to those criteria pigment can be classified as, natural, synthetic, organic, inorganic, pearlescent, luminescent, etc. Pigments generally can be categorized into inorganic and organic pigments (Kumari 2012). Inorganic pigments are a type of pigment which contains various metal ions in the form of carbonates, sulfides, oxides, and silicates. The nature of the metal plays a vital effect in the coloring of the pigments (Divya 2017, Gunter Buxbaum and Gerhard Pfaff 2005). In the production of organic pigments, certain materials become not soluble in the pure form, whereas, others require a metal or an inorganic base to precipitate them. Insoluble coloring materials in the pure form are known as toners and those, which require a base, are called lakes. Synthetic organic pigments are very finely textured and provide clean and intense colors. However, both the light fastness and heat stability of organic pigments are generally lower than that of inorganic pigments (Kumari 2012).

Most of the time inorganic pigments are found in nature as minerals. The degree of opacity, light stability, and chemical resistance of natural inorganic pigment are normally very high. Extender pigments are white inorganic minerals that are relatively deficient in both color and opacity and are commonly used to replace the more expensive prime pigments. These pigments are also referred to as inert pigments because of their optically inert behavior in surface coatings. The extenders are commonly used for surface coatings (Jose et al. 2019).

Pigments are substances that, by wavelength specific absorption, alter the color of transmitted or reflected light. When white light strikes a sample, it may be completely reflected, in which case the substance looks white, or it may be completely absorbed, in which case the substance appears black. If just a portion of the light is absorbed and the remainder is reflected, the reflected light determines the hue of the sample (Gunter Buxbaum and Gerhard Pfaff 2005).

Table 2.1 Classification of inorganic pigment based on optical properties

| Classification of Inorganic pigments | |
|---|--|
| Pigment | General description |
| White pigments | The optic properties are caused by unselective light scattering for illustration; titanium dioxide. And zinc white |
| Colored pigments | The optic properties are caused by selective light immersion and also to a large extent by selective light scattering for example iron oxide red color, and ultramarine color. |
| Black pigments | The optic properties are caused by unselective light immersion for example carbon black, iron oxide black |
| Effect pigment | The optic properties are caused by regular reflection or interference |
| Interference pigments | The optic properties are due to interference (iron oxide on mica) |
| Luminescent pigments | The optical properties are caused by the capacity to absorb radiation and emit it as the light of a longer wavelength |
| Fluorescent pigments | The light of a longer wavelength is emitted after excitation without a delay. for example silver-doped zinc sulfides) |
| Phosphorescent pigments | The light of a longer wavelength is emitted within several hours after excitation for example copper-doped zinc sulfides. |

Source(Gerhard 2017,Buxbaum and Pfaff 2005)

2.5. Colorimetry

Colorimetry is one of the studies of color estimation, which is appropriate to measure color contrasts among tests and it is utilized in business, industry, and the research center to express coloring in mathematical terms. The fundamental reason for Colorimetry is the assurance of a mathematical incentive for a color valency (color stimulant specification) of a colorimetric standard onlooker (hypothetical colorimetric watcher whose sharpness finders relate to the coloring coordinating with capacities characterized by the Commission Internationale de l'éclairage laboratory value (CIElab)(Kumari 2012). This coloring valency can be estimated by L^* , a^* and b^* colorimetric qualities. Any color can have an added substance

combination of the coloring valency of all unearthly radiations showing up in the color stimulus. In Colorimetry, the evaluation of coloring depends on the three-part theory of coloring vision, which expresses that the natural eye has receptors for three essential tones (red, green, and blue) and that all tones are viewed as combinations of these primaries (Divya 2017).

In Colorimetry, these parts are alluded to as X-Y-Z facilitates Colorimetry incorporates three distinct techniques: the adjustment strategy, the tristimulus strategy, and the spectral technique. The assurance and assessment of shading contrasts, be that as it may, is quite possibly the main undertakings of Colorimetry for the turn of events and observing of pigment. Colorimetry is most important to determine and evaluate the color differences value of pigment (KIKUCHI 2015). The CIE Lab color difference formula has achieved the widest popularity. This formula converts the standard color values X, Y, and Z into the L*, a*, and b* values; L* means lightness, a* with +a* and -a* is the red-green axis, and b* with +b* and -b* is the yellow-blue axis. The total color distance ΔE^*_{ab} in the CIE Lab system (L*, a*, b* color space) (Umali and Mahanwar 2012a).

2.6. Uses of Pigment

Pigments have different industrial applications, those are; paints, plastics, artists' colors, printing inks for paper and textiles, varnishes, leather decoration, floor coverings, leather imitates, rubber, cosmetics, ceramic glazes, paper, and enamels (O'Brien 2005). In addition to the above fundamental applications, nowadays, pigments are utilized also for so-called "high-tech" applications such as photoconductors for electrophotography, color filters for liquid crystal displays, electro-luminescent diodes, ink-jet printing inks, and pigment-sensitized solar cells. Pigments have been one of the requisite materials in our life used from conventional coloration to specific state-of-the-art applications (KIKUCHI 2015).

2.7. Inorganic Blue Pigment

Inorganic pigments are mainly occurred as natural mineral sources or obtained synthetically from minerals. Those raw materials are mainly oxides, sulphides of one and more than one metal. These pigments obtain their extraordinary properties through a combination of special manufacturing processes (Buxbaum and Pfaff 2005).

A blue pigment incorporates fundamentally iron blue and ultramarine blue. The ultramarine blue pigment is one of the main individuals from the blue color group of inorganic synthetic compounds. It is accessible in bright blue shades and is resistant to heat and alkali. It is utilized widely in paint, printing ink, paper, and clothing work. Ultramarine was produced by treating aluminum silicate with sulfur. Various forms of Cobalt and Cerulean blue were also introduced in the early 20th century (O'Brien 2005).

2.8. Synthetic Ultramarine Pigments

Ultramarine blue is a deep blue pigment the name "Ultramarine" is "across the sea" this was given to the pigment derived from grinding the mineral. The naturally Ultramarine Pigments occur as a mineral lapis lazuli which is found in very few places around the world at high purity being obtained from Afghanistan and Chile (Gerhard 2017).

Synthetic ultramarines are inorganic blue pigments, commercially available in 3 colors:

- Reddish blue, C.I. Pigment Blue 29: 77007 [57455-37-5]
- Violet, C.I. Pigment Violet 15: 77007 [12769-96-9]
- Pink, C.I. Pigment Red 259: 77007 [12769-96-9]

2.9. Chemical Structure

Ultramarine blue pigment is a three-dimensional aluminosilicate structure with captured sodium particles and an ionic sulfur group. In synthetic ultramarine blue pigment derived from clay by calcination, the equivalent lattice distribution of aluminum and silicon ions is disordered. This contrasts with the ordered array in natural ultramarines. In the most straightforward ultramarine design, equivalent quantities of silicon and aluminum ions are available and the fundamental lattice unit is $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ or $(\text{Na}^+)_6(\text{Al}^{3+})_6(\text{Si}^{4+})_6(\text{O}_2^-)_{24}$ With a net ionic charge of zero as needed for the stability of the structure, there are two kinds of sulfur bunches in ultramarine blue, S^{-3} and S^{-2} , the two species are free radicals stabilized by entrapment in the crystal lattice (Buxbaum and Pfaff 2005).

2.10. Properties of Ultramarine Blue Pigment

Synthetic ultramarine blue colors display escalated shades of blue and moderately powerless violet and pink shading tones. The fundamental blue ultramarine tone is a rich, bright reddish blue. The blue shading tone of the last colors is adjusted by differing the chemical composition and the particle size distribution(KIKUCHI 2015). The pink and violet express significantly weaker and less degrees of color saturation. The last shading nature of business colors is created by granulating to reduce the particle size to the wanted dissemination and hence upgrade coloring strength. Mean particle sizes for the vast majority of the shades are in the reach from 0.7 to 5.0 μm . Fine powders are lighter in shade and rather greener than coarser grades. When used together with white pigments, their color is brighter and more saturated(O'Brien 2005).

Ultramarine blue pigment is thermally steady in various applications to around 400°C, violet to 280°C, and pink to 220°C. All three pigments have excellent light fastness. Ultramarines are not stable against a high concentration of acids. The pigments can be completely decomposed by the action of acids. The color is lost in this case and silica, sulfur, sodium, and aluminum salts, as well as hydrogen sulfide, are formed(Buxbaum and Pfaff 2005). The evolution of hydrogen sulfide under the influence of acids is a useful test for ultramarine. Short-term stability against acids can be achieved by protecting the pigment particles with a coating of impervious silica. Blue and violet pigment grades are stable in dilute alkaline solutions, whereas pink changes its color to a violet shade. Ultramarine pigments are insoluble in water and organic solvents. Therefore, the color does not bleed or migrate from paints or polymers. As a consequence, ultramarines are approved for a wide range of food contact applications (Hamerton, Tedaldi, and Eastaugh 2013). Ultramarine pigments absorb moisture on the external particle surfaces and at the internal surfaces of the sodalite structure. External surface moisture of up to 2% according to particle size is desorbed at about 100°C, but the additional 1% of internal moisture needs 235°C for complete removal(Umali and Mahanwar 2012a). Particles of ultramarine pigments are relatively hard. They are known to cause abrasion in equipment handling either as dry or slurry pigment.

2.11. Application of ultramarine blue pigment

The stability and safety of ultramarine pigments are the basis of their wide range of applications, which include the following:

2.11.1. Plastics manufacturing

Blue ultramarine can be utilized in any polymer; violet ultramarine has the most extreme handling temperature of 280°C, and pink ultramarine has the greatest handling temperature of 220°C. With PVC, corrosive safe grades are normally utilized if the shading blurs during handling. Surface-treated grades are accessible for improved superfluity. Ultramarines don't cause shrinkage or twisting of polyolefin. Ultramarine shades are allowed worldwide for shading food-contact plastic (Buxbaum and Pfaff 2005; Gerhard 2017).

2.11.2. Paints production

Ultramarine blue colors are utilized in beautiful paints, fighting completions, transparent polishes, modern paints, and powder coatings. The transparent nature of the color prompts some noteworthy flamboyant coatings in a blend with impact shades like mica (Buxbaum and Pfaff 2005).

2.11.3. Printing Inks production

Ultramarine colors can be utilized in inks for most printing processes including hot-foil stepping. Letterpress, flexography, and gravure need high-strength grades; lithography needs water-repellent grades; any grade is appropriate for screen inks, texture printing, and hot-foil stepping. Further developed strength grades introduced in a high strong fluid scattering are discovering expanding use in flexographic printing applications (Buxbaum and Pfaff 2005).

2.11.4. Paper and Paper Coatings

Ultramarine pigments are used to enhance the hue of white paper or for colored paper. They can be added directly to the paper pulp, or used in applied coatings. They are particularly suitable for colored paper for children's use (Gerhard 2017).

2.11.5. Detergents

Ultramarine blue pigments are generally used to upgrade the impacts of optical lighting up specialists in working on the whiteness of washed textures. They don't stain or develop with rehashed use (Kumari 2012).

2.11.6. Cosmetics and Soaps

Ultramarine colors are also utilized in beauty care products. Pink isn't suggested for latrine cleansers due to a shading movement to violet. Benefits are finished wellbeing, non-staining, and conformance to every significant guideline (Umale and Mahanwar 2012a).

2.11.7. Toxicology and Environmental Aspects

Ultramarine colors have an exceptional well-being record. No other color has had such a long haul and far-reaching human and natural openness with next to no revealed occurrences of sick impact. The chief uses for ultramarine in prior occasions comprised an overall trial of human security since it was sold and utilized throughout the environment as an added substance for sugar, to create a brightening outcome, and as garments brightening specialist for use in the family wash. Whole populations ate sugar regularly. The use of ultramarine for whitening clothes was and still is, widespread. This represents a test of safety in human ingestion and skin contact on a grand scale. Their only known hazard is the evolution of hydrogen sulfide on contact with acid (Buxbaum and Pfaff 2005; Gerhard 2017; O'Brien 2005).

