Formulation of chlorinated rubber-based traffic marking paint and evaluation of Nano-TiO_2/AMRS composite for its photocatalytic self-cleaning property

By

Yordanos Abay Lema

A Thesis Submitted to the Department of Chemical Engineering School of Mechanical, Chemical and Materials Engineering

Presented for the Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

Adama, Ethiopia

April, 2021

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APPROVAL OF THE BOARD OF EXAMINERS

We, the undersigned, members of the board examiners of the final open defense by Yordanos Abay Lema, have read and evaluated her thesis entitled "**Formulation of chlorinated rubber-based traffic marking paint and evaluation of Nano-TiO_2/AMRS composite for its photocatalytic self-cleaning property**" and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirement of the degree of masters in chemical engineering.

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DECLARATION

I hereby declare that this thesis entitled "**Formulation of chlorinated rubber-based traffic marking paint and evaluation of Nano-TiO_2/AMRS composite for its photocatalytic self-cleaning property**" has been carried out by Yordanos Abay Lema, with the guidance of Dr. Tatek Temesgen and Dr. Melaku Tesfaye. The information derived from the literature has been duly acknowledged in the text and a list of references provided. This work has not been submitted for any other degree or professional qualification.

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
ANOVA	Analysis of variance
$CaCO_3$	Calcium carbonate
CPVC	Critical pigment volume concentration
DTA	Differential Thermal Analysis
EDS/EDX	Energy Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
ISO	International Organization for Standardization
PVC	Pigment volume concentration
KU	Kerb unit
SEM	Scanning electron microscope
SiO_2	Silicon dioxide
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
WHO	World Health Organization
XRD	X-ray diffraction analysis

ABSTRACT

Traffic marking is one of the road safety features that reduce traffic accidents by providing guidance and information for road users. However, during service time, pollutants suspended in the atmosphere deposit on its surface and cause its visibility to decline. The aim of this work was to formulate traffic marking paint using chlorinated rubber and other essential basic components with a modified property towards a self-cleaning ability.

In this research work, toluene and benzene were used as a solvent and tested with different blending ratios to have the better dissolution of the binder targeting a minimum solvent cost. A method of mixture design was followed to formulate the traffic marking paint and optimize the required viscosity taking commercial paints as a benchmark. Different end-user properties including, density, film thickness, adhesion, hardness, non-volatile matter content, water, and thermal resistance were evaluated using ASTM and ISO standard test methods for the selected four different optimal traffic marking paint formulations.

Nano-TiO_2/ Awash Melkasa residue silica composite was prepared and characterized using TGA, XRD, SEM-EDX, and FT-IR. Finally, the optimized traffic paint was modified using the composite to investigate its self-cleaning property.

Solvent blending ratio of benzene to toluene at 35/65 % was observed to dissolve the chlorinated rubber without phase separation with a relatively low cost compared to other mixtures. The cost can be reduced by 2.08$/lit as compared to the cost of 100% toluene use. The obtained viscosity of the formulated traffic paints was observed to vary from 53-114.45 KU. The viscosity of the most common commercially available traffic marking paint ranges from 80-95 KU. Out of a total of 24 different formulations, only four formulations were found to have a viscosity ranging in between the commercial-grade traffic paint viscosity.

Based on the result of end-user property, the optimized paint formulation is found to have a density of 1.311 g/ml, a film thickness of 466.66 µm, zero detachment adhesion, 3H pencil hardness, and 62.6 % of non-volatile matter. Blistering effect was observed after 8 days of the water-resistance test. However, no significant change was observed during the pencil hardness

and adhesion test. Moreover, the optimized traffic paint showed high thermal stability that can withstand a temperature up to 100 ^{o}C without any deformation and crack.

The characterization results of Nano-TiO_2/ Awash Melkasa residue silica composite clearly show that the presence of anatase phase titanium with an average grain size of 13 nm. Finally, the optimized traffic paint was modified using the composite by substituting initially presented pigment (micro anatase TiO_2) by the same amount of composite. A better photocatalytic degradation of methyl blue stain with a contact angle less than 90^{o} was observed after the addition of the composite. With this, it can be concluded that the modified traffic paint has a significant self-cleaning property.

CHAPTER ONE

1. INTRODUCTION

1.1. Traffic marking

The progress of the transportation system has brought about changes in the standard of life. However, the transportation system was also the cause of death for many people because of traffic accidents. The increase in traffic flow, and human error, are the major causes of a traffic accident (Burghardt and Pashkevich 2020). According to the WHO report for the year 2018, the number of road accident deaths a year was around 1.35 million. Road traffic accidents are also the leading cause of death among children and young people aged 5-29. In developing countries, this problem is much more serious than in developed countries (Violence and Prevention 2018). The world health organization report also mentioned the major risk factors of traffic accidents, including speed, driver behavior, missing motorcycle helmet, seat-belts and child restraints, and road infrastructure (Violence and Prevention 2018).

One of the most cost-effective ways to increase road safety is to apply measures related to traffic signaling elements, i.e., road markings and traffic signs (Babić, Babić et al. 2020). Road marking is any materials applied on the road surface to guide, control traffic flow, and convey visual information for road users (Rehman and Duggal 2015). It is one of the traffic management tools that promote the safety of road users by transmitting continuous information about the direction of traffic flow and center and ending of road alignment. Road marking includes lines, signs, and symbols on road infrastructure (Fiolić, Habuzin et al. 2017). Currently, there is no other way to substitute this marking material (Babić, Burghardt et al. 2015).

The presence of road markings on the surface of road infrastructure creates a way of communication between traffic engineers and road users (drivers, pedestrians, and cyclists) by providing continuous information about road alignment and vehicle position, this makes them essential safety features (Malik, Qasab et al. 2016, Coves-Campos, Bañón et al. 2018). Miller, T.R., in 1992 reported that the marking of the road center and end line reduces road traffic accidents by 20% (Miller 1992).

Driving vehicles are a day-to-day task for many of us and it depends on visual information. The driver can receive 90% of information visually, so the presence of road marking can give the driver a range of information, such as information about roadway alignment, vehicle positioning, and other driving-related tasks (Mohamed, Skinner et al. 2019, Babić, Babić et al. 2020).

The driver's failure to scan alignment and its surrounding is a potential source of traffic accidents. More than that, the confusion and uncertainty of road users about the meaning of such marking is one cause of a traffic accident. Hence, the effectiveness, and uniformity of such marking all over should ensure the reduction of traffic accidents due to confusion and uncertainty (Taheri, Jahanfar et al. 2018). The rate of a road traffic accident is higher during night time as compared to daytime, the presences of road marking on road surface have a great contribution in the reduction of a road accident during night time and adverse weather condition such as rain, foggy day (Burghardt, Pashkevich et al. 2019).

The most important problem related to traffic marking is their low resistance to dirt pick up and loss of brightness. Pollutants suspended in the atmosphere which are released from different sources settle on the surface of traffic marking. These dirt materials are made up of different components such as carbon black, organic compound, nitrate, sulfate, and soil particles. The pollutant transported to traffic marking in the form of solid particles or liquid suspension and they leave a permanent stain on the marking surface (Alvani, Darvishi et al. 2018). Deposition of pollutant (dirt) on the surface of traffic marking negatively affect the day and night time visibility of the material and result loss of cognitive perception for the road user. Loss of visibility especially at night time and adverse weather conditions cause an accident. Therefore, to maintain the visibility of traffic marking paint at an adequate level application of new technology called self-cleaning coating is important (Taheri 2017) In recent years the growth of new technology in the field of coating allows the development of new coating products that have either protective or decorative purposes with innovative science (Taheri 2017). A recent development in Nanotechnology has disclosed the production of cleaver coatings such as self-cleaning coating.

The self-cleaning coating is one of the recent technology derived by mimicking nature. Different plants and animals exhibit self-cleaning properties, for example, the leave of lotus plants, rice plants, fish scales, and the wing of butterflies (Ganesh, Raut et al. 2011, Banerjee, Dionysiou et al. 2015). Due to their great significance, self-cleaning coating possesses enormous potential

application in the area of cement, window glass, solar panel, textile, paint, household (bathrooms, kitchen fittings, and non-stick pans), road paving, vehicle side-view mirror and lamp (Parkin and Palgrave 2005, Sethi and Manik 2018). Self-cleaning paints are capable of degrading pollutants present on their surface to maintain their original aesthetic aspect and improve the quality of the environment that they applied. In addition to the usual components, self-cleaning paint consists of photocatalytic particles in their composition (Amorim, Suave et al. 2018). Among different semiconductor materials, Nano-Titanium dioxide found great attention for the development of self-cleaning surfaces. This is because of the special property of TiO_2 such as its great ability to promote the degradation of organic pollutants, super hydrophilicity, chemical stability, non-toxicity, low cost, and large availability (Rocha Segundo, Freitas et al. 2019). TiO_2's self-cleaning mechanism proceeds in two stages: first, the material forms electron-hole pairs when the semiconductor is exposed to ultraviolet rays from solar radiation. The electrons combine to create superoxide radicals with oxygen in the air, and the holes also react to form hydroxyl radicals with moisture in the atmosphere. This free radical degrade the pollutant adhere to the surface. Second due to its super-hydrophilic property, the degraded pollutant washout by water and maintain a clear surface.

Even though Nano-TiO_2 is mainly used for the preparation of the self-cleaning system, their application is restricted due to their high agglomeration phenomena, poor dispersibility of TiO_2, and low adsorption capacity in the application system. The agglomeration of Nano-TiO_2 reduces the active site of the catalysts and specific surface area, this phenomena reduce its photocatalytic efficiency (Zhang, Sun et al. 2020). Supporting Nano-TiO_2 using a mineral carrier or other inorganic carriers can improve the limitation of Nano-TiO_2. Kaolin, diatomite, zeolite, silica are used as supporting materials to Nano-TiO_2 (Wang, Chao et al. 2019). Instead of using natural clay as supporting material for Nano-TiO_2, reuse of byproduct of industries need to be encouraged due to many reasons, such as it reduces landscape need to dispose of the byproduct, minimize disposal cost, and the byproduct can be used as raw material instead of disposing it to the environment.

The aim of this research is a formulation, optimization, and characterization of traffic marking paint using chlorinated rubber as a binder. Then traffic marking paint formulation that has better performance has been selected for the preparation of self-cleaning traffic marking paint. The self-cleaning traffic marking paint was prepared by substituting the pigment titanium dioxide in the

optimum formulation by using Nano-TiO_2 / residue silica composite. Then the photo-catalysis performance of the modified traffic marking paint toward methyl blue removal was investigated. In this study, the silica which is used as a carrier for Nano- TiO_2 is obtained from Awash Melkassa Aluminium Sulphate & Sulphuric acid S.C factory. The photocatalyst Nano-TiO_2/Awash Melkassa residue silica composite was prepared by wet grinding of TiO_2 sol-gel with Awash Melkasa residue silica. Then the photocatalytic effect of the photocatalyst in traffic marking paint and the structure, morphology, and interaction of Nano-TiO_2 with silica was determined.

1.2. Motivation

The purpose of road marking is to improve the safety of road users. The presence of such marks on the road surface has an embracing effect on reducing traffic accidents. Road marking paints are important to inform and guide road users. Their presence is more important during nighttime and adverse weather conditions (i.e. fogy and rainy days).

Ethiopia is one of the developing countries where the amount of death rate due to traffic accidents is high. According to a WHO report, road traffic accidents in Ethiopia cover 29,386 of the total death rate. Most of the traffic marking paint present in Ethiopia lose its visual appearance due to the deposition of pollutant while many of the roads have no traffic marking paint.

The current development of a self-cleaning coating that has the potential of making itself dirt-free has obtained great attention in the world. Nanoparticles are used to develop self-cleaning coating but they have a high agglomeration tendency, low adoration capacity. To reduce the limitation of nanomaterials carrier materials such as clay (kaolin, diatomite) is used. In addition to this, formulation of paint including traffic marking paint is business secrete.

Hence, this research intended to develop traffic marking paint formulation using chlorinated rubber as a binder and modify the formulated traffic marking paint with self-cleaning property using Nano-TiO_2/ Awash Melkassa residue silica composite as photocatalyst. The silica used as the carrier is a by-product of the Awash Melkassa sulfuric acid plant which is currently a waste for the company.

Applying the byproduct of industries instead of damping to the environment has an advantage in terms of reduction of environmental pollution and reduce the use of natural clay carriers such as kaolin, diatomite.

1.3. Statement of problems

A road traffic accident is a one of the leading cause of a loss of human life and economic resource all over the world. In Ethiopia, each year numerous road users lose their lives, and most of them are economically active population. According to WHO data published in 2018 road traffic accident death reached 4.81% of total deaths (LeDuc 2018). The existence of road-making paint contributed to reducing road traffic accidents (Babić, Fiolić et al. 2020). Installing road marking paint provides optical guidance, regulates traffic flow, inform a driver about the oncoming danger, and show driving restriction.

Because of their function, traffic marking paint is exposed to different climatic conditions such as different temperatures and pollutants including organic and inorganic particles, carbon residues, nitrate, sulfate, and soil particles. One of the factors that affect the visibility and brightness of marking paint is the deposition of such pollutants on the surface of traffic marking paint. Loss of the basic property of traffic marking paint i.e its day and night time visibility results in loss of cognitive perception of road users and this will cause traffic accidents (Taheri 2017, Alvani, Darvishi et al. 2018). The deposition of such pollutant cause for the requirement of extensive manpower, time and financial cost to clean and maintain traffic marking paint.

From the personal experience of the author, most of the roads in Ethiopia have either no horizontal, vertical, and pedestrian crossing pavement marking, or most of the markings lost their visibility and color due to the deposition of stain on their surface. Recently, to develop dirt-free material self-cleaning coating using Nano-TiO_2 is widely used. But high agglomeration tendency, low dispersibility, and adsorption capacity of Nano- TiO_2 result in a reduction of its self-cleaning property.

Therefore, this thesis aimed at, the formulation for traffic marking paint without compromising the quality of the paint and modify the formulated traffic marking paint with self-cleaning property using Nano-TiO_2/ Awash Melkassa residue silica composite as a photocatalyst. The

silica is used to reduce agglomeration tendency and helps to increase the adsorption of pollutants near the Nano- TiO_2 surface. The silica used to produce the composite is the waste of Awash Melkassa sulfuric acid factory which is disposed to the environment. Therefore, the reuse of industrial wastes reduces the waste volume and landscape needed to dispose of waste and also minimizes disposal costs. In addition, recycling and usage of the waste as a crier contribute to resource conservation.