2.12. Inorganic blue pigment manufacturing material deposit in Ethiopia

The manufacturing of inorganic ultramarine blue pigment from Ethiopian geo-material, such as Soda ash (from Abbayta Lake), Sulfur (from Afar), Clay (from northern Shewa), Silica (from northern Shewa), Pitch (Hamerton, Tedaldi, and Eastaugh 2013).

2.13. Soda ash deposit in Ethiopia

Ethiopia has several sodium carbonate-bearing lakes such as Abijata, Shalla, and Chitu in the central main Ethiopian rift valley with minable reserves; and Medago,

Dillo, and Alsedo lakes in the Sidama region in south Ethiopia with small reserves. At present, soda ash mining is being carried out by Abijata-Shalla Soda Ash Share Company (ASSASC). At present, it is the only company producing soda ash in Ethiopia. A pilot processing plant was established in 1989 by the Ethiopian Mineral Resource Development Corporation (EMRDC) in line with the agreement signed with Giulini Chemie GmbH, a German-based company (Gidey and Konka 2019). Evaporating saline water from Abijata Lake produces soda ash (Na_2CO_3) for the Abijata-Shalla Soda Ash Share Company in the central Main Ethiopian Rift. Currently, 5000 tons of soda ash with a grade of around 90% are produced annually (Gidey and Konka 2019).

2.14. Sulfur deposit in Ethiopia

Because of the common occurrence of volcanoes in the Ethiopian Rift System, sulfur deposits are more numerous than has been indicated by past exploration. Jelenc (1966) listed six occurrences in Tigray, and Showa. These are, Dallol, Gombo, and Dofan. They present a large potential for sulfur deposits but up to now only it has been properly evaluated. Here the sulfur ore is estimated at 200,000 metric tons and contains 81.21% sulfur (Assefa 1985).

2.15. Clay deposit in Ethiopia

Ethiopia is well provided with industrial clay materials. Refractory bond clays and clays suitable for cement manufacturing occur in Begemeder (Chelga) and Showa (Koka), Alluvial clay deposits for the brick, tile, pottery, and pipe industry occur in Showa (Addis Ababa Area, between Debre Sina and Debre Berhan, Mullo, Karrie, and Zega Wodem), Clay materials for the manufacture of pigment occur in Begemeder and Kaffa. Ceramic clays are common in Ambo, and Showa (Assefa 1985, Tadesse, Milesi, and Deschamps 2003).

2.16. General manufacture methods of inorganic pigment

Inorganic pigments are made using a variety of mechanical and physical-chemical techniques. The procedures are designed to produce pigments with the right composition, crystal structure, and particle size (Gerhard 2017).

2.16.1. Mechanical preparation processes

In both natural and manmade inorganic pigments, mechanical methods are used. According to the principle of scattering, ideal pigments should have mean particle sizes that have the best diffuse reflection behavior. A narrow particle size distribution and the least number of agglomerates and aggregates are also desirable attributes (Gerhard 2017).

In multiple processes, the ore extracted from the gangue is crushed to the appropriate fineness. Separation stages remove the oversized grains from the fine particles, which are then recycled back into the process. Grinding and classification can be done wet or dry, depending on the material's hardness, impurities, and intended application (Gerhard 2017; Hamerton, Tedaldi, and Eastaugh 2013).

2.16.1.1. Crushing and Grinding

For coarse material crushing, two size ranges are distinguished:

- Coarse crushing, also known as breaking, continues from the size of meters down to particles of 1 to 2 cm. Breaking is done in a dry environment at all times.
- Fine crushing, also known as grinding, reduces the size of the material from 1 to 2 cm to roughly 50 μm . Grinding can be done both wet and dry.
- Pulverization produces particles with diameters ranging from 5 to 50 micrometers. Some inorganic pigments and their applications are already appropriate for this range. Wet or dry pulverization is an option (Gerhard 2017). When soluble components need to be separated or a pigment needs to be surface treated directly in suspension, wet pulverization is performed. However, drying is frequently unfavorable because agglomeration can occur. This is why disintegrating grinding is frequently used in conjunction with this technique.

2.17. Precipitation reactions

The direct synthesis of pigments using chemical procedures, particularly precipitation processes, achieves a smaller particle size distribution than grinding. Iron oxide hydroxide (iron oxide yellow), which is generated by the interaction of an iron(II) salt with sodium hydroxide and air in an aqueous solution, is an example of a pigment made directly by precipitation (Gerhard 2017).

The precipitation procedure produces a defined solid with the required color, crystal structure, morphology, and other pigment qualities without any further treatment. The precipitation circumstances that are chosen can have an impact on the features of the particles that are created. During precipitation reactions, nucleus production and crystallization are complicated processes. The pace of nuclei production is determined by the solution's relative oversaturation. The interfacial tension solid/liquid, the lattice energy, and the activation all have a role in the stability of a crystal nucleus of critical size, which means in the equilibrium between resolution and growth (Gerhard 2017).

2.18. Calcination processes

Calcination is the process of heating materials to temperatures above 200°C without applying pressure to achieve one of the following goals:

- crystallite size increase
- improving the crystal structure
- the transition from the solid-state to the liquid state
- solid-state reaction
- gas/solid reaction

Temperature, duration, and sulfur concentration are the most critical process parameters for colored inorganic pigment. The temperatures must be high enough to allow for ion mobility. They should not, however, be too high to avoid excessive particle development and sintering(Gerhard 2017). For each calcination procedure, the best furnace conditions must be found. Impurities or targeted doping can reduce annealing temperature and speed. Adding a few percent of a dopant can lower the annealing temperature by several hundred degrees Celsius (Gerhard 2017). Calcination can be done constantly or intermittently, depending on the throughput. Muffle and drum furnaces that run constantly allow for quick production adjustments (batch production). Only continuous manufacturing is suitable for rotary kilns. It is possible to fire them directly or indirectly. When a defined gas environment must be modified, indirect firing with gas or radiant heaters is used (Gerhard 2017).

2.19. Other methods

Inorganic pigments are also produced using special processes such as flux crystallization, hydrothermal methods, and gas-phase reaction(Gerhard 2017).

2.20. Ultramarine blue pigment production process

Ultramarine blue pigment is prepared from simple, relatively cheap geo-minerals typically clay, feldspar, anhydrous sodium carbonate, sulfur, and a reducing agent (oil, pitch, coal, etc.). The production of ultramarine pigments is carried out in the four steps clay activation, blending and heating of the raw materials, oxidation, and purification and drying (Gunter Buxbaum and Gerhard Pfaff 2005).

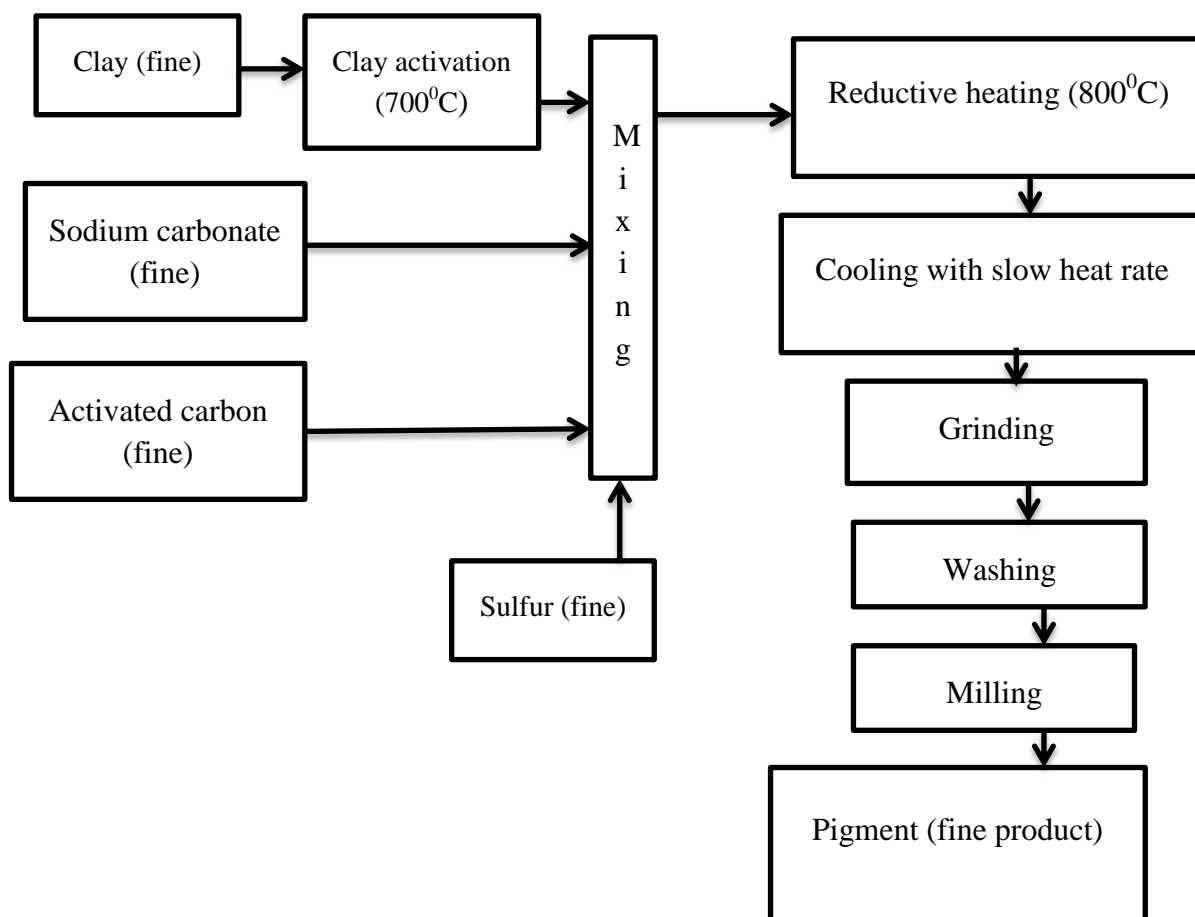


Figure 2.1 Ultramarine blue production process flow diagrams

2.20.1. Clay activation

The clay is heated to about 700°C to destabilize the kaolinite structure by removing hydroxyl ions as water. This can be either a batch process with the clay in crucibles in a directly fired kiln or a continuous process in a tunnel kiln or rotary kiln (Gerhard 2017).

2.20.2. Blending and Heating Raw Materials

The activated clay is blended with the other raw materials and dry-ground, usually in batch or continuous ball mills, to a mean size approaching 63 μm (Umali and Mahanwar 2012b).

2.20.3. Calcination of the prepared sample

Under reducing conditions, the ground mixture is heated to approximately 750 $^{\circ}\text{C}$ in a batch process. This can be done in muffle kilns or directly fired kilns with the mix in covered crucibles of regulated porosity. Solid fuel, oil, or gas can be used as a heating medium. At 300 $^{\circ}\text{C}$, sodium carbonate combines with sulfur and a reducing agent to generate sodium polysulfide. At higher temperatures, the clay lattice reforms into a three-dimensional framework, which is changed into the sodalite structure with entrapped sodium and polysulfide ions at 700 $^{\circ}\text{C}$ (Buxbaum and Pfaff 2005).

2.20.4. Oxidation

When regulated volumes of air are fed into the furnace, it is allowed to cool to around 500 $^{\circ}\text{C}$. Excess sulfur combines with oxygen to generate sulfur dioxide, which exothermically oxidizes the di- and triatomic polysulfide ions to S_2 ; and S_3 ; free radicals, resulting in sodium sulfoxides and sulfur as by-products. When the oxidation process is finished, the furnace cools and is emptied; a full kiln cycle might take several days. The "raw" ultramarine product generally comprises 75% blue ultramarine, 23% sodium sulfoxides, and 2% free (uncombined) sulfur with some iron sulfide (Buxbaum and Pfaff 2005).

2.20.5. Purification and Refinement

Purification and refining can be done in batches or continuously. To eliminate the sulfoxides, the raw blue is crushed and ground, slurred in warm water, then filtered and washed. Reslurrying and wet grinding remove sulphurous contaminants and lower the particle size of ultramarine to 0.1 - 10.0 μm . boiling or cold froth flotation is used to remove contaminants. Gravity or centrifugal separation is then used to divide the liquid into distinct particle size fractions; the remaining fine particles are retrieved using flocculation and filtering. The separated fractions are dried and degraded to produce pigment grades that differ by particle size (Gunter Buxbaum and Gerhard Pfaff 2005).

CHAPTER THREE

3. METHODS AND MATERIALS

The research was comprised of three parts. These involve:

1. Studying the chemical composition of the raw materials (Sulfur, and Clay).
2. Producing blue pigment and examining the effect of reaction temperature, reaction time, and amount of Sulfur.
3. Characterizing the chemical, physical and particular properties of the blue color.

3.1. Materials and Equipment

3.1.1. Materials

Chemicals and fundamental materials in this study considered were including Sulfur, Soda, Clay, Activated carbon, Sodium hydroxide, Hydrochloric acid, and others.

3.1.2. Equipment's

The equipment utilized in this research study are, Ball mill, Aluminum crucible, Nestle and Pastel, a Vacuum flask, Vacuum pump, Filter paper, Oven dryer, Beaker, Muffle furnace, Spatula, Analytical electronic balance, Spectrophotometer CM- 600d, XRD, and FT-IR.

3.2. Source of Raw Material

All raw materials were gathered from distinctive parts of the nation. Clay was collected from the northern region (ankober) locale. Sulfur and Soda were gathered from the remote afar region locale and Juniper Glass Industry locale, respectively.

3.3. Experimental Location

The experiments and tests were conducted at Debre Berhan University, Adama Science and Technology University, Addis Abeba Science and University, Bahirdar institute technology University, and the Ethiopian Geology Survey.

3.4. Experimental Methodology

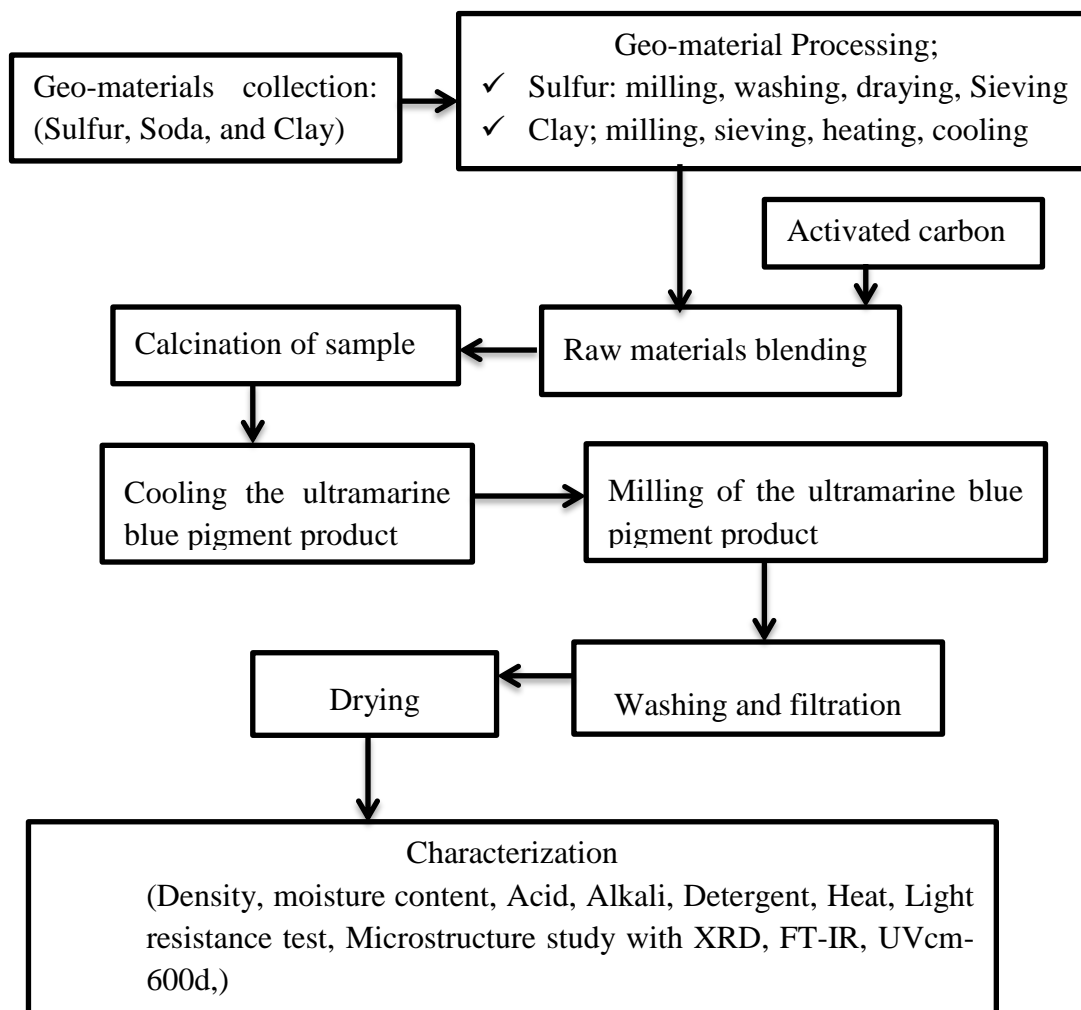


Figure 3.5 The experimental flow diagram

3.4.1. Raw materials preparation and characterization

3.4.1.1. Raw materials preparation

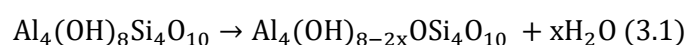
Clay and Sulfur were collected from the mineral location and physically inspected at that point were smashed, crushed, milled, and sieved independently. The finest (pan) parts of the materials were utilized for further process. Purified Soda was collected from the Juniper Glass Manufacturing Industry.

3.4.1.2. Geo-minerals characterization

The chemical composition of the clay, and sulfur, were studied by the complete silicate analysis method, respectively.

3.4.1.3. Clay activation

The clay was activated using a batch kiln process with crucible by muffle furnace. The Clay ($\text{Al}_4(\text{OH})_8\text{Si}_4\text{O}_{10}$) is transformed to meta clay ($\text{Al}_4(\text{OH})_{8-2x}\text{OSi}_4\text{O}_{10}$) by heating the clay to about 700 °C for four hours. The clay structure is destabilized by water removal and meta clay is formed.



3.5. Production of synthetic blue pigment

The synthetic ultramarine blue inorganic pigments were prepared according to the basic pigment manufacturing recipes review and manual (Hamerton, Tedaldi, and Eastaugh 2013). In this study, the experiment was conducted under the following process conditions, reaction temperature 750, 800, and 850 °C, at reaction times 4, 5, and 6 hours and Sulfur composition 20.22, 21.14, and 22.06wt %) and mass proportion was Clay (36.76 Wt %), Reducing agent (4.41 Wt %), sulfur (22.06 Wt %), and Soda (36.76wt %).

3.5.1. Blending and milling

The activated clay was blended with the other raw materials (Sulfur, Soda ash, Activated carbon), and dry ground by batch ball mills was used to obtain mean particle sizes of about below (fig 3.2) 63 μm. Figure 3.2, Shows the blended raw material.



Figure 3.1 Blended raw materials

3.5.2. Sintering (reaction) of the raw materials

The ground powder mixture was collected into a closed crucible, and heated into muffle furnace temperatures of 750,800, and 850 °C under atmospheric conditions, with the batch process for 4,5 and 6 hours.

3.5.3. Cooling

After the calcination process was finished, the crucible was opened and the electric source of the furnace was removed. The raw ultramarine blue pigment was then cooled at the rate of the furnace to cool gradually and for the further oxidation process. Then the raw ultramarine blue pigment was out from the furnace and desiccated for four days to eliminate more different sulfur radicals (different sulfur oxides and others). Figure 3.2, is shown the end product of ultramarine blue pigment.



Figure 3.2 Cooling raw ultramarine blue pigments

3.5.4. Purification of raw ultramarine blue pigment

To eliminate the unreacted sulfur and unwanted material the raw ultramarine blue was crushed and powdered, then slurred in warm distilled water, filtered, and washes repeatedly. The sulfurous impurities and some dust-like materials are released and the ultramarine particle size is reduced by wet grinding. The impurities are floated off by boiling or cold froth flotation. The purified blue pigments were dry for 24 hr. at 80C⁰. Figure 3.3, Shows the purified product of ultramarine blue inorganic pigment.



Figure 3.3 Purified ultramarine blue pigments

3.6. Product Characterization

3.6.1. Moisture content

The amount of water in the ultramarine blue inorganic pigment after it has dried to as moisture content. One gram weight of produced ultramarine blue pigment was measured into the crucible and dried using a blast dryer by adjusting the temperature at 105°C for 2 hours. After completing the drying time the pigment cool for one hour and measures the mass of pigment using electronics balance. Then the moisture content was computed based on the weight reduction (Umale and Mahanwar 2012).

$$\text{The moisture content of pigment(\%)} = \frac{w_2 - w_3}{w_2 - w_1} * 100 \quad (3.2)$$

Whereas;

Empty Crucible weight (w1), Crucible with sample before drying (w2), Crucible weight with sample after cooling (w3)

3.6.2. Resistance to heat

Resistance to the heat of pigment was evaluated according to the heating device. Heat resistance was tested up to 180°C. Measure one gram of pigment sample into Petri-dish using an electronic balance. Then measured sample was put into a 180°C adjusted blast dryer. After 24 hours the heating electrical source of the dryer was removed and the pigment cooled. The CIElab value was measured using a spectrophotometer CM-600d. Then, check the color difference value ($\Delta E_{ab}^* \leq 2$).

The color difference can be calculated as;

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \dots \dots \dots (3.3)$$

Where ΔL^* , Δa^* , Δb^* represent the difference between the before a test and after test CIElab values. Those can be calculated as;

$$\Delta L^* = L_{before}^* - L_{after}^* \dots \dots \dots (3.4)$$

$$\Delta a^* = a_{before}^* - a_{after}^* \dots \dots \dots (3.5)$$

$$\Delta b^* = b_{before}^* - b_{after}^* \dots \dots \dots (3.6)$$

3.6.3. Light resistance studies

The light resistance of the produced ultramarine blue pigment was evaluated by exposing the one gram of ultramarine blue pigment to natural sunlight at the interval of one day and measuring the color coordinates using a spectrophotometer CM-600d. After exposing the same sample produced ultramarine blue pigment to natural sunlight for six days, the color difference (ΔE_{ab}^*) was calculated from the color coordinates of the resultant treated samples and untreated samples.