1.4. Objective

1.4.1. General objectives

- The general objective of this thesis is the development of chlorinated rubber-based traffic marking paint with a self-cleaning property using Nano-TiO_2/ Awash Melkassa residue silica composite as a photocatalysis.

1.4.2. Specific objectives

The specific objectives of the research are:

- Formulation of traffic marking paint
- Optimization and evaluation of wet and dry paint properties of the traffic marking paint
- Synthesis of Nano-TiO_2/ Awash Melkassa residue silica composite from TiO_2 precursor and Awash Melkasa waste residue silica.
- Characterization of the Nano-TiO_2/Awash Melkassa residue silica composite
- Show the effect of Nano-TiO2/ Awash Melkassa residue silica composite on the photocatalytic degradation performance of traffic marking paint.

1.5. Research questions

1. What is the possible composition of paint ingredients to produce optimum quality traffic marking paint?
2. Is it possible to prepare Nano-TiO_2/ Silica composite from TiO_2 precursor and Awash Melkasa residue waste silica?

3. Is it possible to produce traffic marking paint with the self-cleaning property using Nano-TiO_2/ silica composite from TiO_2 precursor and Awash Melkasa residue waste silica?
4. What is the characteristic and the performance of the produced traffic marking paint and its self-cleaning property?

1.6. Significance of the study

Considering the fact that paint formulation including traffic marking paint is business secret, this research aims to develop traffic marking paint with the improved quality needed comparable to that of commercially available traffic marking paint and at the same time offer alternative traffic marking paint in the country with a different formulation.

Importantly, the benefit offered by this research work was modifying the formulated traffic marking paint with the self-cleaning property. This property helps to maintain the optical property of traffic marking paint by degrading pollutants deposit on the paint surface. Indirectly this helps in the reduction of a traffic accident (i.e loss of human life and a lot of huge property) caused by the absence and less effectiveness of traffic marking paint in the country.

Development of self-cleaning traffic marking paint using Nano-TiO_2/Awash Melkassa Silica composite as a photocatalysis will help in the reduction of financial cost invest by road authority to maintain faded traffic marking paint due to deposition of stain. In addition to this, the usage of industrial byproducts in the development of self-cleaning traffic marking paint significantly helps in resource conservation. More importantly, usage of industrial west in the production of self-cleaning traffic marking paint contribute significantly to solving an environmental problem related to the disposal of such waste to the environment.

1.7. Scope of the study

The scope of this research focuses on the formulation of traffic marking paint using chlorinated rubber as a binder. Design-Expert software was employed for developing and optimization of the traffic paint formulation. The study evaluated different wet and dry paint property of optimized paint formulation such as density, viscosity, film thickness, adhesion, hardness, volatile matter, water resistance, and thermal resistance. Furthermore, the optimum paint formulation was modified with self-cleaning property using Nano-TiO_2/Awash Melkasa residue silica composite. The silica used to prepare the composite was obtained from Awash Melkassa Aluminium Sulphate & Sulphuric acid factory and the composite was prepared by wet grinding of the Nano-TiO_2 sol-liquid with the silica. The Nano-TiO_2/Awash Melkasa residue silica composite was characterized by FT-IR, XRD, and EDS instrumentation techniques. Then the self-cleaning ability of the modified traffic marking paint was evaluated by taking methyl blue as a model pollutant and sun as a light source.

CHAPTER TWO

2. LITERATURE REVIEW

Roads, airport runways, bridges, etc. need to contain certain markings to ensure the safety of road users. Such road surfaces are marked for lane markings, pedestrian crossings, directional markings, and other markings (Parekh 2020). Traffic markings are unique traffic management tools that act as safety marking to provide continuous information to road users about the direction of the traffic movement, longitudinal guidance, roadside alignment, and other traffic-related information without making the driver turn his attention away from the road.

Traffic markings help the drivers stay on the road, which will help reduce road traffic accidents. According to Miller, T.R., the appearance of road marking on the road surfaces has reduced traffic accidents by 20% (Miller 1992).

2.1. Road marking materials

Currently, there are different traffic marking materials used to mark the road, highway, pedestrian cross, and parking lots. These materials are classified based on different criteria such as based on material type, the solvent used, and durability. Traffic marking materials based on material types are divided into paint, thermoplastic, plural component system, and tapes. Traffic marking material is also classified according to the solvent they use; waterborne, solvent-born, and solvent-free. Another method to categorize traffic marking material is durability. Based on this traffic marking classify as durable (such as epoxy, thermoplastic, and tap) and non-durable (such as water-based and solvent-water road marking paint) (Babić, Burghardt et al. 2015, Mohamed, Skinner et al. 2019).

Traffic marking material is composed of three major components which are a binder, pigment, and glass beads. Binder is an adhesive material that is responsible for the adhesion of marking material to the road surface. The pigment is another component of road marking that incorporates color for marking. Glass bead is retro-reflective material that can enhance the visibility of marks especially at night, while also protecting the base layer (Mohamed, Skinner et al. 2019,

Burghardt and Pashkevich 2020). Traffic marking materials that are most widely used around the world are; thermoplastic, performed tap, two-component marking, and paint.

2.1.1. Thermoplastic

Thermoplastic traffic marking is one of the most commonly used traffic marking composed of four general components; binder (resin), pigment, filler, and glass beads. It is a dry homogeneous mixture of these components at high temperatures (Dotson 2018). Then it performed to the desired shape. Since they are in solid form reheating of thermoplastic road marking material at 200 ^{O}C is needed during the time of application to melt them (Babić, Burghardt et al. 2015).

Contrasted with traffic marking paint, thermoplastic markings have high durability and lasts for 3 to 6 years. But they require a high amount of energy in terms of heat during production and application, this maximizes environmental impact (Babić, Burghardt et al. 2015). The application of thermoplastic marking in high humid areas is poor due to the failure of the adhesion to the road surface and the long-term durability of such marking is influenced by road surface moisture and air temperature (Carlos A. Lopez August 2004). So effective installation of such marking requires surface cleaning and moisture removal before applying the marking on the road surface (Asdrubali, Buratti et al. 2013).

2.1.2. Performed tap

Preformed marking tapes are typically composed of a composite structure consist of a support base of calendared rubber compound, a self-adhesive layer, and a topcoat anti-wear layer incorporating anti-skid material and retroreflective elements (Garbe and Hedblom 2019). Marking tapes are typically pre-manufactured and supplied in the continuous roller of various lengths and widths.

Preformed marking tapes are cold applied. Such marking material has an advantage over other marking materials because they do not require expensive application equipment, they do not require drying time (Le Normand, Boehme et al. 2019, Carlos A. Lopez August 2004). Performed tap has better visibility, retro reflectance, durability and they have a temporary or removable option than road marking paint (Garbe and Hedblom 2019).

Even though they have a lot of benefits, tap road marking material has also drawbacks such as higher initial cost and slow application procedure. The other challenging issue related to preformed tap road marking is the replacement of tap with a new one. Tapes should always be removed before the placement of new markings but the removal of such markings is a challenge and is the major drawback to their use (Carlos A. Lopez August 2004).

2.1.3. Two-component marking

Two-component traffic marking is made by the reaction of two chemical compounds on sit. The first compound consists of binder, pigment, and filler while the second component is a catalyst that accelerates the settling time of marking on the road (Asdrubali, Buratti et al. 2013).

2.1.4. Traffic marking paint

Traffic marking paint is the oldest and most widely used traffic marking material, consisting of binders, pigments, fillers, solvents, and additives. During application, the solvent will evaporate from the surface of the wet fill to form a dry solid film (Pashkevich, Bartusiak et al. 2020). Based on the type of solvent they use traffic marking paint classifieds into two; water-based and solvent-based paint (Asdrubali, Buratti et al. 2013).

2.1.4.1. Water-based traffic marking paint

Water-based traffic marking paint is environmentally friendly marking paint that uses water as a solvent. They consist of high molecular weight acrylics and styrene-acrylic latex as a binder (Sward and Koleske 2012). They have many advantages such as less volatility, safety against fire risk, a good hygienic condition during application and production, ease to clean, and low odor (de FA Mariz, Millichamp et al. 2010).

Traffic marking paint needs to have short track free time, especially in high traffic volume roads to reduce traffic delay. Even though water-based paint has many advantages, one of the limitations of water-based paint traffic marking paint is its drying time. Due to the low evaporation rate of water, they take a longer time to dry. The drying time of water-based road marking paint depends on the relative humidity of the atmosphere in which it is applied. On a

humid day, the paint takes a long time to dry, this causes the distraction of traffic flow (de FA Mariz, Millichamp et al. 2010).

As an environmentally friendly alternative to a solvent-based counterpart, the different formulation has been developed by different researchers. But the main limitation of water-based traffic marking paint is their slow drying time, the problem is resolved by techniques such as applying a thin layer of paint film instead of a thick film. The reason behind applying thick paint film is to obtain high durable paint that can resist erosion due to traffic volume and environmental conditions. Therefore applying a thin layer of water-based paint is less wear-resistant and removes easily within a short period (Sun and Zhang 2012).

In addition to applying a thin film of paint on the road surface to reduce drying time, other methods were also developed by the researcher to resolve the problems. Pirotta, M.G., A. Sanfilippo, and A.P. Trapani, (Pirotta, Sanfilippo et al. 2000) reduce the drying time of water-based paint using ion exchange resin. The ion exchange resins are insoluble, dry, solid, and extremely hydrophobic. When this resin is connected to freshly applied paint they absorb water and cause fast drying of the film. The limitation of usage of ion exchange resin is the sulfonic acid group present in the resin react with the polymeric binder (acrylic resin) of water-based paint and therefore result weakening of the resin. In addition to this, the brown color of ion exchange resin changes the color of white traffic marking paint.

2.1.4.2. Solvent-based traffic marking paint

Because of its quick drying time characteristics, solvent-based traffic marking paint has been commonly used for a long time. Solvent-based paint consists of a binder, pigment, organic solvent, and additives. Aromatic, aliphatic, alcohol may be the organic solvent that is used here. Compared to water-based paint, solvent-based paint has a quick-drying period and can be used in various environmental conditions (Sward and Koleske 2012, Pandey and Kiran 2020).

Chlorinated rubber paint is used for a long duration of time due to the better property of chlorinated rubber. The chlorinated rubber which is used as a binder to the paint provides water and chemical resistance, abrasion resistance, and durability. Due to their anti-corrosive property, they are used in marking coating, swimming pools, and traffic paint (Thames and He 2002).

Coughlan, T.N.,(Coughlan 1992) develop road marking paint using plasticize chlorinated rubber as a binder for the application of airport runaway. The formulated paint consists of titanium dioxide pigment, mineral extender such as talc, barium Sulfate, diatomite, plasticize chlorinated rubber binder, methyl ethyl ketone, and toluene solvent and additives (such as wetting agent, bentonite, and acid stabilizer).

Miller, D.R., and J.E. Wolfe, (Miller and Wolfe 1980) formulated traffic sign paint, which can be used without heating at ambient temperature to speed up the drying time of the paint. They use chlorinated rubber and medium oil glycerin phthalic alkyd as a binder, chlorine paraffin plasticizer, titanium dioxide pigment, extender (aluminum silicate and magnesium silicate), methylene chloride solvent, and additives such as anti-skinning agent and epichlorohydrin.

2.2. Traffic marking paint composition

Traffic marking paint consists of a base (pigment) layer and a reflective layer. The base layer of road marking paint provides color, adhesion to the road surface, and holds the retroreflective element (glass bead).whereas the retroreflective element is responsible for the retro-reflection of the paint and protects the base layer from wear. The base layer of road marking paint is composed of four ingredients, which are: resin (binder), pigment, solvent, and additives (Burghardt and Pashkevich 2020).

2.2.1. Resin (binder)

The most significant component of the paint that is used as the glue is the binder. Binder holds other components of the paint and is responsible for adhering the paint to the substrate (Pandey and Kiran 2020). The binder used in paint manufacturing is composed of polymer materials (such as resin and dry oil), and its main function is to form a film after applying the paint to the substrate, surface adhesion, hardening, chemical, and solvent resistance (Humans 1989, Mannari and Patel 2015). In the painting industry, a wide number of both natural and synthetic binders are used. A natural binder such as rosin, linseed oil, castor oil, and soyabean oil is used in paint industries. Alkyd resin, acrylic resin, epoxy resin, polyurethane resin, and chlorinated rubber, etc., are the most widely used synthetic binders (Humans 1989).

2.2.2. Pigment

The pigment is one of the indispensable components of any paint (Perera 2004). It is a substance containing fine particulate solids, which is practically insoluble in the application media and is used for its coloring and protective properties (Brock, Groteklaes et al. 2000). They are used in paint formulation to impart certain properties to the paint, such as color, opacity, mechanical properties, and durability (Mannari and Patel 2015).

The pigment used in the coating industry classifies based on its color, chemical nature, and process of manufacturing. Based on color, the pigment is classified as a white pigment (titanium dioxide, zinc oxide), black pigment (carbon black, iron oxide black), and colored pigment such as red pigments, orange pigments, yellow pigments. According to their chemical nature pigment classified into two groups: organic pigments such as azo pigments, and inorganic pigments like titanium dioxide, iron oxide red, nickel titanate yellow, zinc sulfide, cadmium sulfide. The pigment is also classified based on process manufacturing as natural and synthetic (Mannari and Patel 2015). Titanium dioxide is the dominant white pigment in today's coating industry considering its usage in almost all types of products. Since the coating industry is a major consumer of titanium dioxide pigment more than half of the titanium dioxide produced goes to paint production (Sward and Koleske 2012, Mannari and Patel 2015).

As a white pigment, titanium dioxide is of outstanding importance due to its high reflective index (high opacity), maximum whiting capacity, and outstanding performance properties. It exists in three crystal phases, rutile, anatase, and brookite. Among the three titanium dioxide pigments, Brookite has no commercial significance in the field, while rutile and anatase are manufactured industrially in large quantities and used as a pigment (Buxbaum 2008). In each of the three titanium dioxide crystals form, the titanium atom in the lattice is surrounded octahedrally by six oxygen atoms, and each oxygen atom is surrounded by three titanium atoms, but they differ in the way the octahedra are linked through their corners and edges (Mannari and Patel 2015).