3.6.4. Density determination

The density of pigment was determined according to ASTM D-153. The density of the pigment was measured by the pycnometer method at a standard temperature of 25°C and one atmospheric pressure. A pycnometer is a piece of equipment that is applicable to determine the density of the homogeneous solid object which does not dissolve in working liquid (water). First, I measured the weight of the pycnometer collectively with inserted sample (m_o+m_s), and water was added and decide the weight of M_{H_2O} (measured weight minus m_o+m_s). The extent of introduced water V'_{H_2O} was bought as;

$$V'_{H_2O} = \frac{m'_{H_2O}}{\rho_{H_2O}} \dots \dots \dots (3.7)$$

The volume of measured solid sample V_s is the difference between the volumes of water that fills the empty pycnometer V and volume V'_{H_2O}

$$V_s = V - V'_{H_2O} = \frac{m_{H_2O} - m'_{H_2O}}{\rho_{H_2O}} \dots \dots \dots (3.8)$$

The density of measured object ρ_s can be obtained

$$\rho_s = \frac{m_s}{V_s} \dots \dots \dots (3.9)$$

Whereas m_o is the mass of an empty pycnometer and m_s is the mass of the sample, ρ_s is the density of the sample, ρ_{H_2O} is the density of water.

3.6.5. Chemical resistance test

The ASTM D-4274-88 standard was used to determine acid and alkali resistance, whereas ASTM D-2248a was used to determine detergent resistance. Acid-resistant test; the ultramarine blue pigment was immersed in 5%,10%, and 15% solution of HCl(37w/w), alkali resistance test: the ultramarine blue pigment was immersed in 5%, 10,% and 15% solution of NaOH (99.6wt%), Detergent resistant test; the ultramarine blue pigment was immersed in a solution of detergent (Largo) for three days. After each of the above tests was performed the samples were dried and CIElab color value (L^* , b^* , a^*) tested using spectrophotometer CM-600d.

3.6.6. X-ray diffraction (XRD)

The structural examination was carried out by using powder X-ray diffraction. The X-ray diffraction (XRD) patterns of the calcined powders of optimum samples were taken to confirm the formation of the phase and structural identification are obtained from an X-ray powder diffractometer using Cu-K α radiation in a 2θ range of 10° to 80° . The main reason for the use of powder X-ray diffraction in this work was to investigate sample purity and crystalline structure.

3.6.7. Fourier transform infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a method for determining the qualitative and quantitative properties of IR-active compounds in organic or inorganic solid, liquid, or gas samples. It is a quick and low-cost approach for analysing crystalline, microcrystalline, amorphous, or film-like substances. Another advantage of using infrared technology is that it may offer information on the "light elements".

3.6.8. Color values

Spectrophotometer CM-600d is one of the essential devices which is applicable to measure solid-state CIElab color value (L^* , b^* , a^*). In this thesis, a spectrophotometer was used to determine the coloring value L^* , a^* , and b^* values. The lightness or darkness is determined by L^* (the higher the L^* value, the lighter the brightness, and vice versa), while the redness or greenness is determined by a^* (+ve a^* = redness and -ve a^* = greenness) and b^* indicates the yellowness or blueness (+ve b^* = yellowness and -ve b^* = blueness).

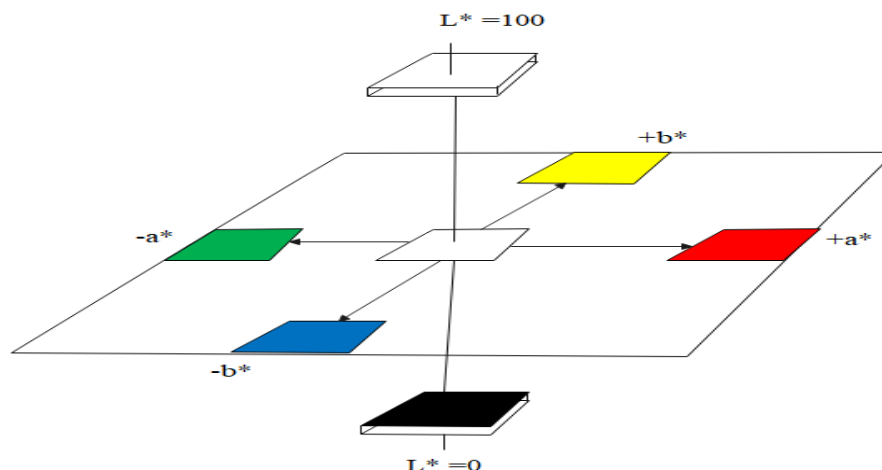


Figure 3.4 The CIElab color space system

3.6.9. Parameters effect on blue color

In this study, the factors that affect the chemical reaction of ultramarine blue pigment were examined based on the one variable at a time approach. Therefore, the reaction time ranges from 3 ½ to 7 hours, reaction temperature from 700⁰C to 950⁰C and sulfur concentrations 19.12 to 22.06Wt%. In this approach, only the effect of one variable was examined, while the others were assumed to be constant. Hence, varying the reaction time to 3 ½, 4, 4 ½, 5, 5 ½, 6, 6 ½, 7 hours and fixing the reaction temperature 800⁰C and weight of sulfur 22.06Wt%; reaction temperature varying 700,750,800,850,900,950⁰C and fixing the reaction time 5hr and weight of sulfur 22.06Wt%. In the same manner sulfur concentration varying 19.69, 20.00, 20.30, 20.59, 0.89, 21.18, 21.48, 21.77, 22.06, 22.34Wt% and fixing the reaction time 5hr and reaction temperature 800⁰C, respectively.

3.7. Statistical Design of Experiment

3.7.1. Response surface method of analysis (RSM)

For this research, I was use the response surface method of analysis with central composite by selecting three basic factors such as calcination temperature; residence time, and the composition ratio of Sulfur. The response surface method of analysis is a group of mathematical and statistical techniques useful for the analysis and modeling of problems. Central Composite design is a response surface design that apart from the 3 level factors has axial or star point and also provides high-quality predictions of linear and quadratic interaction effects of parameters that affect the process.

Therefore, in this study, I was tested the blue color strength (-b) of the pigment by performing 20 experimental runs according to design expert output.

Table 3.1 Experimental runs

| Std | Factor 1 | Factor 2 | Factor 3 | Response |
|-----|------------|--------------------------------|-------------------------|------------------|
| | A:Time(hr) | B:Temperature(⁰ C) | C: Sulfur amount (gram) | Color value (b*) |
| 1 | 4 | 750 | 55 | |
| 2 | 6 | 750 | 55 | |
| 3 | 4 | 850 | 55 | |
| 4 | 6 | 850 | 55 | |
| 5 | 4 | 750 | 60 | |
| 6 | 6 | 750 | 60 | |
| 7 | 4 | 850 | 60 | |
| 8 | 6 | 850 | 60 | |
| 9 | 3.32 | 800 | 57.5 | |
| 10 | 6.68 | 800 | 57.5 | |
| 11 | 5 | 715.91 | 57.5 | |
| 12 | 5 | 884.09 | 57.5 | |
| 13 | 5 | 800 | 53.3 | |
| 14 | 5 | 800 | 61.7 | |
| 15 | 5 | 800 | 57.5 | |
| 16 | 5 | 800 | 57.5 | |
| 17 | 5 | 800 | 57.5 | |
| 18 | 5 | 800 | 57.5 | |
| 19 | 5 | 800 | 57.5 | |
| 20 | 5 | 800 | 57.5 | |

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1. Raw Material Characterization Result

4.1.1. Sulfur composition

The chemical composition of sulfur was determined using the complete silicate analysis method. Table 4.1; shows the finding of the analysis. The Iron oxide content is low that mineral is suitable for making blue pigment production.

Table 4.1 Complete silicate analysis of local Sulfur

| Sulfur Sample | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | MnO | P ₂ O ₅ | TiO ₂ | H ₂ O | S |
|---------------|------------------|--------------------------------|--------------------------------|-------|-------|-------------------|------------------|-------|-------------------------------|------------------|------------------|-------|
| Wt% | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.34 | <0.01 | 0.15 | <0.01 | 1.76 | 82.24 |

4.1.2. Clay composition

Table 4.2; Display the result of the clay composition analysis. The clay composition has a sufficient amount of aluminum oxide and silicon dioxide for the formation of sodium aluminosilicate complex from the reaction. From the obtained color we observed that this mineral is applicable for blue color manufacturing.

Table 4.2 Complete silicate analysis of Clay

| Clay Sample | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | MnO | P ₂ O ₅ | TiO ₂ | H ₂ O | LOI |
|-------------|------------------|--------------------------------|--------------------------------|-----|------|-------------------|------------------|-------|-------------------------------|------------------|------------------|-------|
| Wt% | 56.38 | 18.34 | 1.48 | 3.1 | 0.22 | 0.8 | 3.26 | <0.01 | 0.22 | 0.09 | 5.54 | 10.96 |

4.2. Product Characterization Result

4.2.1. Moisture content

The moisture content was computed based on the weight reduction. The average sample pigment moisture content is 1.15Wt%. The calculation part is presented in appendix (7A.).

4.2.2. Heat, light, and chemical stability testing

In this research, the Ethiopian geo-material product such as clay, soda ash, sulfur, and activated carbon was used for the production of synthetic ultramarine blue pigment, and the chemical and specific properties of ultramarine blue were identified. The color

stability of the inorganic pigment is normally considered to be good when the ΔE^*_{ab} value is less than two ($(\Delta E^*_{ab}) \leq 2$), which is the industrially acceptable limit of color difference (ΔE^*_{ab}).

Table 4.3 Reference sample produced ultramarine pigment CIElab value

| Sample | L* | a* | b* |
|------------------------------------|------|-------|-------|
| Blue pigment value before the test | 36.6 | -5.95 | -12.9 |

4.2.2.1. Heat resistance

Resistance to the heat of pigment was evaluated according to the heating device. Heat resistance was tested at 180°C. The heat resistance of this blue pigment was tested by using a blast dryer oven for 24hours and measuring the CIElab value (table 4.4). In this experiment, I have seen that the appearance of blue color pigment does not change. Table 4.4, this experiment shows that the produced ultramarine blue pigment has high heat resistance. The ΔE^*_{ab} is evaluated by equation number 3.3. The ΔE^*_{ab} value is found within the standard range value of blue color ($(\Delta E^*_{ab}) \leq 2$)

Table 4.4 Heat resistance test CIElab value and color difference

| Sample | L* | a* | b* | ΔE^*_{ab} |
|--|-------|-------|--------|-------------------|
| Blue pigment value after testing at 180°C test | 36.61 | -5.94 | -12.89 | 0.017 |

4.2.2.2. Light resistance

The light resistance of the normal ultramarine blue shade was assessed from experimental information obtained parameters (Table. 4.5). The color difference value is also calculated from the CIElab value. The calculated value lay within the standard information range of blue color value.

Table 4.5 Lightness stability test result in CIElab and color difference value

| Staying time (in a day) | L* | a* | b* | ΔE^*_{ab} |
|----------------------------|-------|-------|--------|-------------------|
| 0 | 36.6 | -5.95 | -12.9 | 0.000 |
| 1 | 36.6 | -5.95 | -12.9 | 0.000 |
| 2 | 36.59 | -5.95 | -12.9 | 0.010 |
| 3 | 36.5 | 5.93 | -12.89 | 0.100 |
| 4 | 36.49 | -5.92 | -12.87 | 0.117 |
| 5 | 36.46 | -5.9 | -12.86 | 0.153 |
| 6 | 36.44 | -4.99 | -12.84 | 0.975 |

4.2.2.3. Acid resistance

ASTM D-4274-88 standards were used to determine acid resistance. The acid resistance of this synthetic ultramarine blue pigment was tested by immersing 2 grams of product in 250ml of 15%, 10%, and 5% of HCl (37w/w) solution for one hour. The acid resistance test result is shown in table 4.6, at 15% of HCl (37wt/wt) the pigment molecule dissolved and lost its color identity. The calculated color difference value has greater than the standard value. As a result, at this and higher acid concentration, the pigment has no resistance. The pigment slightly dissolves in acid at 10% of the HCl (37w/w) solution tested, and the calculated color difference value is greater than standard, implying that the pigment is not effectively resisted acid solution with this concentration. At 5% of the HCl (37w/w) solution test, the pigment has not dissolved in the acid solution and no color change was observed the calculated color difference value was also under the standard one.

Table 4.6 Acid resistance test CIElab value and the color difference value

| Acid test concentration | L* | a* | b* | ΔE^*_{ab} |
|-------------------------|-------|-------|--------|-------------------|
| 5% con. of HCl | 37.4 | -4.9 | -11.99 | 1.477 |
| 10% con. of HCl | 38.01 | -4.82 | -11.61 | 2.22 |
| 15% con. of HCl | 39.63 | -4.68 | -11.32 | 3.645 |
| | | | | |

4.2.2.4. Alkali resistance

ASTM D-4274-88 standards were used to determine alkali resistance. The alkali resistance of this synthetic ultramarine blue pigment was tested by pouring two grams of this ultramarine blue pigment into a 250ml NaOH solution for one hour. The result table 4.7 shows that at 5% NaOH (99.6%) solution the pigment was not dissolved by alkali solution and the calculated color difference value has under industrial standard, this indicates that the pigment resistance to alkalis on this concentration and also at 15% and 10% NaOH (99.6%) alkali solution test shown that negligible effect on pigment material and the calculated color difference is under the industrial standard. Generally, I had concluded that those concentrations of alkali solution the pigment have not been affected.

Table 4.7 Alkali resistance test CIElab and the color difference value

| Alkali resistance test concentration | L* | a* | b* | ΔE^*_{ab} |
|--------------------------------------|-------|-------|--------|-------------------|
| 5% con. Of NaOH | 36.62 | -5.87 | -12.88 | 0.085 |
| 10% con. of NaOH | 36.64 | -5.87 | -12.87 | 0.12 |
| 15% con. of NaOH | 36.65 | -5.85 | -12.85 | 0.13 |

4.2.2.5. Detergent resistance

ASTM D-2248a standard was used to determine detergent resistance. The detergent has a low alkali concentration; due to this reason, the result of this test was not changed. From table 4.8, we see that the ΔE^*_{ab} value is less than two ($\Delta E^*_{ab} \leq 2$) which indicates that under standard, the pigment has resistant to detergent.

Table 4.8 Detergent-resistant tests CIElab and the color difference value

| Sample | L* | a* | b* | ΔE^*_{ab} |
|---|-------|-------|-------|-------------------|
| Blue pigment value after detergent test | 36.61 | -5.95 | -12.9 | 0.01 |

4.2.3. Density

The density of the pigment was measured by the pycnometer method at a standard temperature of 25°C and one atmospheric pressure. Appendix 7B, contains the detailed calculation, the calculated density of the pigment is 2.54g/cm⁻¹.

4.2.4. X-ray diffraction result

The crystalline nature and phase purity of the synthesized ultramarine blue pigments were characterized by powder X-ray diffraction (XRD). The intense and sharp diffraction peaks reveal the crystalline nature of ultramarine blue pigments ($\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$). Synthetic ultramarines have a sodalite-cubic crystal structure. Figure.4.1 shows the XRD patterns of produced ultramarine blue pigment calcined under different conditions. The crystalline nature of this ultramarine blue pigment shown from XRD data using matches application has a cubic sodalite structure.

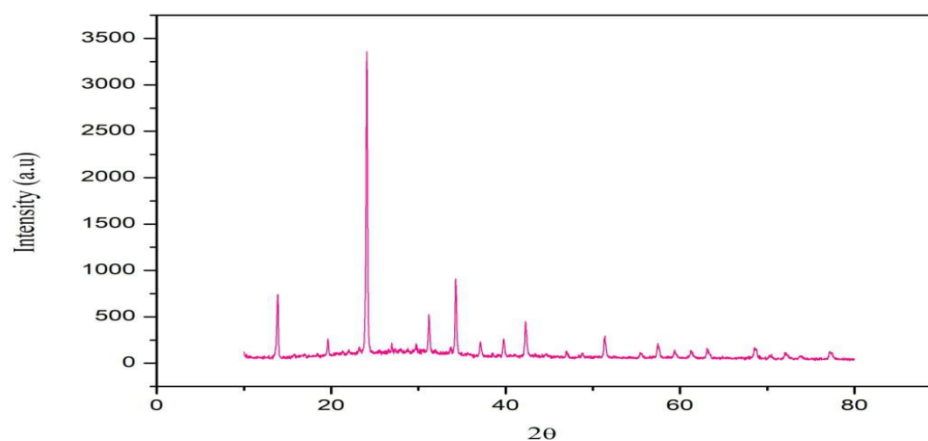


Figure 4.1 XRD pattern of ultramarine blue

4.2.5. Fourier transform infrared spectroscopy

Table 4.2 shows the Strong broad band ultramarine blue pigment is dominated due to the stretch of the Si-O-Si bond; these regions are regions 1146 and 1013 cm^{-1} . Less intense spectrum bands are in the region of $706, 656$, and 466 cm^{-1} , which may be related to the Si-OH stretch. The weak broad band of ultramarine blue pigment is in the region of 1626 cm^{-1} , this happens due to O-H bending. The highest broad absorption at 3450 cm^{-1} is due to hydroxyl groups (Si-OH groups) or from water.

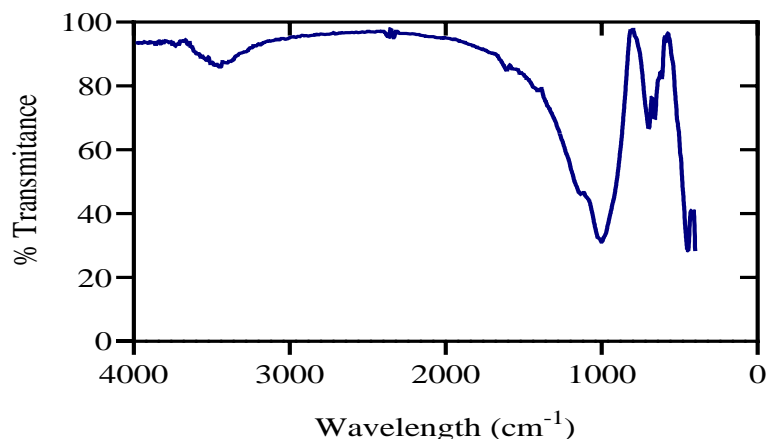


Figure 4.2 FT-IR ultramarine blue pigment

4.3. The influence of parameters on pigment coloring value

In this thesis reaction time, reaction temperature, and the amount of sulfur in a given formulation were the main parameters for the production of ultramarine blue pigment. The reaction time is needed to complete the reaction, reaction temperature used to achieve respective activation energy of a reaction, and sulfur amount are also the main for blue coloring of pigment.

4.3.1. Time influence on pigment blue coloring value (b^*)

To assess the more negative value of correlation coordinate (b^*), the major influence of contact time on blue coloring value (b^*) was investigated. The experiment's goal is to determine the time at which the pigment's minimum negative b^* value occurs. The coloring coordinate value ($-b^*$ value) decreased from 3 1/2 to 5 1/2 hours, or the b^* value decreased from $b^* = -5.4$ to -12.99 . When the time is increased from 6 to 7 hours, the blue coloring (b^*) value decreases from -10.87 to -6.78 , indicating that as the time increases, the pigment loses its coloring identity.

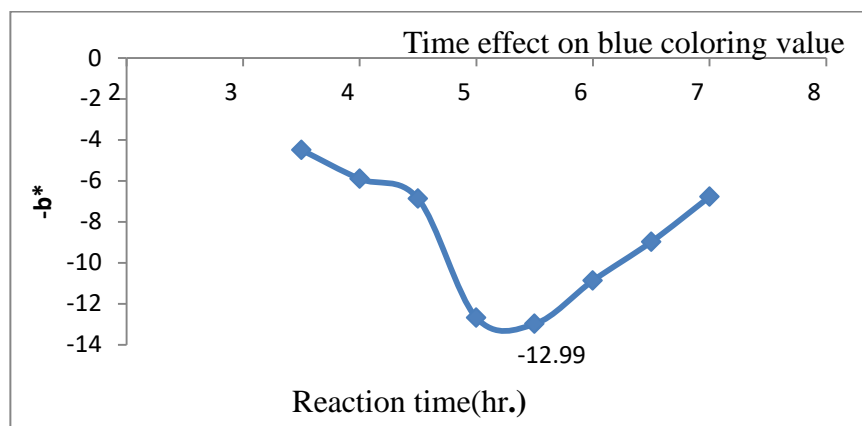


Figure 4.3 Reaction time effect on coloring value (b^*), reaction temperature 800°C , sulfur amount (22.06wt %)

4.3.2. Sulfur amount influences pigment blue coloring value (b^*)

The concentration of sulfur had a significant effect on the blue coloring value (b^*). The obtained result is depicted in graph Figure 4.3. The result showed that increasing the sulfur amount (Wt % in raw sample pigment from 19.69 to 22.06 decreased the blue coloring (b^*) value pigment from -4.98 to -13.02 and after this become constant. This result demonstrates that as the sulfur amount increases, the blue coloring effect becomes more pronounced. As a result, sulfur is the primary linear parameter influencing the blue coloring of ultramarine blue pigment.

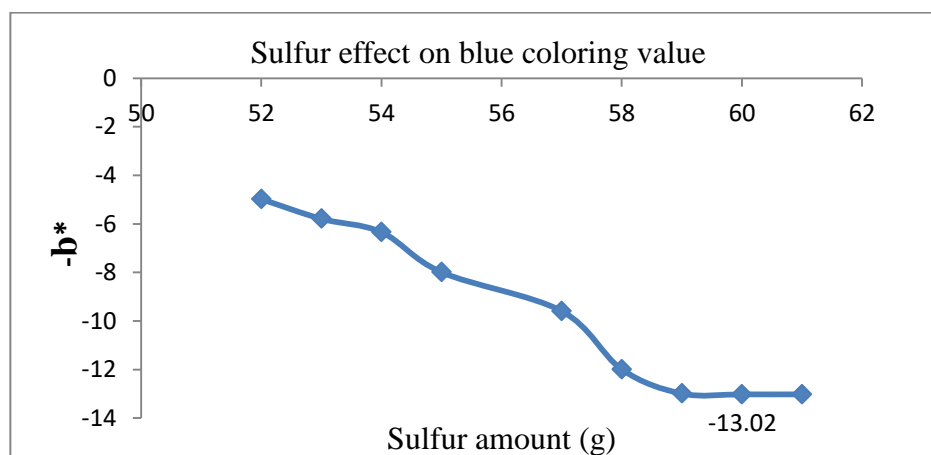


Figure 4.4 Sulfur amount effect on coloring value (b^*), reaction temperature 800°C , reaction time 5hr.

4.3.3. Temperature influence on pigment blue coloring value (b*)

The blue coloring value (b*) was significantly affected by the reaction temperature. The obtained result is shown in graph Figure 4.4, and it shows that as the reaction temperature increases from 700 to 850 °C, the result of blue coloring (b*) value decreases from -3.2 to -12.79, and above 900°C temperature, the result of coloring b* value becomes positive (1.01), indicating that at high temperatures, the pigment loses its chemical identity.