Rutile titanium dioxide is thermodynamically more stable. Compared with the anatase phase, it has a high reflective index (2.75) and high hiding power. This is because of the compact arrangement of atoms in the rutile phase. Anatase titanium dioxide has a less compact

arrangement of atoms and respectively they have a low reflective index (2.55) as compared to the rutile phase and they have better photocatalysis property.

Extender: are an important part of almost all coating formulation (Ewulonu, Igwe et al. 2016). They are naturally occurring white minerals and synthetic white inorganic pigments (Funke 1984). An extender is a substance comprising particles that are practically insoluble in the paint vehicles (Winkelaar 2009). They enhance the certain property of paint such as flow characteristics, settling tendency, abrasion resistance, etc.(Ewulonu, Igwe et al. 2016).

In most cases, because the extender pigments are inexpensive, they are used to reduce the cost of expensive TiO_2 by filling the coating volume with minimal impact on performance. Calcium carbonates, kaolins (aluminum silicates), talcs (magnesium silicates), mica (hydrous aluminum potassium silicates), silica (silicon dioxide), wollastonites (calcium metasilicates), and barite (barium sulfate) most commonly used extender pigment used in the paint industry (Perera 2004).

2.2.3. Solvent

A solvent is a liquid comprising one or more components that are volatile under the specified dry condition and can dissolve a binder without a chemical reaction. Most of the binder used in the paint formulation is solid or highly viscous that needs to be diluted to a lower viscosity for easy processing, easy application. Solvent has a great role in paint processing, application, and film formation. During the production of paint, the solvent reduces the viscosity of the binder and assists the wetting of the pigment particle in the pigment dispersion process. In the time of application of paint on the surface of the substrate solvent also assist in better flow and leveling, which improves the appearance and gloss of coatings. After the application of paint, the solvent needs to be evaporated to form a dry film (Mannari and Patel 2015).

2.2.3.1 Solvent classification

There are many different solvents used in the production of the coating. A solvent is frequently classified into three based on its function as a prime solvent, latent solvent, and diluent solvent (Sward and Koleske 2012). A prime solvent is also known as the true or active solvent is a solvent capable of dissolving a binder. The latent solvent does not dissolve a resin, but they enhance the solvency of the prime solvent. A diluent solvent is a volatile liquid that cannot dissolve the given

binder alone, but they used in combination with prime solvent to reduce the cost and to balance the evaporation rate of paint The organic solvent used in coating also broadly classified based on its chemical structure into three this is; hydrocarbon solvent, oxygenate solvent, and other solvents (Mannari and Patel 2015).

Hydrocarbon solvent: A hydrocarbon solvent is an organic compound whose molecules are composed of carbon and hydrogen atoms. The vast majority of these types of solvents came from the fractional distillation of petroleum oil and some of which are of vegetable origin. Owing to this hydrocarbon solvents are considered as being natural products (Sward and Koleske 2012).

Since hydrocarbon solvents are of natural origin, they are a good solvent for natural or natural modified resins. For example, the hydrocarbon solvent is a good solvent for rosin, dry oil, and petroleum resin. Hydrocarbon solvent is further classified into aliphatic, aromatic, naphthenes, and terpenes(Sward and Koleske 2012). Aliphatic hydrocarbon is a saturated organic molecule that is a mixture of straight-chain(normal paraffin) and branched-chain (isoparaffin) hydrocarbons, with some cycloparaffin (Mannari and Patel 2015). Aliphatic hydrocarbon characterizes by low odor, low cost, low specific gravity, and weak solvency (Sward and Koleske 2012). A Mineral sprite is an example of an aliphatic hydrocarbon solvent that is used most widely in the paint industry (Mannari and Patel 2015).

Aromatic solvent is cyclic, an unsaturated compound that has high solvency than an aliphatic hydrocarbon solvent. Toluene, mixed xylene are commonly used aromatic solvents used in the coating industry. A terpene is the other form of hydrocarbon solvent, such solvents are of plant origin and obtained from pine trees. Terpentine, dipentene and pine are the major solvents in this category. The fourth types of hydrocarbon solvent are Naphthenes. Most aliphatic hydrocarbon solvents contain some amount of cycloparaffin or naphthenes. Most of the properties of such kinds of solvent (solvency, specific gravity, and odor) lay between aliphatic and aromatic solvent. Cyclohexene is an example of naphthenes hydrocarbon solvent (Sward and Koleske 2012, Mannari and Patel 2015).

Oxygenated solvent: The oxygenated solvent is an organic compound, molecules of which consist of carbon, hydrogen, and oxygen. They are an important group of solvents in the coating industry due to their strong solvency power and wide range of volatility availability. Unlike hydrocarbon solvents, the oxygenated solvent is synthetical produce. As a result, they are an active solvent for

most of the synthetic resin. The most important types of oxygenated solvents used in the coating industry are alcohols, ketones, ester, and glycol ether (Sward and Koleske 2012).

Other solvents: Other solvent is an organic compound, molecules of which consist of carbon, hydrogen, and atoms other than oxygen such as chlorine, nitrogen, and inorganic compound (water and supercritical carbon dioxide) (Sward and Koleske 2012). Chlorinated hydrocarbon solvent is an example of other solvent that contains chlorine atoms in the molecules. for most of the resin used in the coating industry, chlorinated hydrocarbon has better solvency than the corresponding hydrocarbon solvent (Mannari and Patel 2015).

2.2.3.3. Performance requirements of solvent

Due to a large number of solvents available to solubilize and disperse other components of paint (such as a binder, pigment, and additives) selection of an optimum solvent mixture for formulating a paint is challenging. Different factors affect the choice of solvent and the use of the solvent mixture. Some of these factors are solvency, evaporation rate, viscosity, toxicity, and cost (Lambourne and Strivens 1999).

Solvency: is the main performance criteria of solvent. The need for solvent in paint composition is to dissolve a resin to yield a solution with a viscosity suitable for the application (Mannari and Patel 2015). The term solvency for coating formulators refers to the ability of a solvent to dissolve the resin, to hold the resin in the solution in the presence of a diluent, and efficiently reduce the viscosity of the resin and paint. The solvency of a given resin in a solvent is indirectly determined by measuring its compatibility in the solvent (Sward and Koleske 2012).

Evaporation rate: The choice of solvent-based on the evaporation rate is important to control the appearance, and paint film defects. A solvent is not a part of the dry film, it must leave the wet paint film by evaporation. But the solvent needs to evaporate from the surface of a wet paint film at a controlled rate to obtain a uniform and defect-free film. Fast and slow evaporation of solvents has its impact on the property of the dry paint film. Fast evaporation of solvents from wet film help in reducing the sagging of paint on a vertical surface and reduce the drying time of paint film. But fast evaporation of solvent results in an increase of viscosity of wet film, this event may affect the flow and leveling of wet film. The difficulty of wet paint film to flow and level on the

surface of the substrate results in nonuniform dry paint. This may lead to poor gloss and appearance of paint film (Mannari and Patel 2015).

On the other hand, slow evaporation of the solvent is important to provide better flow and leveling of the wet film but it may result in run and sagging of paint on a vertical surface. Due to slow evaporation, solvents may become trapped in the film as it cures, thus impairing performance properties of the paint such as drying time. Therefore, for good film formation, the solvent needs to evaporate from the paint film at a controlled rate (Sward and Koleske 2012, Mannari and Patel 2015).

Toxicity: solvent is not a part of dry film, it evaporates after application of the paint to the substrate. Evaporation of the organic solvent has a great contribution to volatile organic compound emission to the environment. A worker is exposed to such organic solvent during paint production as well as during application which causes serious health problems. Therefore, a solvent with minimal toxicity should select for paint production (Hassan, Elnagar et al. 2013, Jhamb, Liang et al. 2020).

Cost: Coating industries are the largest users of organic solvent where, from the total raw material cost in the coating industry, the cost for solvent covers one-third. To become economically feasible the solvent with a low cost per kg need to be used (Barry, Morose et al. 2017, Jhamb, Liang et al. 2020).

2.2.4. Additives

Besides the above three components, paint also contains other material called additives, which may directly influence the coating properties or may modify the properties of the major ingredients. Additives are any substances that are added in a small amount in paint formulation to improve the certain property of paint during manufacturing, storage, application, and transportation. According to their functions, additives used for paint and coating are divided into many groups. Some of the additives used in paint are drier, dispersing agent, anti-skinning agent, defoamer, thickening agent, and their function is mentioned below (Bieleman 2008, Mannari and Patel 2015).

2.2.4.1. Driers

Dring of paint without any addition of catalyst may take many times, which is not desirable from a practical point of view. The curing speed of paint may accelerate significantly by using a catalyst. These catalysts are called driers (Gezici-Koç, Thomas et al. 2016). Driers are transition metal that accelerates the curing or hardening of paint film that contain oxidizable component (Funke 1984).

Dryers used to speed up the drying time of paint film are commonly classified into two dominant classes: primary dryers and secondary dryers. Primary driers (active dryers) are called surface or skin dryers. They catalysis the auto-oxidation curing process but when primary dryers are used alone, they will cause the surface of paint film to rapidly convert to near solid and this will result in the underlying film does not reach an advanced state of oxidation. Cobalt and manganese are commonly used as active dryers (Brock, Groteklaes et al. 2000).

Lead, calcium, zinc, or zirconium are secondary dryers that enhance the drying of a paint film. When such types of driers are used in combination with primary driers they give films that do not surface-dry as rapidly and cure though more uniformly. Secondary driers are sub-classified into two: through driers and auxiliary driers. Though driers include zirconium, strontium, aluminum and auxiliary driers include calcium, potassium, and lithium. Among the other types of driers secondary driers, Zirconium and calcium are the most widely used ones in combination with primary driers to facilitate uniform curing of the paint film.

2.2.4.2. Wetting and dispersing agent

Pigment and filler are important components of paint, and they need to disperse and stabilized throughout the paint to ensure consistent color, better quality, and durability. Dispersion is the uniform distribution of solid particles (that is, pigments and fillers) into liquid media of paint(resin and solvent). Pigments for coatings are typically supplied as powdered materials wherein primary particles form larger agglomerates so during dispersion the adhesive strength between solid particles needed to be overcome. Uneven distribution pigment in liquid media results in various undesirable further to paint such as poor color strength and development, sedimentation, and poor application characteristics (Bieleman 2008). This indicates the optimum

dispersion of pigment particles in resin solution is critical for better performance of the paint. The pigment dispersion process occurs in three steps which are wetting, dispersion, and stabilization (Müller 2010).

During the wetting of pigment particles, a binder solution wets the pigment particle and causes for replacement of pigment/ air interface by pigment/ liquid interface. After pigment particles are wetted, the next step is a dispersion of pigment agglomerate. During this pigment agglomerates, flocculated is broken up and reduce particle size through mechanical energy. Pigment dispersion must be stabilized to prevent the re-flocculation of pigment particles. If pigment dispersion is not stabilized during the production process, storage, and application processes some defects may arise such as color deviation, sedimentation, and viscosity change (Bieleman 2008).

Therefore, appropriate measures are used to keep the individual pigment particles at distances from one another so they cannot re-flocculate. To optimize pigment wetting and stabilization in resin solution additives are used which are called wetting and dispersing agents. Wetting and dispersing agent are added in small amounts to paint formulation to facilitate dispersion of pigment and filler into liquid media(binder and solvent) (Bieleman 2008, Zubielewicz 2012). They mainly improve the wetting of pigment particles and helping to maintain the stability of pigment dispersion (Bieleman 2008).

Wetting additives accelerate the wetting of pigment particles by reducing the surface tension between liquid media (binder solution) and solid surface(pigment surface). This wetting agent affects the breakdown of agglomerate, speeds up the dispersion process, and reduces the energy required during the pigment dispersion process. Such wetting agents are surface-active agents of low molecular mass (Brock, Groteklaes et al. 2000, Bieleman 2008).

Via two processes, dispersants stabilize the dispersion of pigments: electrostatic stability and dimensional stability. Electrostatic stabilization is dependent on electrical charge repletion. The dispersant modifies the surface charge, allowing a mobile ion cloud to form around the particle. Provided that the electrostatic repulsion forces are greater than the attractive force between pigment particles when two particles approach each other (Brock, Groteklaes et al. 2000).

During steric stabilization, dispersing agents contain both binder-compatible segments and pigment-affinitive groups (Brock, Groteklaes et al. 2000). For example, polymeric wetting agents

are absorbed on the pigment surface by various anchoring segments in the polymeric molecules, and the other part remains dissolved in the liquid media. Based on this method dispersing agents prevent re-flocculation of solid particles in paint formulation (Bieleman 2008).

2.2.4.3. Antiskning agent

To speed up the drying of paint film dryers are added to the paint composition (Weijnen and Brandjes 2019). Dryers are a catalyst used to accelerate the drying of paint for example metal oximes (john weijnen 2017, Tantawy and Alomari 2019). When air drying paint composition consists of dryers exposed to air, they will rapidly convert to a dry polymeric matrix. Even though dryers are added to ensure drying of the paint film, rapid surface drying may also occur resulting in the skin (Weijnen and Brandjes 2019).

Skinning is generally the result of early film forming on the liquid coating material's surface. The paint can react with air over the composition and form a thin skin, mainly during storage of the paint (john weijnen 2017). Such undesirable skin formation results in a loss of consistency in paint formulation, such as the skinning phenomenon, which deteriorates the quality of the paint, affects the strength of the dryers and affects the drying profile of the remaining paint.

To prevent this undesirable skinning of paint and to improve storage stability of paint additives called anti-skinning agents are added to the paint composition (Weijnen and Brandjes 2019). Antiskining agent is an additive that is added to the paint formulation to temporarily inhibit or delay oxidative curing of paint during production and storage (Mannari and Patel 2015).