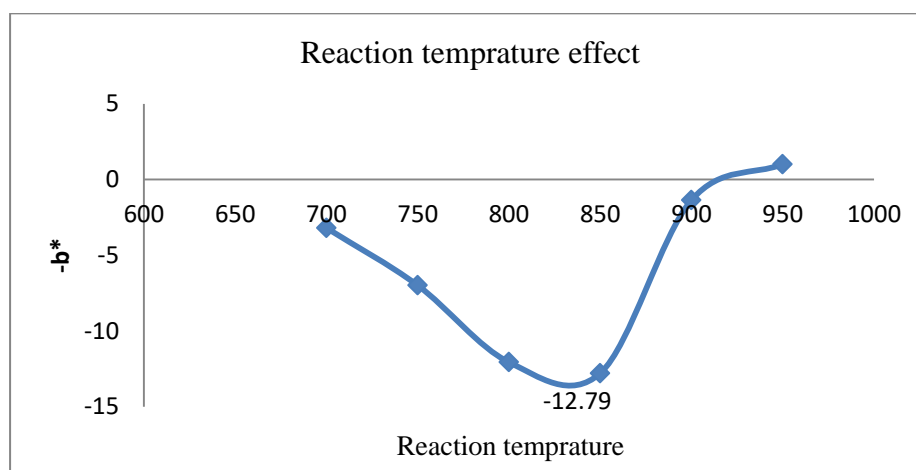


Figure 4.5 Reaction temperature effect on coloring value (b*), reaction time 5hr, sulfur amount (22.06wt %)

4.4. Statistical Design of Experiments (DOE) Result

4.4.1. Response surface method of analysis (RSM)

In this research design expert (response surface method analysis with central composite) was used for modeling statistical analysis and optimization of significant parameters reaction time, reaction temperature, and sulfur amount for the production of ultramarine blue pigment. To investigate the optimal level and therefore the influence of every parameter in the blue coloring strength study was made by batch type solid-state calcination process using a muffle furnace. However, 20 run experiments were performed using central composite design (CCD) to determine the maximum blue coloring strength or minimum blue coloring value (-b*) and optimization of those parameters conducted with design expert 7.0 (trial version) the result that generated from CCD are listed as table 4.10, below. Hence, in this paper, the design expert analysis was performed using the blue coloring response value (b*) because blue coloring value (b*) is the major measuring parameter of blue color ultramarine

pigments but the other parameters measure the lightness value (L*) and greenness value (a*)

Table 4.10 Experimental runs CIElab value

| Std | Factor 1 | Factor 2 | Factor 3 | Response |
|-----|------------|-------------------|-------------------------|------------------|
| | A:Time(hr) | B:Temperature(0C) | C: Sulfur amount (gram) | Color value (b*) |
| 1 | 4 | 750 | 55 | -5.59 |
| 2 | 6 | 750 | 55 | -7.72 |
| 3 | 4 | 850 | 55 | -9.45 |
| 4 | 6 | 850 | 55 | -9.94 |
| 5 | 4 | 750 | 60 | -8.48 |
| 6 | 6 | 750 | 60 | -10.7 |
| 7 | 4 | 850 | 60 | -10.16 |
| 8 | 6 | 850 | 60 | -10.77 |
| 9 | 3.32 | 800 | 57.5 | -5.4 |
| 10 | 6.68 | 800 | 57.5 | -9.26 |
| 11 | 5 | 715.91 | 57.5 | -5.09 |
| 12 | 5 | 884.09 | 57.5 | -9.88 |
| 13 | 5 | 800 | 53.3 | -9.78 |
| 14 | 5 | 800 | 61.7 | -12.88 |
| 15 | 5 | 800 | 57.5 | -12.9 |
| 16 | 5 | 800 | 57.5 | -11.99 |
| 17 | 5 | 800 | 57.5 | -12.87 |
| 18 | 5 | 800 | 57.5 | -12.9 |
| 19 | 5 | 800 | 57.5 | -12.9 |
| 20 | 5 | 800 | 57.5 | -12.9 |

4.4.2. Analysis of variance (ANOVA)

In this research, the experiment results analysis was done by using analysis of variance with quadratic regression model analysis of the significant model term. To determine whether or not the quadratic model is significant, it is needed to perform an analysis of variance (ANOVA). The probability (P-values) values were used as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. F-value is a test for comparing model variance with (error) variance. It is calculated by a model mean square divided by a residual mean square. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. Table 4.11, shows the

smaller the P-values are the significance of the corresponding coefficient the bigger p-value also the opposite one.

Table 4.11 ANOVA for response surface quadratic model

| Source | Sum of Squares | df | Mean Square | F-Value | P-value | |
|-----------------|----------------|----|-------------|---------|----------|-----------------|
| | | | | | Prob > F | |
| Model | 124.93 | 9 | 13.88 | 41.69 | < 0.0001 | significant |
| A-time | 10.44 | 1 | 10.44 | 31.36 | 0.0002 | |
| B-temperatures | 18.48 | 1 | 18.48 | 55.5 | < 0.0001 | |
| C-sulfur amount | 11.67 | 1 | 11.67 | 35.04 | 0.0001 | |
| AB | 1.32 | 1 | 1.32 | 3.97 | 0.0745 | |
| AC | 5.51E-03 | 1 | 5.51E-03 | 0.017 | 0.9002 | |
| BC | 2.34 | 1 | 2.34 | 7.04 | 0.0242 | |
| A ² | 45.7 | 1 | 45.7 | 137.26 | < 0.0001 | |
| B ² | 42.93 | 1 | 42.93 | 128.94 | < 0.0001 | |
| C ² | 1.94 | 1 | 1.94 | 5.82 | 0.0366 | |
| Residual | 3.33 | 10 | 0.33 | | | |
| Lack of Fit | 2.65 | 5 | 0.53 | 3.88 | 0.0814 | not significant |
| Pure Error | 0.68 | 5 | 0.14 | | | |
| Cor Total | 128.26 | 19 | | | | |

In this research the Model F-value was 41.69 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, BC, A₂, B₂, and C₂ are significant model terms, values greater than 0.1000 indicate the model terms are not significant.

Table 4.12 Correlation coefficient (R²) for blue coloring value

| | | | |
|-----------|--------|----------------|--------|
| Std. Dev. | 0.58 | R-Squared | 0.974 |
| Mean | -10.08 | Adj R-Squared | 0.9507 |
| C.V. % | 5.73 | Pred R-Squared | 0.836 |
| PRESS | 21.03 | Adeq Precision | 20.279 |

The quality of the model developed was evaluated based on the coefficient, R² value. The model developed seems to be the most effective at high R² statistics which are closer to unity because it will give a predicted value closer to the actual value for the

response. During this experiment, the R^2 value was 0.974 which is closer to unity, the "Pred R-Squared" of 0.836 is in reasonable agreement with the "Adj R-Squared" of 0.9507, "Adeq Precision" measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio is also 20.279 which indicates an adequate signal. Therefore, this model can be used to navigate the design space.

4.4.3. Development of regression equation

The results of blue coloring value (b^*) from the interaction of the three main process factors sulfur amount, reaction temperature, and reaction time was used for the model generation. A second-order quadratic regression was performed to estimate the response function as a second-order polynomial after the examination of the model fit summary revealed that a quadratic model was statistically significant for the response (CIElab) value. The resulting model equation which expresses the relationship between the interactions of the blue coloring factors and the response CIElab value (b^*) is shown below in terms of coded values and terms of actual factors.

The final empirical model Equation in Terms of Coded Factors for blue coloring of pigment can be written as follow:

Final Equation in Terms of Coded Factors:

$$b^* = -12.72 - 0.87 * A - 1.16 * B - 0.92 * C + 0.54 * B * C + 1.78 * A^2 + 1.73 * B^2 + 0.37 * C^2 \dots \dots \dots (4.0)$$

From this equation, the negative coefficient value indicated that negatively affects blue coloring while positive coefficient values represent the factors' positive relationship to blue coloring.

Final Equation in Terms of Actual Factor

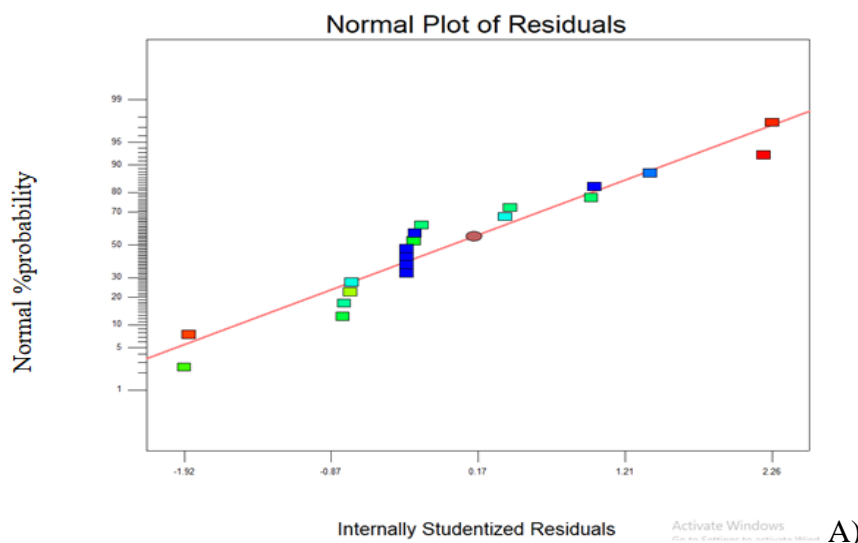
$$b^* = +940.50468 - 24.57895 * A - 1.41752 * B - 10.52695 * C + 4.33000E - 003 * B * C + 1.78083 * A^2 + 6.90411E - 004 * B^2 + 0.058658 * C^2 \dots \dots \dots (4.1)$$

4.4.4. Model diagnoses

Model diagnostic plots are the graphical summarise for case statistics. The plots of residuals showed how well the model satisfies the residual assumptions of the analysis of variance. Different model diagnostics were plotted (selected cause statistics) from

the view menu. To compare the plot distribution (the straight line) was using a normal probability plot of standardized residual.

- The normal probability plot shows whether the residuals have a normal distribution and, as a result, follow the straight line. Expect some scatter even with normal data. The normal probability plot of standardized residual was plotted in Figure 4.5 (A); the data as shown from the graph are distributed normally close to the diagonal line. So, this implies no apparent problem.
- The residuals Vs expected response values have been examined to see if the assumption of constant variance is correct. A random scatter plot should be used (constant range of residuals across the graph). Figure 4.5 (B), shows the standardized plot residuals versus predicted (run 'number) was tested to check for constant errors and therefore the residuals were scattered.
- Figure 4.5 (C) shows the standardized plot residuals versus run numbers were tested to check for constant errors and therefore the residuals were scattered. The plot shows a random scatter. Trends indicate a time-related variable lurking in the background. Blocking and randomization provide insurance against trends ruining the analysis.
- The purpose of predicted response values versus the actual response values is to detect a value, or group of values, that are not easily predicted by the model. Figure 4.5(D), shows the experimental values for CIE value (b^*) versus the predicted value. The developed model was quite close to the experimental values which indicated that the model is well-fitted.