Anti-skinning agents may act as anti-oxidant to prevent oxidative crosslinking of binders or they form complex with transition metal salt driers to prevent skin formation in the can. But during the application of paint to the substrate anti skinning agent need to evaporate to reduce their impact on the drying of the paint film. When the coating composition is applied to a substrate, the surface area is increased, enabling the anti-skinning agent to evaporate. Evaporation of the anti-skinning agent destroys the complex between the anti-skinning agent and the metal salt driers. This phenomenon enables the catalytic activity of the metal ions to be restored and the paint to dry. (john weijnen 2017)**.**

Antiskining agents used in paint composition to prevent undesirable skin formation are organic additives based on hydroxylamine derivatives, phenols, amino compounds, and oximes of aldehydes and ketones (john weijnen 2017). During the choice of this anti-skinning agent for a given paint formulation different criteria need to be considered such as the ability of anti-skinning agents to prevent skin formation, rating an adequate drying potential of paint, odor, toxicity, and coloristic effect (Weijnen and Brandjes 2019). Among the different groups of anti-skinning agents, oxime is the most widely used group in the paint and coating industry due to its well-balanced property(Weijnen and Brandjes 2019). In practice, methyl ethyl ketoxime (MEKO) is typically regarded as the most effective and widely used anti-skinning agent(john weijnen 2017).

2.2.4.4. Defoamer

The paint contains surface-active substances to improve a particular property. For example, wetting and dispersing agents are used to improve the wetting and stabilization of pigment and filler in liquid media. Even-though the existence of such surface-active material has great importance in paint formulation they have also an undesirable side effect. They stabilize air introduce in paint composition during production, packaging, and application in the form of foam (Brock, Groteklaes et al. 2000). Stabilization of foam begins when the surface-active substance(e.g. wetting and dispersing agent) accumulate on the surface of the air/ liquid interface. Then when the air bubble is loaded with surface-active substance rises upward agglomeration of the air bubble (foam) is formed (Bieleman 2008).

Foam is an undesirable phenomenon that may cause optical defects in the coating surface, containers are not properly filled at the packaging stage, and also foam formation diminishes the protective function of the coating (Brock, Groteklaes et al. 2000). To prevent such a negative impact of foam, a suitable defoamer or foam inhibiting agent adds to the paint formulation.

Defoamers are used to remove the existing stabilized foam (Mannari and Patel 2015). They are low surface-tension liquids that have controlled incompatibility in the system to be defoamed, along with positive penetration and a positive spreading coefficient. On the other hand to avoid surface defect such as craters in paint film defoamer need to be compatible with the binder (Bieleman 2008).

The defoamer breaks the foam through the following working mechanism; the first defoamer enters the foam lamella. Second, they spread across the air/liquid interface, and then stabilizing surfactant molecules are displaced. This phenomenon leads to a decrease in the cohesive strength of the lamella that causes the foam to burst and collapses. Mineral oil and silicone defoamer are examples of defoamer used in paint formulation (Mannari and Patel 2015).

2.3. Formulation of traffic marking paint

Formulating of paint starts with the determination of raw material and its proper amount. Paint including traffic marking paint is a blend of different ingredients that are pigment, filler, binder, solvent, and additives. Therefore the selection of proper types of ingredients and their amount is important to formulate paint with good performance (Idris and Rashan 2017). In addition to a selection of ingredient types, the pigment volume concentration (PVC) is a useful guide parameter for paint formulators. Many paint film properties such as mechanical, transport, corrosion property change as a function of PVC (Darvish, Naderi et al. 2014). Pigment volume concentration is the ratio of pigment volume to the total volume of solid paint. It can be calculated as follow;

$$\mathrm{PVC} = (\mathrm{Vp} + \mathrm{VE})/(\mathrm{Vp} + \mathrm{VE} + \mathrm{VB}) \qquad \text{Eq 1. 1}$$

Where: Vp is a volume of pigment; VE is a volume of the extender; VB is a volume of binder.

The limiting value of PVC in paint formulation is known as critical pigment volume concentration (CPVC) (Končan Volmajer, Steinbücher et al. 2019). Critical pigment volume concentration is the PVC at which the binder concentration is sufficient to fill the void between the pigment and filler (Müller and Poth 2011). CPVC constitutes a significant transition point in the property of the paint film. Owing to the presence of air pockets, when the pigment volume concentration is greater than CPVC, the paint film becomes discontinuous. This implies that there is no adequate binder between the pigment and the extender particles to fill the hole. When the concentration of the pigment volume is lower than the CPVC, due to the presence of enough binder to hold the pigments and to fill the gap between them, the paint film continues (Končan Volmajer, Steinbücher et al. 2019). CPVC of paint consist single pigment and a mixture of pigment can be calculated as follow;

$$CPVCi = 1/(1 + (OAi * \rho i/93.5)) * 100\% \quad \text{Eq 2. 1}$$

$$CPVCmix = \Sigma(Wi/\rho i)/(\Sigma Wi/(\rho i * CPVCi)) \quad \text{Eq 2. 2}$$

$$CPVCmix = \Sigma(Wi/\rho i)/(\Sigma Wi/(\rho i * CPVCi)) \quad \text{Eq 2. 3}$$

Where: OA_i is the oil absorption value of component i, ρ_i is the density of component i. W_i is the weight fraction of component i, $CPVC_i$ is the critical pigment concentration of a single pigment.

2.4. Performance of road marking materials

Road users and road authorities strongly demand better-performing traffic marking materials. The efficient performance of this material provides optical guidance for road users (Babić, Burghardt et al. 2015). This event will ensure the safety of road users including drivers, pedestrians, and motorists.

Public administrators need traffic marking material that can provide better performance because administrators will invest a lot of money to maintain the proper performance levels. Each road management department has its selection criteria and guidance to select marking material that meets operating conditions. The Performance (durability and visibility) of traffic marking material, price, and local conditions are selection criteria that influence the selection of marking material by the administrator (Babić, Burghardt et al. 2015, Mohamed, Skinner et al. 2019).

The performance of traffic marking judge by two criteria, durability and visibility. The term durability measures the resistance of marking material to damage due to traffic volume and environmental effects. The durability of road marking is expressed by the percentage of material remaining on the surface of the road over time (Mohamed, Skinner et al. 2019). The durability of

road marking has a direct impact on visibility, periodic marking renewal schedule, and also overall maintenance cost (Babić, Ščukanec et al. 2018).

To achieve its goal, road marking must be visible in all traffic and weather conditions. The visibility of road marking refers to the brightness of the marking, which is directly related to nighttime visibility and daytime visibility. During the daytime, road users recognize road markings by the color contrast between the marking and the road surface. Recognition of road marking by road users is not a problem during the daytime because a sufficient amount of light is present during the daytime. The problem is during the night time or in the condition of low visibility (Babić, Ščukanec et al. 2018, Mohamed, Skinner et al. 2019).

Even though the number of vehicles traveling during the night is lower than daytime, a road traffic accident is high during night time this is because the quantity and quality of visual cues accessible to the drivers are limited (Burghardt 2018). At night, road users recognize road marking based on their nighttime visibility. Nighttime visibility of road marking is a function of luminescence contrast between markings and road surfaces. Luminous contrast is generally determined by the road marking retro-reflectivity (Babić, Ščukanec et al. 2018). Retro-reflectivity of road marking plays a significant role in guiding road users during nighttime.

The most important problem related to traffic marking is their low resistance to dirt pick up and loss of brightness. Pollutants suspended in the atmosphere which are release from different sources settle on the surface of traffic marking. These dirt materials are made up of different components such as carbon black, organic compound, nitrate, sulfate, and soil particles. The pollutant transported to traffic marking in the form of solid particles or liquid suspension and they leave a permanent stain on the marking surface (Alvani, Darvishi et al. 2018). Deposition of pollutant (dirt) on the surface of traffic marking negatively affect the day and night time visibility of the material and result loss of cognitive perception for the road user. Loss of visibility especially at night time and adverse weather conditions cause an accident. Therefore, to maintain the visibility of traffic marking paint at an adequate level application of new technology called self-cleaning coating is important (Taheri 2017).

In recent years the growth of new technology in the field of coating allows the development of new coating products that have either protective or decorative purposes with innovative science

(Taheri 2017). A recent development in Nanotechnology has disclosed to the production of cleaver coatings such as self-cleaning coating.

2.5. Self-cleaning coating

Environmental pollution, dust, and particulate materials in the air may easily make outdoor materials dirty. The accumulation of dirt on the surface of the material causes the optical properties of such materials to be preserved by intense cleaning. Material cleaning requires extensive manpower, resources, and financial resources (Zhang, Lei et al. 2019). Therefore, smart coating such as self-cleaning material is required to reduce extensive manpower and cost required for cleaning of the material. Recently self-cleaning coating using Nano size particles have obtained great attention in the different application area (Taheri 2017). Self-cleaning technology is derived from nature, many plants and animals exhibit self-cleaning property. For example left of the lotus plant, butterfly wings, and the exoskeleton of some insects. This technology has many advantages related to the reduction of the maintenance cost, elimination of tedious manual effort, and also reduction of time required to clean the surface (Ganesh, Raut et al. 2011).

Self-cleaning coating is classified into two: hydrophilic and hydrophobic coating. Both types of self-cleaning coating clean the surface by their different property toward the water. Hydrophilic coating cleans itself by making water film over the surface and washes off dirt and impurities that adhere to the surface. Whereas in the hydrophobic coating, the water droplet slid and roll over the surface to clean the surface. In addition to cleaning dirty by making water film, hydrophilic coating using metal oxide have the additional property of chemically break down dirt deposit on the surface of the material by sunlight assisted cleaning mechanism. The hydrophilicity or hydrophobicity of the material is determined by measuring the wetting angle, which is the angle formed by a water droplet with the surface of the material. Hydrophilic self-cleaning material has a wetting angle of less than 90^{o} whereas the hydrophobic material has a wetting angle greater than 90^{o} (Ganesh, Raut et al. 2011, Ragesh, Ganesh et al. 2014). This research only focused on the hydrophilic self-cleaning coating.

2.5.1. Hydrophilic self-cleaning coating

The hydrophilic coating chemically breaks dawn dirt absorbed on its surface when it is exposed to sunlight, the process is called photocatalysis. In the photocatalysis process, the organic pollutant decomposed into none or less toxic matters with the help of solar energy. Among many semiconductors, titanium dioxides have become a potential candidate for the preparation of self-cleaning coating due to their outstanding property such as photocatalysis activity, chemical stability, cost-effectiveness, and availability (Ragesh, Ganesh et al. 2014, Zhang, Sun et al. 2020).

When TiO_2 surface irradiated under UV light with energy equals to or greater than its bandgap energy, excited charge carrier (electron and hole) are generated on the surface. That means when light irradiated on the surface of TiO_2, the electron is excited from the valance band of TiO_2 to the conduction band and crate hole in the valance band. These charge carriers migrate to the surface and the electron reduces oxygen present in the air to generate superoxide radicals ($^{\bullet}O^{-}$). The hole can also oxidize the surface adsorbed water and generate hydroxyl radical ($^{\bullet}OH$). This free radical attack nearby organic pollutants and degrade into carbon dioxide and water. A schematic illustration of the photocatalytic reaction is shown in figure 1. Cleaning of the material surface by the degradation of organic pollutants deposit to its surface into water and carbon dioxide at an atmospheric condition called cold composition. Different types of organic pollutants in the solid, liquid, and gas phases can be degraded by the cold composition process (Cook and Baumeister 2005, Ganesh, Raut et al. 2011, Banerjee, Dionysiou et al. 2015).

In addition to its photocatalysis TiO_2 surface also become super-hydrophilic under UV Light irradiation (Liu and Jiang 2012). This two photo-induced property of TiO_2 (i.e. photocatalysis and super-hydrophilicity) is the base for the self-cleaning property of TiO_2 contain surface. Titanium dioxide exists in three crystal structures; anatase, rutile, and brookite. Among the three anatases, TiO_2 show better self-cleaning property (Quagliarini, Bondioli et al. 2012).

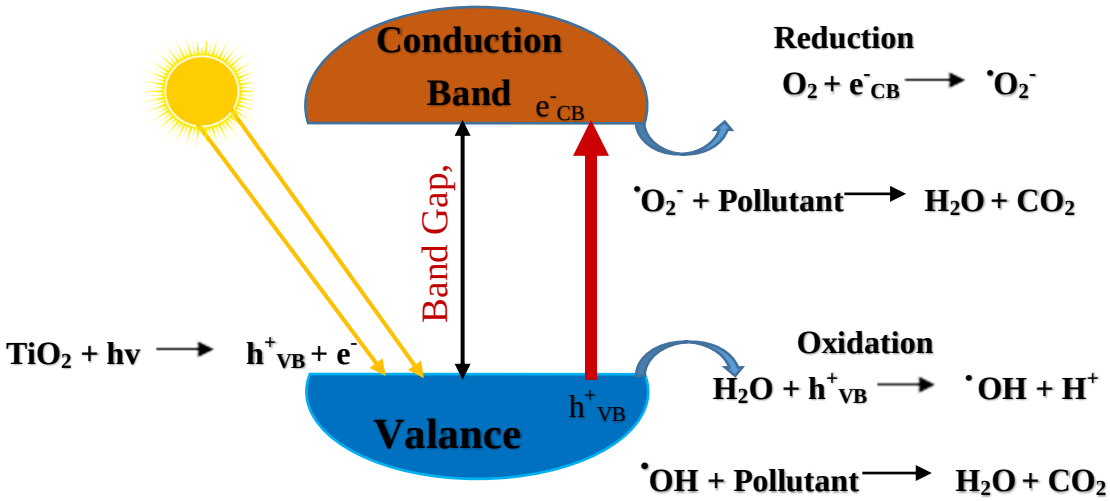


Figure 2. 1. Schematic illustration of photocatalysis reaction of TiO_2

In the recent year, self-cleaning coating using titanium dioxide as a photocatalysis have been used in different application areas such as cement, window glass, solar panel, textile, paint, household (bathrooms, kitchen fittings, and non-stick pans), road paving, vehicle side-view mirror and lamp (Parkin and Palgrave 2005, Sethi and Manik 2018). Recently the principle of self-cleaning coating also applies in the development of traffic marking paint. Traffic marking paint exposed to different weather conditions and pollutants (such as organic, inorganic, and soil particles) during their service life. Deposition of such pollutants causes a gradual loss of the daytime and nighttime visibility of traffic marking paint (Taheri 2017). In addition to this deposition of pollutants on the surface of paint require intensive cleaning. Cleaning of such dirt from the paint surface is labor-intensive, requires time, finical (Zhang, Lei et al. 2019). The application of self-clearing traffic marking paint could maintain the optical property of traffic marking paint and also reduce the maintenance cost.

Taheri, M., et al., (Taheri 2017) prepare self-cleaning traffic marking paint based on acrylic resin and anatase nanoparticles. The formulated traffic marking paint is composed of acrylic resin as a binder, commercial Nano-TiO_2 particles, calcium carbonate filler, and toluene as a solvent and additives (anti-settling agent and dispersing agent). The formulated paint consists of anatase nanoparticles that remain clean after a period of use as compared to the traffic marking paint without anatase nanoparticles. They observe the self-cleaning ability of traffic marking paint on the degradation of dirt by taking a photograph. Bricout, X.(Bricout 2012) prepare road marking

paint with self-cleaning property using anatase titanium dioxide. The road marking paint has both photocatalytic and hydrophilic properties.

Even though Nanosized titanium dioxide has great importance for the development of self-cleaning coating due to their photocatalysis and super hydrophilic property, some factors limit their application scope for the development of self-cleaning coatings such as their poor adsorption property and high agglomeration tendency (Liu, Zhao et al. 2020). Previous studies show usage of different adsorbents such as silica, zeolite, clay, and carbon black as a supporting material can improve dispersion and adsorption capacity. Due to their adsorbing property, such supporting material increases the availability of pollutants on the surface of Nano-TiO_2 and enhances the photocatalysis efficiency of titanium dioxide (Nosrati, Olad et al. 2015, Sun, Deng et al. 2017, Liu, Zhao et al. 2020).

Silicon dioxide is used as a supporting material for titanium dioxide due to its chemical inertness, transparency to UV radiation, large surface area, and high thermal stability. Silica from the different sources used as supporting material for Nano-TiO_2 including fumed silica, zeolites, clay. To prepare Nano-TiO_2/silica composite different methods are used such as chemical vapor deposition method, impregnation, precipitation method, and sol-gel method but among such methods the most promising methods are sol-gel and precipitation due to their low-cost production (Hendrix, Lazaro et al. 2015).

Many attempts have been done on preparing Nano-TiO_2/ silica composite for self-cleaning application. Zhang, M., et al.,(Zhang, Lei et al. 2019) prepared SiO_2/TiO_2 nanocomposite by a sol-gel method using titanium butoxide as a metal source and Tetraethyl orthosilicate (TEOS) as a silicon source. The prepared composite is coated on a glass substrate for self-cleaning application. But it is an efficient way to improve resource utilization using industrial byproducts as support material for the preparation of the composite instead of buying sources for supporting material. Usage of industrial byproduct that has high silica content helps to reduce the cost of the composite.

In addition to this usage of a byproduct of the industry has also a positive impact on the reduction of environmental pollution caused by the disposal of the residue to the environment. Sun, S., et al. (Sun, Deng et al. 2017) prepare Nano-TiO_2 coated SiO_2 microsphere composite by wet grinding of Nano-TiO_2 sol-gel and SiO_2 microsphere followed by proper calcination to obtain composite.

The SiO_2 microsphere used to prepare the composite was obtained from industries, produces as a byproduct during the production of fused zirconia. The composite shows better performance on the photocatalytic degradation of methyl orange in the aqueous solution.

To the best of our knowledge, there is no report on the preparation of Nano- TiO_2/Awash Melkasa residue silica composite photocatalysis and its application for the preparation of self-cleaning traffic paint.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials and Consumables

The major component of road marking paint; chlorinated rubber was supplied by Tarak chemicals.Ltd (www.tarakchemicals.com), titanium dioxide was supplied by Shanghai Jianghu Titanium white product CO. LTD (www.jianghuchemical.com), calcium carbonate was supplied by Vickers laboratories limited (http://www.viclabs.co.uk), dispersing agent (Byk 104s) and ant-settling agent (Bentonite –L-10) was supplied by BYK (byk-chemie gmbh), anti-skinning agent supplied by Rockwood Additives Ltd (BYK Additives. Ltd), driers (Combination driers) was supplied by Patcham.Ltd (https://www.patchamltd.com), plasticizer (Linseed oil) bought from a local market, toluene (methylbenzene) was supplied by Loba Chemie Pvt. Ltd. (https: //www.lobachemie.com), benzene bought from Local market, TiO_2 precursor (Titanium(Iv)butoxide) was supplied by SIGMA-ALDRICH (http://www.sigmaaldrich .com) and Ethanol was supplied by Dallul pharmaceuticals PLC.

Equipment and apparatus used for this research were beakers, weighing balance, measuring cylinder, petri dish, mechanical Stirrer, ball mill, muffle furnace, digital viscometer, panicle hardness tester, thickness gauge, tape, cutter, oven, and metal pycnometer, ultrasonic bath.

3.2. Methods

3.2.1. Binary solvent selection for the formulation of paint

The compatibility of a mixture of benzene and toluene with chlorinated rubber was examined experimentally. The blending ratio of the binary solvent is listed in Table 3.2. The solvent blends in which the chlorinated rubber fully dissolves with a minimum cost of solvent were selected as optimum and used for the whole paint formulation. Each experiment done was duplicate.

Table 3. 1. Mixing ratio of benzene and toluene.

Run	1	2	3	4	5	6	7	8
Benzene to toluene ratio	100/0	85/15	75/25	65/35	0/100	15/85	25/75	35/65

3.2.2. Experimental design for traffic paint formulation

Design-Expert software was used to determine the optimum proportion of traffic marking paint formulation. Binder (chlorinated rubber), pigments (titanium dioxide), extenders (calcium carbonate), and solvents (benzene and toluene) are major components of the traffic marking paint and selected as dependent variables in the experimental design. Among different methods in design expert software, mixture design was selected to determine the effect of each component of traffic marking paint on its end-user property. Analysis of variance (ANOVA) was performed to determine the influence of each factor (a component of paint) on the response. In ANOVA, P-value were used to evaluate the significance of the DoE proposed model and the interaction of each factor.

The formulation of traffic marking paint was developed by taking (Coughlan 1992) as starting formulation and by making a lot of preliminary experiments. Established along with the starting formulation and preliminary experiment, the ingredient of traffic marking paint; binder, pigment, extender, and solvent cover 86 wt. % of the paint recipe and the rest i.e. plasticizer and additives (dispersing agent, anti-settling agent, anti-skinning agent, deformed, and driers) cover 14 wt. % of the paint recipe.

Science pigment volume concentration is a highly influential parameter in paint property, pigment volume concentration (PVC) which is the ratio of pigment volume to the total volume of solid paint and critical pigment volume concentration (CPVC) of traffic marking paint were determined before formulating the paint. The PVC of traffic marking paint was calculated by considering the upper and lower limit value of the paint ingredients using Eq 3.1. The CPVC of the traffic marking paint was also measured by the oil absorption method using Eq 3.2. Titanium dioxide (Shanghai Jianghu Titanium white product CO. LTD) has an oil absorption value of 26 and a density of 3.9 g/cm^3. Calcium carbonate (Vickers laboratories limited) has an oil absorption value

of 40 and a density of 2.7 and the chlorinated rubber (Tarak chemicals. Ltd) has a density of 1.6g/cm^3. Therefore the traffic marking paint was formulated at pigment volume concentration (PVC) in the range between 43.1-44.9 and the CPVC was between 46.5-46.7.

$$PVC = (Vp + VE)/(Vp + VE + VB) \quad \text{Eq 3. 1}$$

$$CPVCi = 1/(1 + (OAi * \rho i/93.5)) * 100\% \quad \text{Eq 3. 2}$$

$$CPVCmix = \Sigma(Wi/\rho i)/(\Sigma Wi/(\rho i * CPVCi)) \quad \text{Eq 3. 3}$$

Where: V_P is pigment volume, V_E is extender volume, V_B is binder volume, OAi is the oil absorption value of component i, ρ_i is the density of component i. W_i is the weight fraction of component i, $CPVC_i$ is the critical pigment concentration of a single pigment.

To develop predictive models, 24 formulations were developed using Design-expert software. The factors and their varied range defined by experimental design software are listed in table 3.3.

Table 3. 2. Factors and levels in the experimental design.

Variable	**Level**	
	low (-1)	**high (+1)**
A: Pigment(Titanium dioxide)	5	16
B: Extender(Calcium carbonate)	25	35
C: Binder (Chlorinated rubber)	5	20
D: Solvent	35	45

Considering these design criteria, the output of the software was a set of 24 possible formulations. Based on mixture design, the effect of ingredients of the traffic marking paint on its viscosity was evaluated and the optimum combination was determined. Viscosity for each of 24 experimental runs was determined according to ASTM D 562-01 standard test method. The experimental run and the response (viscosity) obtained from the software is presented in Table 3.4. To minimize an error each experimental run was done duplicate, and the average value of the response (viscosity) was taken.

Table 3. 3. Formulation and run order proposed by mixture experimental design.

	Component 1	Component 2	Component 3	Component 4	Response
Run	A:Pigment(Titanium dioxide)	B:Extender(Calcium carbonate)	C:Binder (Chlorinated rubber)	D:Solvent	Viscosity
	%wt.	%wt.	%wt.	%wt.	KU
1	5.0	26.0	20.0	35.0	
2	16.0	25.0	5.0	40.0	
3	7.7	28.4	8.4	41.5	
4	9.0	31.0	11.0	35.0	
5	5.0	25.0	15.5	40.5	
6	5.0	26.0	20.0	35.0	
7	6.7	27.9	14.9	36.5	
8	9.8	25.0	11.8	39.3	
9	5.0	40.0	6.0	35.0	
10	11.0	25.0	15.0	35.0	
11	11.0	25.0	15.0	35.0	
12	16.0	27.5	7.5	35.0	
13	5.0	35.5	5.0	40.5	
14	5.0	31.0	5.0	45.0	
15	5.0	25.0	11.0	45.0	
16	9.8	31.8	5.0	39.3	
17	11.0	25.0	5.0	45.0	
18	5.0	31.2	11.2	38.7	
19	11.0	35.0	5.0	35.0	
20	5.0	33.0	13.0	35.0	
21	11.0	35.0	5.0	35.0	
22	5.0	33.0	13.0	35.0	
23	6.7	34.9	7.9	36.5	
24	5.0	40.0	6.0	35.0	

3.2.3. Preparation of traffic marking paint

Based on the formulation constant amount of dispersing agent (BYK 104s), ant-settling agent (BentoLITE-L-10), anti-skinning agent (BYK ALTANA group), and plasticizer were added to solvent (a combination of benzene and toluene) under mechanical mixing at a mixing speed of 200 rpm for 5 min as per a method of (Hadizadeh, Pazokifard et al. 2020) with little modification. Then the powder ingredient of the paint composition; pigment (TiO_2) and extender ($CaCO_3$) were gradually dispersed into the mixture using mechanical mixing at the speed of 1,500 rpm for 10 minutes. Thereafter, chlorinated rubber as a binder was added to the mixture and mixed for 5 min at 1,500 rpm as described by (Hadizadeh, Pazokifard et al. 2020).

Then the mixture was milled for 30 min at a rotation speed of 150 rpm using a ball mill to make a smooth coating by avoiding any pigment and extender agglomeration. Lastly, the drier (Patcham driers) were added and mix for 5 minutes as described by (Hadizadeh, Pazokifard et al. 2020). Figure 3.1 illustrates schematically the applied process flow diagram for the production of traffic marking paint.

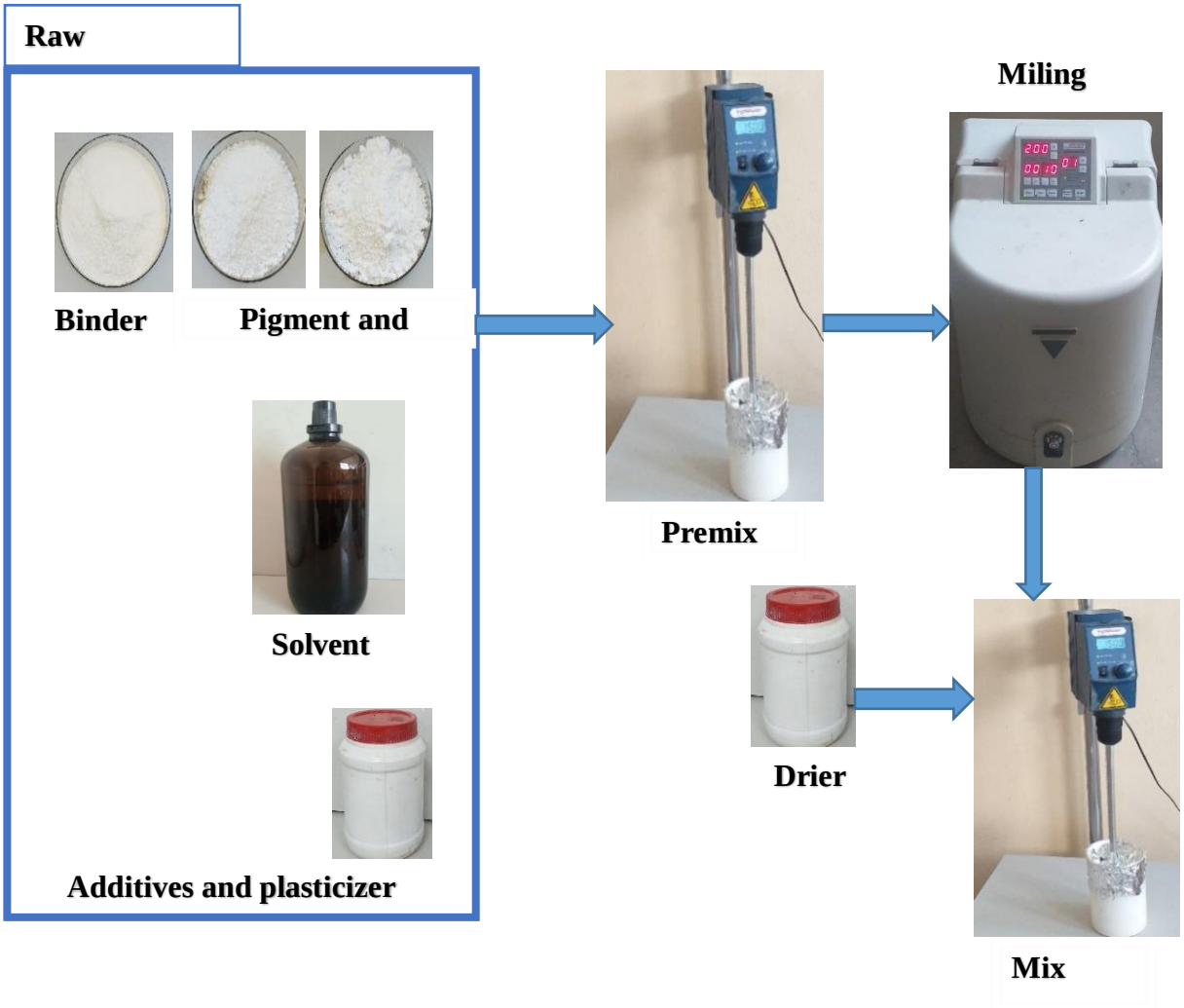


Figure 3. 1. Schematic diagram of the overall process of traffic marking paint manufacturing operation.