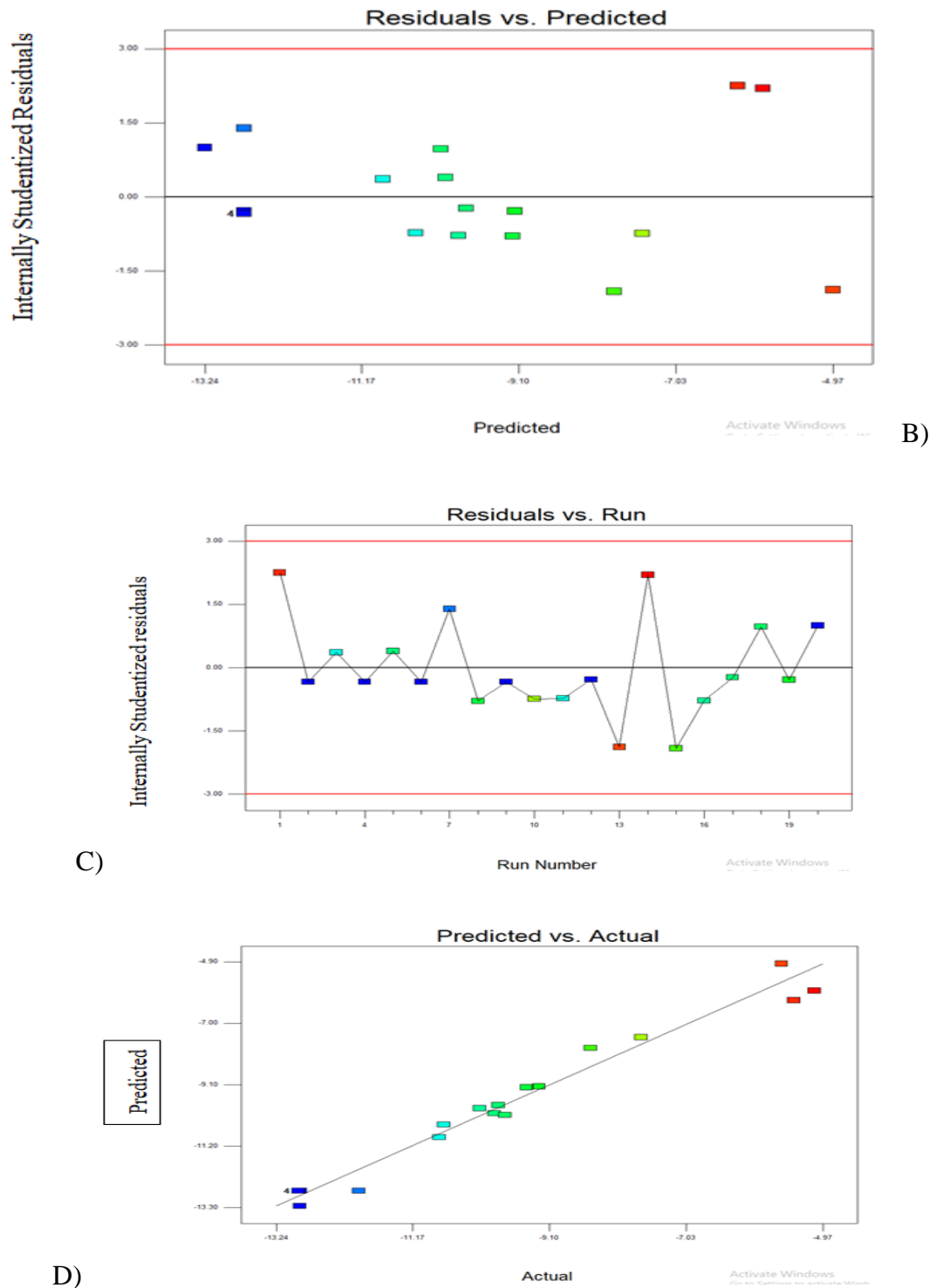


Figure 4.6 Model diagnose plot, A) actual Vs residual plot, B) residuals versus predicted plot C) residuals versus run plot, D) CIE value (b^*) versus predicted.

4.4.5. Interaction effect of the process variables

The residual diagnosis reveals no statistical problem, so now let's generate response surface plots. For the graphical interstation of the interactions, the use of countered and three-dimension regression model is highly recommended for significant effect factors on ultramarine blue pigment. Such a three-dimensional surface can provide useful information about the behavior of the system within the experimental design; facilitate an examination of the effect of the experimental factors on the response and the interaction effect between the independent factors.

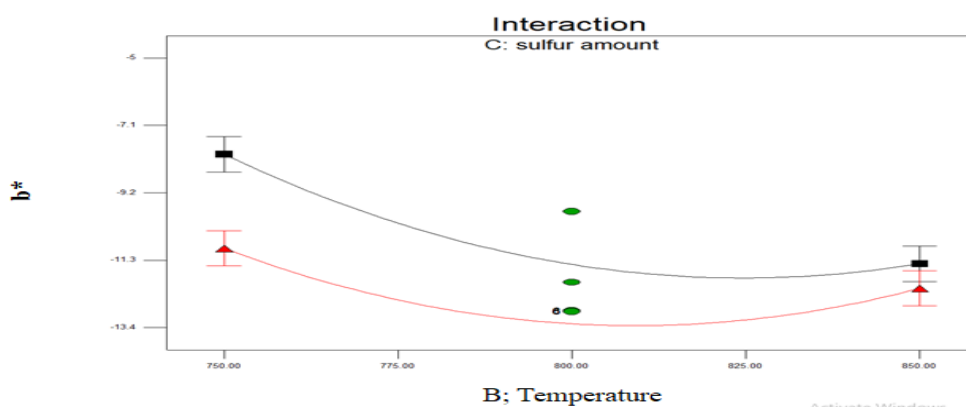


Figure 4.7 The interaction effect of sulfur amount and reaction temperature

4.4.6. The combined effect of reaction temperature and sulfur amount on blue coloring value (-b*)

The combined effect of reaction temperature and Sulfur amount on blue coloring value (-b*) at the constant time (4hr and 52 mint) is shown in figure 4.7. It can be seen that the minimum requiring blue coloring value $b^* = <-8.89$ was achieved. From this, it had been observed that the blue coloring value decreased with the increasing Sulfur amount (Wt %), and reaction temperature also affect the compilation reaction of pigment raw material.

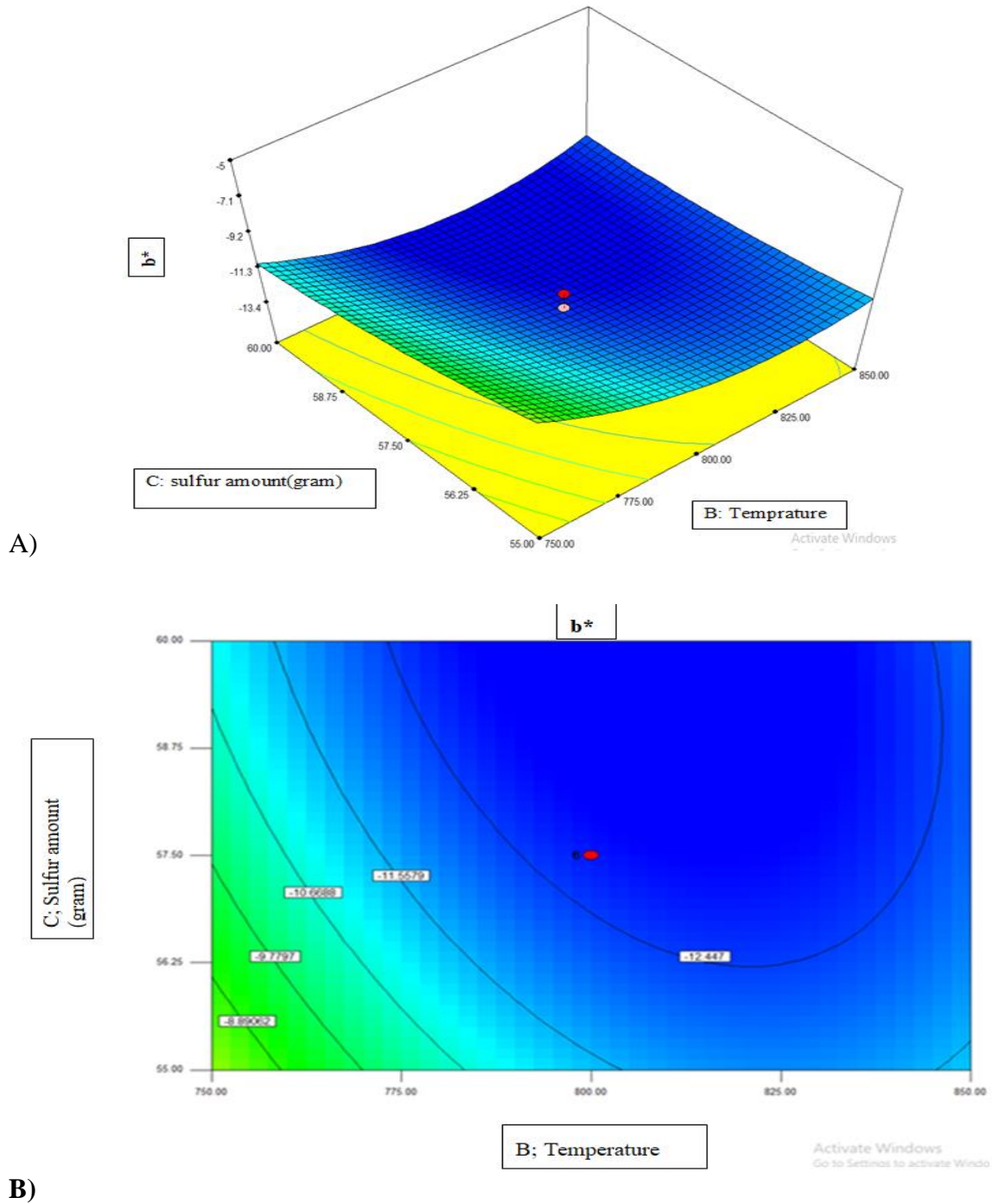


Figure 4.8 Combined Effect of Reaction Temperature and Sulfur Amount on Blue Coloring Value ($-b^*$) A) 3D plot, b) counterplot

4.4.7. Validation of the developed model

Model validation or the experimental confirmation is the final step within the optimization process using the response surface model. To confirm the optimization result, an experiment was performed under the predicted condition with the very best desirability (1) selected to be verified. The predicted and experimental results of the blue color ($-b^*$) value obtained at optimum conditions are listed in table 4.13. The optimum blue coloring value was obtained at optimum using reaction time, reaction temperature, and sulfur amount. It had observed that the experimental value (-13.02) obtained was in good agreement with the value predicted (-13.13) from the model, with a relatively small error between the predicted and the actual value, which was only 0.11 indicating that the regression quadratic model was valid and accurate in predicting the response. The desirability ramp for the optimization of the response and also the variables are shown in the appendix fig (7.1).

Table 4.13 Optimum condition and model validation

| Time(hr.) | Temperature(°C) | Sulfur amount (g) | Blue coloring value(-b*) | |
|---------------------|---------------------|-------------------|--------------------------|--------------|
| | | | Predicted | Experimental |
| 4.87(4:52.2 hr.) | 799.84 | 60 | -13.1315 | -13.02 |

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this study, the production of ultramarine blue pigment from locally available raw materials, such as soda ash, sulfur, clay, and activated carbon had been investigated based on the batch-type solid-state calcination method. The prepared ultramarine blue pigment was characterized by physical, chemical, and microstructure analysis such as moisture content, heat resistant, light-resistant, acid resistant, alkali resistant, detergent, crystalline structure, functional group and density were determined. The blue coloring value (b^*) influenced process parameters where reaction time, reaction temperature, and sulfur amount (Wt %) were examined; the reaction time was increased from 3 ½ to 7 hours. The blue coloring value became progressively more negative b^* value from 3 1/2 to 5 1/2 hours (b^* value -4.49 to -12.99) and above 5 ½ hours the blue coloring was less negative, in this study the reaction temperature highly affected on blue coloring value (b^*). When the temperature increases from 700 to 850 °C the more blue value or more negative blue coloring b^* value becomes decreased from -3.2 to -12.79 and increase the coloring value at 950 °C ($b^*=1.01$), this indicates that at 950 °C temperature the pigment loses its chemical and physical identity. The sulfur amount is also a highly affecting parameter in the ultramarine blue production process. In this study, whenever the sulfur amount (Wt %) increases from 19.69 to 22.06 Wt% the blue coloring value (b^*) becomes more negative the value decrease from -4.98 to 13.02, and above this sulfur composition coloring value becomes constant.