3.2.4. Selection of optimum traffic paint formulation

Based on the result of viscosity, the paint sample that had viscosity ranging in between the commercial-grade traffic paint viscosity (i.e.809-1350 cp) was selected. For each optimum road marking formulation different end-user property test was done, these are density, adhesion, hardness, film thickness, volatile content of road marking paint, water immersion test, and thermal resistance. Each test was done according to ASTM and ISO standard test method, and the detailed discerptions of how each test held describe in the experimental section. After doing each

test the paint formulation that has good performance was selected as the optimum paint formulation.

3.2.5. Modification of road marking paint using Nano TiO_2/ Awash Melkassa industrial waste silica composite as photo-catalyst

i. Pretreatment of Awash Melkassa S.C byproduct silica and composite preparation: Kaolin is the main raw material of Awash Melkassa Aluminium Sulfuric Acid factory to produce aluminum sulfate and high silica contain kaolin is a by-product of the company. The silica from the by-product of Awash Melkassa S.C was dried in the oven at 105 ^oC for 24 hours. The dried sample was then milled at 250 rpm using a ball mill for 15 minutes and sieve to obtain a particle size less than 63μm (Hadjltaief, Gálvez et al. 2019). In accordance with a thermogravimetric analysis result, silica with a particle size of less than 63μm was outgassed at a temperature of 900 ^oC.

The outgassed silica was used to prepare Nano TiO_2/ silica photo-catalysts. The preparation of Nano TiO_2/ silica composite was done as described by (Sun, Deng et al. 2017). The preparation of the composite classified into three steps such as preparation of Nano-TiO_2 sol-liquid; depolymerization of SiO_2; and preparation of Nano TiO_2/ Awash Melkassa residue silica photo-catalyst and a detailed description of the method described below;

Preparation of Nano-TiO_2 Sol-liquid: 8.5 mL of tetrabutyl titanate was initially dissolved in 10 ml of the ethanol solution. The combined solution was uniformly stirred and marked as Solution A. The mixture of acetic acid and hydrochloric acid (volume ratio 2.5:1) was then dissolved into 10 mL of ethanol solution. The obtained solution was marked as Solution B. Solution B was then slowly added into Solution A and 19.35 ml of the ethanol and water mixture (water 0.85 mL) was also added into Solution A. The mixture was then vigorously stirred for 12 h at room temperature and the stirred mixture was aged for 48 h to obtain the stable nano-TiO_2. Light brown sol-liquid was finally obtained.

Depolymerization of Awash Melkassa residue silica: due to the agglomeration effect of residual silica**,** depolymerization and dispersion of the silica are important. The silicon materials were added to the ethanol solution to form a suspension. The suspension was mixed using high speed

dispersing machine at the speed of 1000 rpm for 30min again the suspension was ultrasonic for 30 min. Finally, the dispersed SiO_2 was obtained.

Preparation of Nano-TiO_2/Awash Melkassa residue silica composite: Firstly, the dispersed SiO_2 was added into the aged nano-TiO_2 sol-liquid to form the Nano-TiO_2/SiO_2 mixture. Secondly, the Nano-TiO_2/SiO_2 mixture was stirred for 60 min using a high-speed dispersion machine at speed of 1000 rpm. Then, the Nano-TiO_2/ Awash Melkasa residue SiO_2 sol-liquid composites were put in a drying oven at 80 ^oC for 3 hrs and calcined in a chamber electric furnace at 500 ◦C for 2 h. Finally, the Nano-TiO_2/ Awash Melkasa residue SiO_2 composite was obtained. Figure 3.2. Show the schematic diagram of the overall process of production of Nano-TiO_2/Awash Melkasas residue silica photo-catalysts.

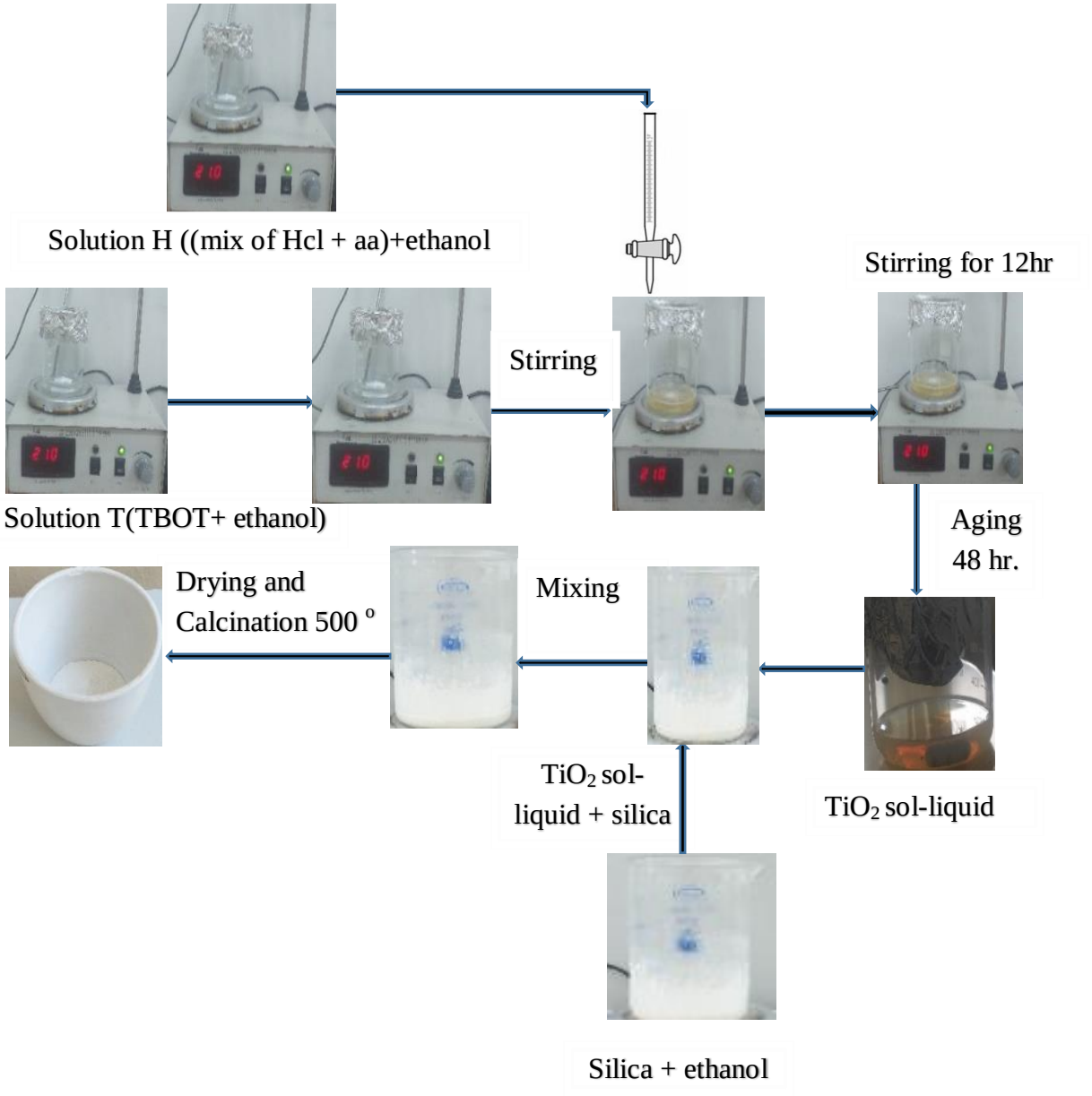


Figure 3. 2. Schematic diagram of the overall process of production of Nano-TiO_2/silica photo-catalysts.

ii. Formulation of modified road marking paint with self-cleaning performance: The optimum formulation of road marking paint that has better end-user property was selected to prepare self-cleaning road paint. The self-cleaning road paint was prepared by replacing the pigment of the formulated traffic marking paint with the Nano-TiO_2/Awash Melkassa residue silica photo-catalyst. Based on the recipe dispersing agent (BYK 104s), ant-settling agent

(BentoLITE-L-10), anti-skinning agent (BYK ALTANA group), added to solvent (a combination of benzene and toluene) under mechanical mixing at mixing speed of 200 rpm for 5 min. Then, Nano-TiO_2/SiO_2 composite was added to the mixture and mix for 5 min at the same mixing speed. The mixture was sonicated for 30min to avoid agglomeration. The extender ($CaCO_3$) was gradually dispersed into the mixture under mechanical mixing at the speed of 1500 rpm for 10 minutes. Thereafter, the binder (chlorinated rubber) and plasticizer was added to the mixture and mix for 5 min at the same mixing speed. Lastly, driers were added to the mixture and mix for 5 min.

3.3. Experimental Design

3.3.1. Protocol followed for the characterization of road marking paint

Preparation of test panel: Aluminum metal plat with dimensions of 150-100mm was prepared as described in ISO 1514 standard. The metal plate was cleaned before usage. The aluminum metal plate was used for a cross-cut, pencil hardness, water resistance, and thermal resistance test. The paint was applied on the metal plate using a film applicator at a wet film thickness of 466.66 µm. Then, the test panel was allowed for air drying for several hours depending on the test method procedure.

Viscosity Measurement: The viscosity of different road marking paint samples was measured using a digital display viscometer (VK-2000, MYR KREBS viscometer); according to ASTM D562-0l test practice at atmospheric temperature. The paint sample was poured into a 250 ml beaker. The beaker was then placed on a digital viscometer after it had been switched on. Then the spindle attached to the machine was dipped into the sample in a beaker. The spindle was allowed to rotate for 40 seconds. The viscosity reading was taken in the Kreb unit (KU). The spindle was raised and the beaker can be removed, following which the spindle was thoroughly cleaned. The viscosity of traffic marking paint measurement using a VK-2000 viscometer at an atmospheric temperature is shown in figure 3.4.

Figure 3. 3. Viscosity measurement of traffic marking paint.

Density Measurement: The density of the road marking paint sample was measured using a metal pycnometer according to ISO 2811 test practice. The weight of an empty metal pycnometer was first weighted using digital weight balance. Then the value was recorded (M1). The paint sample was poured into the metal pycnometer and any excess paint was cleaned off from the pycnometer. The metal pycnometer with the paint was weighted (M2) to obtain the density of the road marking paint. Two tests were done and the average value was calculated.

$$\text{Density } (\rho) = \frac{\text{M1} - \text{M2}}{\text{V}} \qquad \text{Eq 3. 4}$$

Where = M1 is the mass of empty metal pycnometer; M2 is the mass of metal pycnometer filled with paint sample and V is the volume of the metal pycnometer. The weight of an empty pycnometer and a pycnometer with a sample is shown in Figure 3.3.

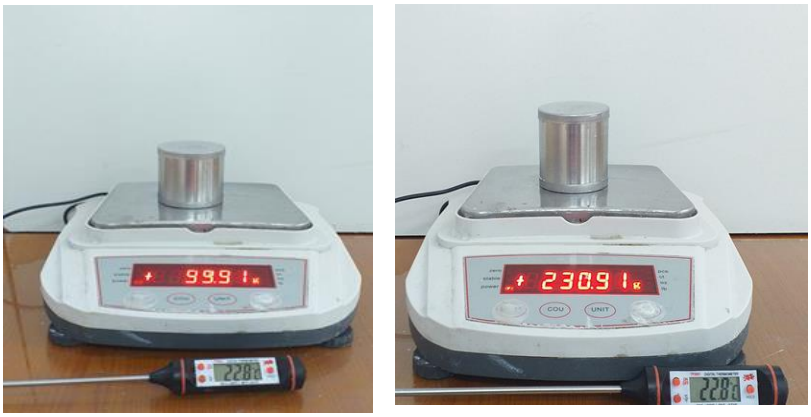


Figure 3. 4. A weight measurement of empty pycnometer and pycnometer with the sample.

Film thickness measurement: the wet film thickness of traffic marking paint was measured using a hand-held immersion gauge called Elcometer 112 wet film thickness gauge according to the ASTM D4414 standard test method. Elcometer 112 wet film thickness gauge has a series of teeth along with the ending of different lengths.

Before measuring the wet film thickness of traffic marking paint, the paint was applied on an aluminum metal plate. Then the gauge was placed on the freshly applied painted surface. The ending of the gauge is supported by two teeth of the same length for measurement control and the other teeth have different length and they are shorter than the control teeth. After applying the thickness gauge on freshly applied traffic marking paint, the last tooth that leaves a mark in the paint film was taken as the wet film thickness of traffic marking paint.

Adhesion test: In accordance with the ISO 2409 standard test procedure, the adhesion of the coating layer to the substrate was measured. The traffic marking paint was applied on an aluminum metal platform before the test began and the plate was allowed to dry for 24 hours. In this test, using the cutter to create a grid of small squares at right angles to each other, six 3 mm spaced cuts were made in two directions.

Then 75mm long pressure adhesive tape was applied over the lattice parallel to one set of cut. To ensure good contact of the tap with film, the tap was firmly rubbed with an eraser. Finally, the tap was removed by grasping the free end and pulling in a single smooth action. Adhesion of road marking paint with the substrate was then assessed by comparing the fraction of coating removed from the grid of squares against the ISO 2409 standard ratings.

Hardness test: The hardness test of dry road marking paint film was determined according to ISO 15184 standard using pencil hardness tester, Wolff-Wilborn pencil hardness tester. The pencil hardness test is a constant-load scratch test. It uses pencil leads of different hardness grades (6B (soft)–6H (hard)) as the scratch stylus. The same normal load with indenters of different hardness is applied to the samples. The hardest pencil grade that does not cause damage to the coated specimen is considered as the pencil hardness of the coating.

The traffic marking paint was applied to the aluminum metal plate using a film applicator before the start of the test and was allowed to dry for 48 hours. The painted metal plate was then mounted on a horizontal surface. At a 45° angle, the pencil mounted on the pencil hardness tester was placed firmly against the film. Starting from soft pencil 6B up to the hardest pencil that causes failure to the surface of the paint film was used. The pencil hardness tester with a pencil pushed away from the operator. During the operation, the tester applies 10N on the surface of the paint film. Finally, the hardest pencil that does not cause damage to the painted panel was recorded as the pencil hardness of the road paint. figure 3.4 shows the Wolff-Wilborn pencil hardness tester.

Figure 3. 5. Wolff-Wilborn pencil hardness tester.

Determination of Volatile matter contains road marking paint: Volatile matter contains in road marking paint was determined according to ASTM D2369 standard test method. A designated quantity of coating specimen was weighed into an aluminum foil dish containing 3 mL of toluene

dispersed, and heated in an oven at 110℃ for 60 min. The percent volatile was calculated from the loss in weight. Two tests were done and the average value was calculated.

$$VA = 100 - ((W2 - W1)/SA * 100) \quad \text{Eq 3. 5}$$

Where= VA is the weight percent of volatile: W1 is the weight of aluminum foil dish: W2is weight of aluminum foil dish with sample after heating: SA is the weight of the specimen.

The weight percent solids content (nonvolatile matter) of road marking paint was also determined by difference.

$$NA = 100 - VA \quad \text{Eq 3. 6}$$

Where= NA is weight percent solids content (nonvolatile matter): VA is the weight percent of volatile.

Testing water resistance of traffic marking paint using water immersion: In accordance with the ASTM D870 test process, the water-resistance of the road marking paint film was determined. The paint was applied to an aluminum metal plate before the start of the test and allowed to dry for 48 hours to ensure the removal of all the solvent from the paint film

The water bath was filled with distilled water and its temperature was set at 38 ^{o}C. Then, in the water bath, the painted aluminum metal plate was placed. The painted metal plate was removed from the water bath after 8 days. The evaluation of the sample was held after the removal of the sample from the bathe. Then, any effect such as color change, blistering, loss of adhesion, and softening was observed and reported.

Temperature resistance of traffic marking paint: the effect of heat on paint film was determined according to ISO 3248 standard test method. The effect of heat on traffic marking paint was determined by placing the coated aluminum metal plat in a drying oven at 100 ^{o}C for 10 hr. Before starting the test, the specified area was quantified on the surface of the paint to control the expansion or contraction of the paint film due to heat. On average the sun peak for 10hr (from 9 am to 4 pm) during the day. Then by considering this, the sample was placed in an oven for 10 hr per day and in each of 1hr, the expansion or contraction of the paint film was determined by measuring the area. The test was done for 3 consecutive days.

3.3.2. Characterization of silica and Nano titanium dioxide/ silica photo-catalysts

Thermogravimetric analyses (TGA): Thermal gravimetric analysis (TGA) analysis was performed using the flow rate of Nitrogen at 20.0 mL/min to determine the thermal stability of the Awash Melkassa residue silica. The temperature was adjusted between 25 ℃ to 1000 ℃ with a heating rate of 10 ℃/min and the decomposition of sample weight (%) against temperature (℃) was recorded.

XRD analysis: the X-ray diffraction (XRD) pattern of silica and Nano-TiO_2/ silica and Nano-TiO_2 was performed with an X-ray diffractometer using 40Kw Cu-Ka radiation over bragged angle range 10-80° (Roongraung, Chuangchote et al. 2020) to survey the crystal structure of Awash Melkassa residue silica, Nano-TiO_2, and Nano-TiO_2/silica composite. The obtained diffraction pattern was refined using high scholar plus software. The average crystalline size of Nano-TiO_2 was calculated using the Scherrer equation using Eq 3.7.

$$D = K\lambda/\beta cos\theta \qquad \text{Eq 3. 7}$$

Where D is average crystalline size: K is the shape factor (0.9):λ is the wavelength of X-ray radiation: θ is Bragg angle of corresponding diffraction peak:β is full width at half maxima (FWHM) of main diffraction peak (Roongraung, Chuangchote et al. 2020)

The distance between the atomic layer of crystal was also calculated using Bragg's low using Eq 3.8.

$$n\lambda = 2dsin\theta \qquad \text{Eq 3. 8}$$

Where n is an integer: d is the distance between the atomic layer: θ is an incident angel: λ is the wavelength of an incident X-ray beam (Mallakpoura and Shahangia 2012).

FI-TR analysis: The surface functional group of Awash Melkassa residue silica, Nano-TiO_2, and Nano-TiO_2/silica composite were examined by Fourier transferred infrared radiation (FTIR with Model name FTIR-6600 type A and Serial number A013861790). FTIR attenuated with total reflectance (ATR) mode in the range of 4000 to 500 cm-1 with 4 cm-1 resolution and 64 scan rates.

SEM-EDS: The elemental composition of Awash Melkasa residue silica before and after heat treatment, and Nano-TiO_2/silica composite was examined using Bruker's electron microscope analyzers SEM on EDS.

3.3.3. Evaluation of Self-cleaning performance of road marking paint

Self-cleaning property test: The self-cleaning property of Nano TiO_2/silicon modified traffic marking paint was determined by the distraction of stains of methyl blue day (mg/lit) as a model pollutant. The traffic paint applied on the aluminum metal plate was stained with 100 µl of methylene blue solution with a concentration of 10 and 20ppm. Then it dries with air in dark condition for 24 hrs and exposed to sunlight from February 24, 2021, to February 26, 2021, for a total of 12 hr. The photographic image of the paint film was taken at a regular time interval to evaluate the change in methyl blue dye color. For comparison, the self-cleaning property of traffic marking paint without composite was evaluated with the same procedure.

Wettability investigation of the modified road marking paint: To assess the hydrophilic and hydrophobic characteristics of self-cleaning road marking paint film surface, the contact angle of a water droplet on the surface of the paint film was measured using a high-resolution camera. The water droplet dripped slowly on the surface of the paint film using a droplet then the photograph was taken instantly. The water contact angle analysis was performed using Image J software. The water contact angle of the paint film was measured before and after sunlight exposure and all test was done duplicate.

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1. Binary solvent selection for the formulation of paint

Solvent-based traffic marking paint is the dispersion of pigment, extender, binder, and additives within the organic solvent. During the application of traffic paint, the solvent evaporates from the surface of the road and forms a dry film. Even though the solvent is not an integral part of the dry paint film, they are an important component of the paint. They have a significant role in the paint production, application and film formation process (Mannari and Patel 2015).

Selection of solvent and determination of their composition is an important step in paint formulation. For the formulation of traffic marking paint, chlorinated rubber was selected as a binder. Chlorinated rubber is soluble in most organic solvents such as toluene, benzene but they are insoluble in aliphatic hydrocarbon and alcohols.

In this research work, toluene and benzene were selected as a solvent during the traffic paint formulation. The solubility of chlorinated rubber in the selected solvents with different blending ratios was performed in order to find the best formulation based on solubility performance and cost. As indicated in figure 4.1 benzene and toluene at different blending ratios were used to dissolve 15g of chlorinated rubber. Then solubility of the resin in those solvents was analyzed by sensory analysis.

The mixing of chlorinated rubber with benzene to toluene blend ratio of 100/0 shows phase separation after the mixture is withdrawn from the mixer. According to (Freitag and Stoye 2008), chlorinated rubber is soluble in aromatic hydrocarbon including benzene and insoluble in alcohol. However, during the experiment, it was very difficult to dissolve chlorinated rubber using locally available benzene and it is because of the purity of benzene. The benzene used in this research work was bought from the local market which has a 10% ethanol blended (Gabisa and Gheewala 2020). Since chlorinated rubber is insoluble in alcohol, the presence of ethanol in benzene influences the solubility of chlorinated rubber.

Owing to the presence of toluene, the solubility of the binder within the specified benzene to toluene blend ratio of 85/15, 75/25, 65/35 was considerably enhanced as the blending composition of toluene increased. For the aforementioned formulations, phase separation was observed as a major problem.

Complete solubilization of chlorinated rubber was observed for benzene to toluene blending ratios of 15/85, 25/75, 35/65, and 0/100. From this, it can be concluded that toluene can be considered as a true solvent, while benzene obtained from the local market (10% ethanol blended) can be taken as a diluent solvent. True solvents are solvents that can dissolve the binder, while diluent solvents are solvents that do not dissolve the binder but are used to reduce the true solvent cost.

The cost estimation of each solvent blend ratio in $/lit is presented in Table 4.1. The solvent solution with a mixing ratio of 100/0, 85/15, 75/25, and 65/35 has a low cost relative to the 35/65,25/75,15/85, and 0/100 mixing ratios. Even if a lower-cost index was observed for the higher content of benzene, the primary objective of solubilizing the chlorinated rubber can not be achieved. Therefore, a minimum cost of solvent blend without compromising the solubilization effect can be achieved at benzene to toluene blending ratio of 35/65. The cost of solvent at 100% toluene reduced from 14.46$/lit to 12.38$/lit while using the 35/65 ratio blend and the cost reduction accounts 14.4% from the initial. Based on this observation the subsequent formulation was performed using a 35/65 blending ratio.

Table 4. 1.The solvent blend ratio and solubility result of chlorinated rubber.

Run	**Benzene to toluene ratio**	**Chlorinated rubber (g)**	**Solubility**	**Cost ($/lit)**
1.	100/0	15	Insoluble	0.57
2.	85/15	15	Insoluble	2.66
3.	75/25	15	Insoluble	4.05
4.	65/35	15	Insoluble	5.44
5.	15/85	15	Soluble	9.60
6.	25/75	15	Soluble	10.99
7.	35/65	15	Soluble	12.38
8.	0/100	15	Soluble	14.46

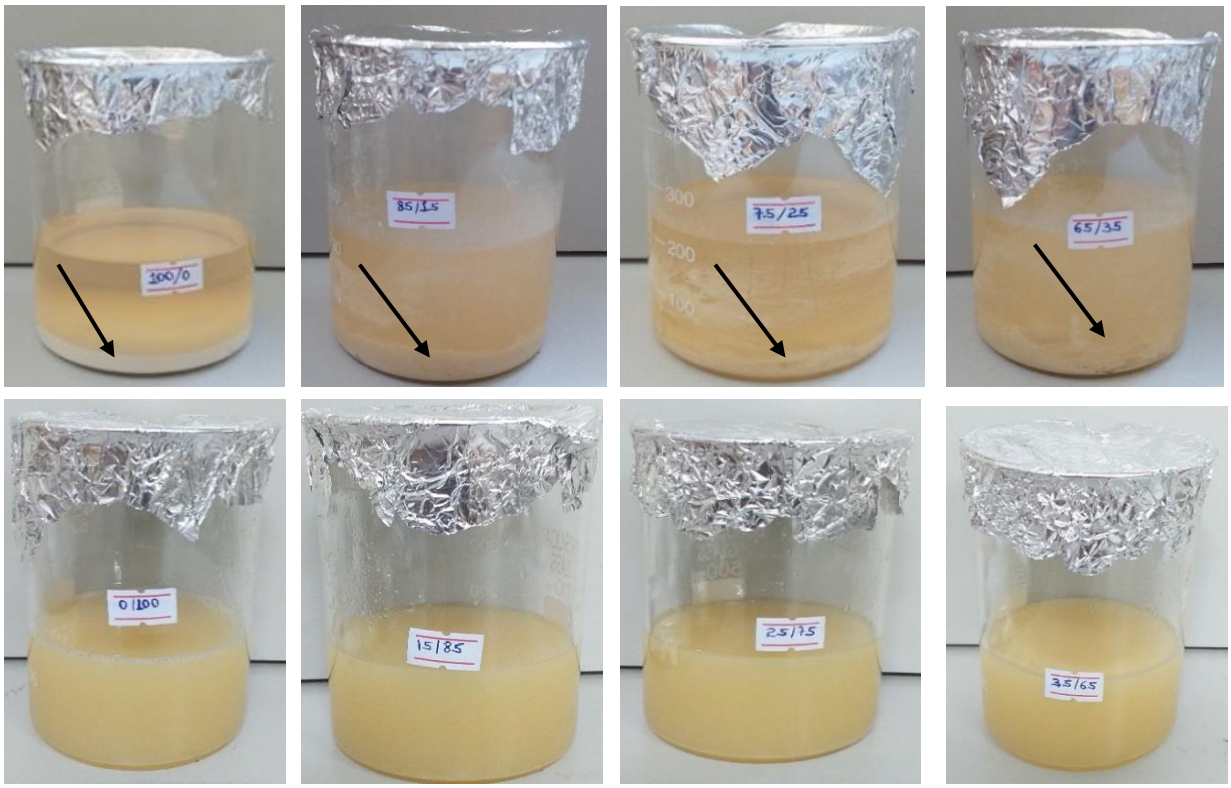


Figure 4. 1. Mixing of chlorinated rubber with benzene and toluene with different blending ratios of solvent.

4.2. Formulation of traffic paint: Mixture design

The viscosity of traffic marking paint was measured using a VK-2000 viscometer at an atmospheric temperature. Each of the 24 experimental runs was done duplicate and the average value of the viscosity was taken. The result obtained for the viscosity of each sample is shown in Table 4.2. The result was analyzed by experimental-design software to determine the possible correlations of factors (components of the paint) and the response (viscosity).

The measured value of viscosity for traffic marking paint samples with different formulations was in the range of 53-114.45 KU (2.23-24.81 poise). Practically most commercially available chlorinated rubber-based traffic marking paint has a viscosity within the range of 80-95 KU (8.09-13.5 poise) (Brand name TT-P-115F, EF serious high VOC chlorinated rubber traffic paint). The result of the response value revealed that samples in run 4, 7, 10, and 20 show viscosity within the acceptable range as compared to other samples.