The developed mathematical modelling for the production of blue ultramarine blue pigment using design experiments appears to be an effective tool for prediction and understanding of interaction effect between factors. The optimal ultramarine blue was obtained as reaction time, reaction temperature, and sulfur amount (Wt %), and this was found to be 4.87 hours (4 and 52 min), 799.84 °C, and 22.06 w% respectively. Therefore the optimum deep blue coloring value becomes reaches ($b^*=-13.02$).

5.2. Recommendation

From this study Production of ultramarine blue from locally available Ethiopian raw materials such as soda ash, activated carbon (reducing agent) sulfur, and kaolin had been shown to have the potential to produce this ultramarine blue pigment in our country. Thus, in the next study, the following works should be explored the production of ultramarine blue pigment from local raw materials.

- I. In this study hiding power and tinting, strength tests were not checked due to the lack of laboratory in our country (color strength detecting spectrophotometer) so, for the next study those characteristics would need to investigate.
- II. The study should continue with final objective of establishing a plot plant and manufacturing with a collaboration of investors.

6. REFERENCES

- Assefa, Getaneh. 1985. "Future Prospects." *The mineral industry of Ethiopia: present conditions and future prospects GETANEH* 3(3): 341–45.
- Buxbaum, Gunter, and Gerhard Pfaff. 2005. *Industrial Inorganic Pigments: Third Edition Industrial Inorganic Pigments: Third Edition*.
- Divya, S. 2017. *Synthesis , Characterization and Optical Properties of Blue and Green Inorganic Pigments for Coloring Applications Thesis Submitted to Cochin University of Science and Technology*.
- Dp-, Plot N O, and Saykha Estate. "Of Proposed Project for Manufacturing of Pigments of M / s . Nirva Pigments."
- Gerhard, Pfaff. 2017. 3 Inorganic pigments *Inorganic Pigments*.
- Gidey, Berihu, and Bheemalingeswara Konka. 2019a. "Challenges Associated with Quality of Soda Ash, Abijata Lake, Central Main Ethiopian Rift, Ethiopia Berihu." *Momona Ethiopian Journal of Science* 11(1): 124.
- 2019b. "Challenges Associated with Quality of Soda Ash , Abijata Lake , Central Main Ethiopian Rift , Ethiopia." 11(1): 124–39.
- Gunter Buxbaum and Gerhard Pfaff. 2005. *Also of Interest : High Performance Pigments Paints , Coatings and Solvents Industrial Organic Pigments Automotive Paints and Coatings Color Chemistry Industrial Color Testing*.
- Hamerton, Ian, Lauren Tedaldi, and Nicholas Eastaugh. 2013. "A Systematic Examination of Colour Development in Synthetic Ultramarine According to Historical Methods." *PLoS ONE* 8(2).
- Jose, Sheethu, Deepak Joshy, Soumya B. Narendranath, and Pradeepan Periyat. 2019. "Recent Advances in Infrared Reflective Inorganic Pigments." *Solar Energy Materials and Solar Cells* 194(January): 7–27. <https://doi.org/10.1016/j.solmat.2019.01.037>.
- KIKUCHI, Takeshi. 2015. "PREPARATION OF NOVEL AZO PIGMENTS AND

CLARIFICATION OF THE EMITTING STATE OF A UNIQUE FLUORESCENT PIGMENT.” 1(September): 2–10.

Kumari, Sandhya. 2012. “Synthesis, Characterization and Optical Properties of Rare Earth – Transition Metal Based Environmentally Friendly Red and Yellow Pigments.” : 190.

Müller, Bodo, and Ulrich Poth. 2007. 36 Pigment & Resin Technology *Coatings Formulation*.

O’Brien, Duncan Lee John. 2005. “Preparation of Environmentally-Friendly Inorganic Pigments.”

Shinohara, Atsushi. 2017. 71 IRYO - Japanese Journal of National Medical Services *Role of Regional Medical Support and Collaboration Center in Regional Medical Care Support Hospitals*.

Tadesse, Solomon, Jean Pierre Milesi, and Yves Deschamps. 2003. “Geology and Mineral Potential of Ethiopia: A Note on Geology and Mineral Map of Ethiopia.” *Journal of African Earth Sciences* 36(4): 273–313.

Umale, Shweta, and Prakash Mahanwar. 2012a. “Characterization and Application of Naturally Occurring Mineral Based Pigment in Surface Coating.” 2012(November): 1101–7.

2012b. “Characterization and Application of Naturally Occurring Mineral Based Pigment in Surface Coating.” *Journal of Minerals and Materials Characterization and Engineering* 11(11): 1101–7.

7. APPENDIX

A. Moisture content determination (%)

Trail one

Crucible weight (w1) =40.063

Crucible with sample (w2) =41.063

Result after cooling

Crucible weight with sample (w3) =41.052

Trail two

Crucible weight (w1) =40.134

Crucible with sample (w2) =41.134

Result after cooling

Crucible weight with sample (w3) =41.035

$$\text{moisture content\% in the trail (1)} = \frac{w_2 - w_3}{w_2 - w_1} * 100$$

$$= \frac{41.063 - 41.052}{41.063 - 40.063} * 100 = 1.1\%$$

$$\text{moisture content\% in trail (2)} = \frac{w_2 - w_3}{w_2 - w_1} * 100$$

$$\frac{41.134 - 41.122}{41.06 - 40.063} * 100\% = 1.2\%$$

$$\text{Average moisture content (\%)} = \frac{\text{trail (1)} + \text{trial (2)}}{2} = 1.15\%$$

B. Density determination (g/cm³)

mass of sample, $m_s = 1.5\text{gram}$

Mass of pycnometer with the sample, $m_o + m_s = 18.5\text{gram}$

Total mass with distilled water, $m_o + m_s + m'_{H_2O} =$

42.86 Mass with distilled water, $m'_{H_2O} = 42.86 - m_o + m_s = 24.362$

$$V'_{H_2O} = \frac{m'_{H_2O}}{\rho_{H_2O}} = \frac{24.362\text{g}}{0.998 \frac{\text{g}}{\text{cm}^3}} = 24.41\text{cm}^3$$

The volume of pycnometer $V = 25\text{cm}^3$

Volume of sample $V_s = 25 - 24.41 = 0.59\text{cm}^3$

$$\text{Density of sample, } \rho_s = \frac{m_s}{V_s} = \frac{1.5\text{g}}{0.59\text{cm}^3} = 2.54\text{g/cm}^3$$

Table 7.1 Amount of Sulfur influence on coloring value

| Amount Sulfur | b* value |
|---------------|----------|
| 52 | -4.98 |
| 53 | -5.79 |
| 54 | -6.34 |
| 55 | -7.99 |
| 57 | -9.59 |
| 58 | -11.99 |
| 59 | -12.99 |
| 60 | -13.02 |
| 61 | -13.02 |

Table 7.2 Time influence on coloring value

| Time | b* value |
|-------|----------|
| 3 1/2 | -4.49 |
| 4 | -5.9 |
| 4 1/2 | -6.87 |
| 5 | -12.68 |
| 5 1/2 | -12.99 |
| 6 | -10.87 |
| 6 1/2 | -8.98 |
| 7 | -6.78 |

Table 7.3 Temperature influence on coloring value

| Temperature | b* value |
|-------------|----------|
| 700 | -3.2 |
| 750 | -6.99 |
| 800 | -12.06 |
| 850 | -12.79 |
| 900 | -1.36 |
| 950 | 1.01 |

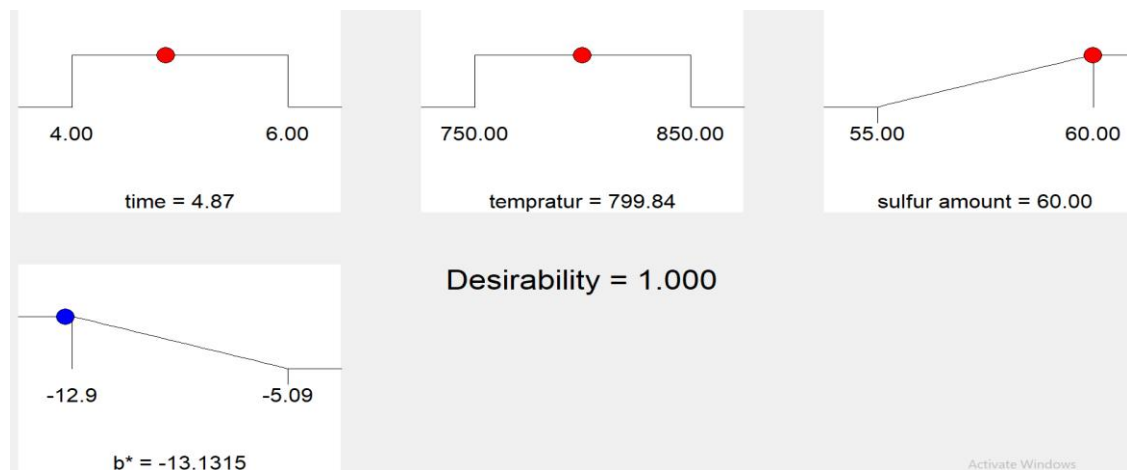


Figure 7.1 Numerical optimization results

Table 7.4 Sequential Model Sum of Squares [Type I]

| Sequential Model Sum of Squares [Type I] | | | | | | |
|--|---------|----|---------|-------|----------|-----------|
| Sum of | Mean | F | p-value | | | |
| Source | Squares | Df | Square | Value | Prob > F | |
| Mean Vs Total | 2031.32 | 1 | 2031.32 | | | |
| Linear Vs Mean | 40.59 | 3 | 13.53 | 2.47 | 0.0993 | |
| 2FI Vs Linear | 3.67 | 3 | 1.22 | 0.19 | 0.9018 | |
| Quadratic Vs 2FI | 80.67 | 3 | 26.89 | 80.76 | < 0.0001 | Suggested |
| Cubic Vs Quadratic | 1.38 | 4 | 0.34 | 1.06 | 0.4514 | Aliased |
| Residual | 1.95 | 6 | 0.33 | | | |
| Total | 2159.58 | 20 | 107.98 | | | |

Table 7.5 Lack of Fit Tests

| Lack of Fit Tests | | | | | | |
|-------------------|---------|----|---------|-------|----------|-----------|
| Sum of | Mean | F | p-value | | | |
| Source | Squares | df | Square | Value | Prob > F | |
| Linear | 86.99 | 11 | 7.91 | 58 | 0.0002 | |
| 2FI | 83.32 | 8 | 10.41 | 76.39 | < 0.0001 | |
| Quadratic | 2.65 | 5 | 0.53 | 3.88 | 0.0814 | Suggested |
| Cubic | 1.27 | 1 | 1.27 | 9.31 | 0.0284 | Aliased |
| Pure Error | 0.68 | 5 | 0.14 | | | |

Table 7.6 Model Summary Statistics

| Std. | Adjusted | Predicted | Column1 | Column2 | Column3 | Column4 |
|-------------|-----------------|------------------|----------------|----------------|----------------|----------------|
| Source | Dev. | R-Squared | R-Squared | R-Squared | PRESS | |
| Linear | 2.34 | 0.3165 | 0.1883 | -0.0067 | 129.12 | |
| 2FI | 2.54 | 0.3451 | 0.0428 | -0.3397 | 171.83 | |
| Quadratic | 0.58 | 0.974 | 0.9507 | 0.836 | 21.03 | Suggested |
| Cubic | 0.57 | 0.9848 | 0.9518 | -1.1904 | 280.94 | Aliased |



Figure 7.2; Laboratory Equipment Figure