Table 4. 2. Formulation of traffic marking paint proposed by mixture experimental design and the result of viscosity test.

	Component 1	Component 2	Component 3	Component 4	Response
Run	A:Pigment(Titanium dioxide)	B:Extender(Calcium carbonate)	C:Binder (Chlorinated rubber)	D:Solvent	Viscosity
	%wt.	%wt.	%wt.	%wt.	KU
1	5.0	26.0	20.0	35.0	114.45
2	16.0	25.0	5.0	40.0	57.4
3	7.7	28.4	8.4	41.5	58.2
4	9.0	31.0	11.0	35.0	81.85
5	5.0	25.0	15.5	40.5	72.6
6	5.0	26.0	20.0	35.0	114.45
7	6.7	27.9	14.9	36.5	93.35
8	9.8	25.0	11.8	39.3	65.85
9	5.0	40.0	6.0	35.0	71.1
10	11.0	25.0	15.0	35.0	93.65
11	11.0	25.0	15.0	35.0	93.65
12	16.0	27.5	7.5	35.0	68.55
13	5.0	35.5	5.0	40.5	59.45
14	5.0	31.0	5.0	45.0	53
15	5.0	25.0	11.0	45.0	56.6
16	9.8	31.8	5.0	39.3	58.25
17	11.0	25.0	5.0	45.0	53.9
18	5.0	31.2	11.2	38.7	69.2
19	11.0	35.0	5.0	35.0	65.1
20	5.0	33.0	13.0	35.0	88.85
21	11.0	35.0	5.0	35.0	65.1
22	5.0	33.0	13.0	35.0	88.85
23	6.7	34.9	7.9	36.5	68.55
24	5.0	40.0	6.0	35.0	71.1

4.2.1. Response surface analysis

Analysis of variance (ANOVA) was performed to determine the influence of each factor (a component of paint) on the response. Different response surface plot generated by the DoE software and each plot shows how the response (i.e. viscosity of traffic marking paint) vary as a function of the proportion of the four ingredients of paint(pigment, extender, binder, and solvent) at a constant amount of plasticizer and additives.

4.2.1.1. Effect of paint ingredients on viscosity

The 2D contour plot and 3D graph indicated in Figure 4.2 shows the effect of the different formulation of the paint on the viscosity of traffic marking paint. The color spectrum shows the pattern of the change in the viscosity of the traffic paint sample as a function of the change in the formulation (a combination of the three components; pigment, extender, and binder at a constant level of the fourth solvent component). The viscosity of the paint sample was observed to vary from 53 to 114.45 KU (2.23-24.81 poise).

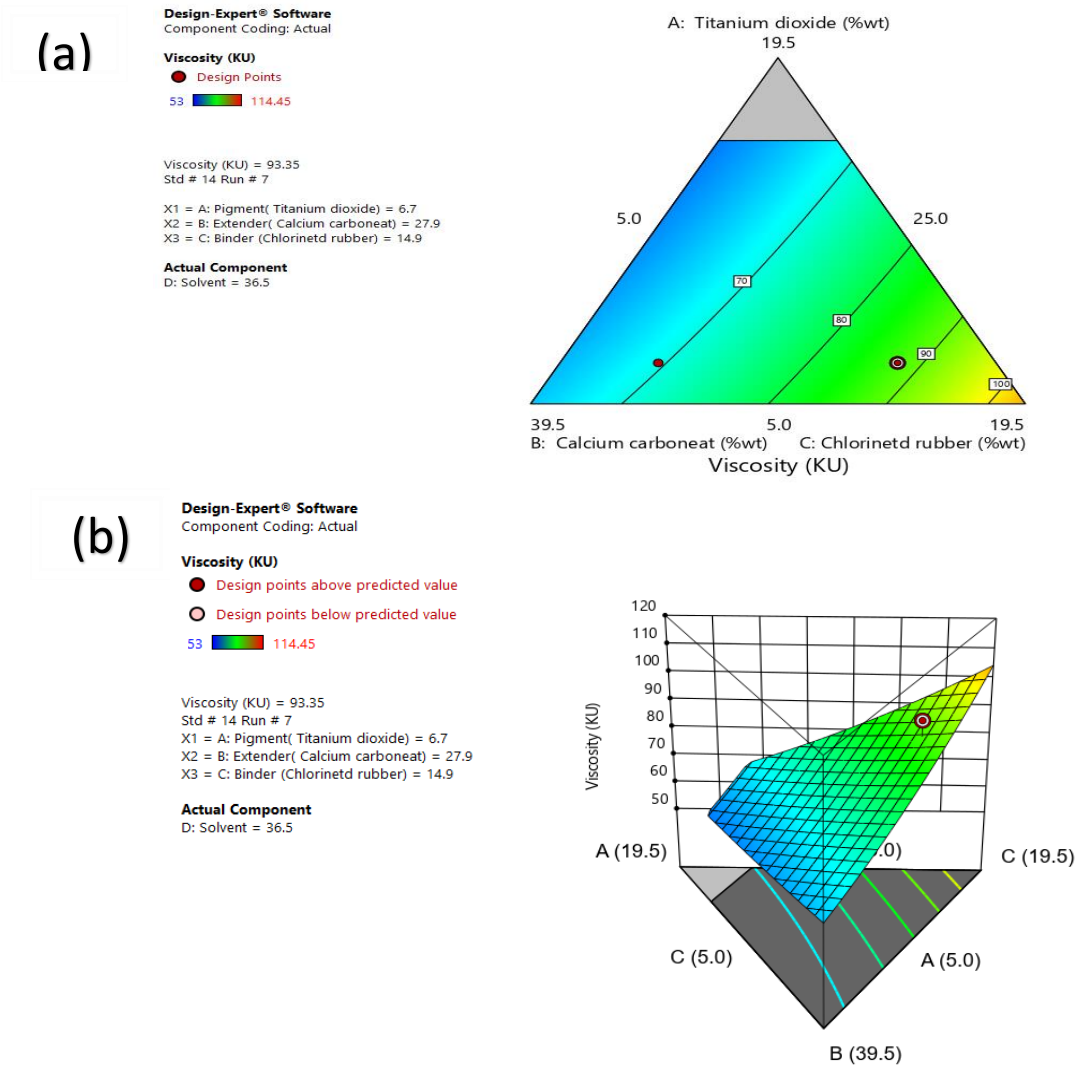


Figure 4. 2. Contour plot (a) and 3D graph (b) of viscosity as a function of different levels of traffic marking paint ingredients.

The trace plot in figure 4.3 shows how the viscosity of traffic marking paint change with a change in the amount of each ingredient in paint formulation while keeping the other constant. As seen in the figure, chlorinated rubber has a huge impact on the viscosity of the paint.

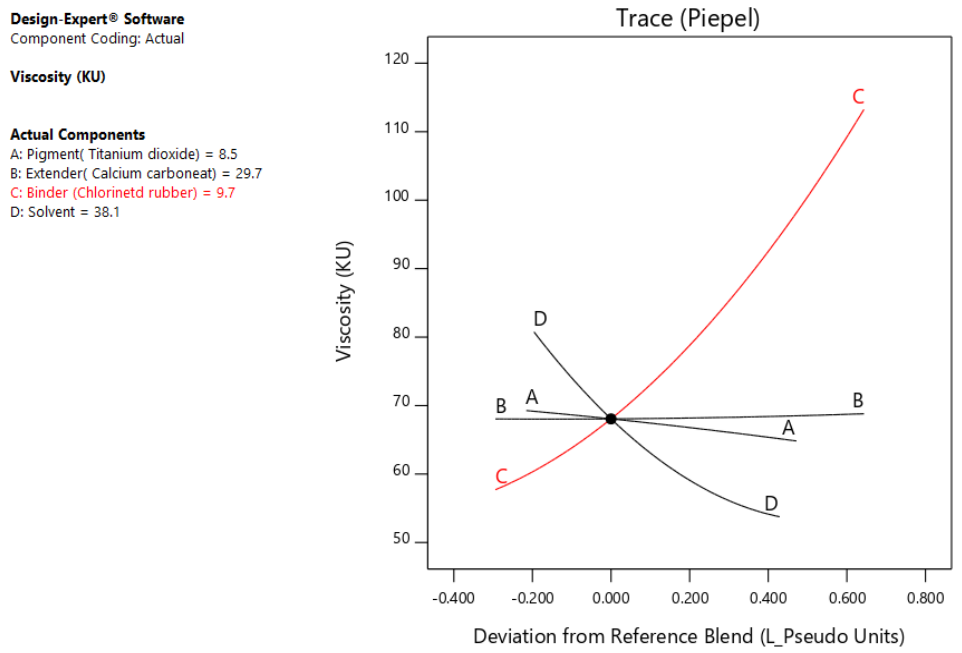


Figure 4. 3. Trace plot of the viscosity of traffic paint.

The suggested model for the interactions between the composition of the paint ingredient and viscosity value was found to be quadratic, according to the study of variance (ANOVA). Table 4.3 reports the ANOVA findings for the viscosity of various samples of traffic paint. The model is significant, as seen in the table (model p-value< 0.05). Each individual component of the paint ingredient has an impact on viscosity. The macromolecular entanglement of the chlorinated rubber and the solvent characteristics towards elastomeric polymer can highly influence the flow characteristics of the paint which can be related to viscosity. The high interaction effect of solvent to polymer will help facilitate uniform dispersion of fillers within the entangled macromolecular structure that can further improve the binding effect after the removal of the solvent. Increasing a solvent amount can cause disentanglement of the polymeric chains which is a major reason for the reduction of paint viscosity. The increasing of the solid content of the paint also increases the viscosity of the paint. relatively, the low viscosity of paint is required during production in order to have a uniform and complete desperation of the solid content in chlorinated rubber matrix using minimum energy conception. Similarly, relatively low viscosity can also help to apply the paint easily on the road. However, low viscosity can also negatively affect the storage capacity and spreadability during application. Therefore, optimum viscosity is required targeting less

spreadability and easy to flow during application; high density during storage and minimum power consumption during production. Most of the commercially available traffic paint viscosity varies from 80-95 KU. Out of 24 experiments performed in this research work the viscosity of only four formulations coincides within the range of commercial available traffic paints viscosity. From the ANOVA result, it can be confirmed that the contribution of the linear factor is significant with P-value less than 0.05. the linear factors increment of binder, pigment, the extender has been observed to increase the viscosity, while the linear increment of solvent amount decreases the viscosity.

Most importantly, the ANOVA result indicates that the binary interaction of binder to solvent (CD) has a significant effect with a p-value less than 0.05. The viscosity of the vehicles (binder solution) is dependent on the macromolecular entanglement of chlorinated rubber. As stated above, increasing the amount of true solvent (toluene) decreases the entanglement of the binder that can further reduce the viscosity of the paint (Mannari and Patel 2015). As the binder contain increased from 5- 20 wt % and as the solvent amount decreased from 45 to 35 wt.%, the viscosity of the paint was observed to increase from 53 to 114.45 KU. At the maximum amount of solvent (45wt%), the increment of binder from 5 to 11 wt% increases the viscosity only by 6.8 % (56.6 KU). For a fixed amount binder at 5wt.%, the viscosity is observed to increase by 22.8% (65.1 KU) if the solvent amount is reduced by 10wt.%. Further increment of the viscosity to 67.6% (88.85 KU) is obtained during binder increment from 5 to 13 wt.% at 35 wt.% of solvent. From this result, it can be concluded that the required viscosity range that considers with commercially available paints can be obtained for the solvent and binder amount converging to 35wt.% and 15 wt.% respectively and the result also indicates binder and solvent has a high impact on the viscosity of the paint.

Furthermore, the interaction between the paint extender-binder(BC), extender- solvent (BD) is also significant with a p-value less than 0.05. This indicates that the binary interaction of extender, binder, and solvent has a positive effect on viscosity (response). As the solid content of the paint increases, the viscosity of the paint is also increased. the homogeneity of the dispersed phase of the solid contained (pigment and extender) within the binder matrix can be highly affected by the increment of viscosity. This problem can be encountered by the addition of an optimum solvent amount.

The model indicates that the interaction between AB, AC, and AD is not significant (p-value >0.05), which implies pigment-extender, pigment-binder, and pigment–solvent respectively do not affect the viscosity. For a fixed amount binder (5wt.%) and solvent (45wt%), insignificant viscosity increment (1.7%) is observed for the respective change of pigment and extender from 5 to 11 wt% and 31 to 25 wt%. For a fixed amount of extender (25wt.%) and solvent (45 wt.%), an insignificant viscosity increment (2.19%) is observed for the respective change in pigment from 5 to 11 wt.% and binder from 11 to 5 wt.%. The pigment-solvent interaction has also an insignificant effect on the viscosity. For the change in the pigment and solvent from 16 to 11 wt% and 40 to 45 wt% respectively, viscosity increment by 6.09 % is observed. This indicates that the interaction of pigment-extender, pigment-binder, and pigment–solvent is insignificant as compared to the interaction of binder- solvent, extender-binder and extender- solvent.

Table 4. 3. ANOVA for the viscosity of the sample.

ANOVA for Quadratic model

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	
Model	7323.68	9	813.74	207.91	< 0.0001	significant
Linear mixture	6787.4	3	2262.47	578.07	<0.0001	
AB	1.03	1	1.03	0.2621	0.6167	
AC	13.5	1	13.5	3.45	0.0845	
AD	6.16	1	6.16	1.57	0.23	
BC	26.06	1	26.06	6.66	0.0218	
BD	26.59	1	26.59	6.79	0.0207	
CD	344.36	1	344.36	87.99	<0.0001	
Residual	54.79	14	3.91			
Lack of fit	54.79	9	6.09			
Pure error	0	5	0			
Cor total	7378.47	23				

4.3. Selection of optimum traffic paint formulation

To obtain optimal paint formulation, optimization of traffic marking paint formulation was also carried out by considering the range of viscosity of commercially available chlorinated rubber-based traffic marking paint. The allowed viscosity range was set between 80 to 95 KU for the formulated paint. Taking into account the appropriate viscosity range for the paint and the effective interaction of ingredients (factors), the DoE mixture formed an optimized yellow zone region, as shown in Figure 4.4. The amount of paint ingredient that should be used for the preparation of optimized traffic marking paint is shown by each point in the yellow zone.

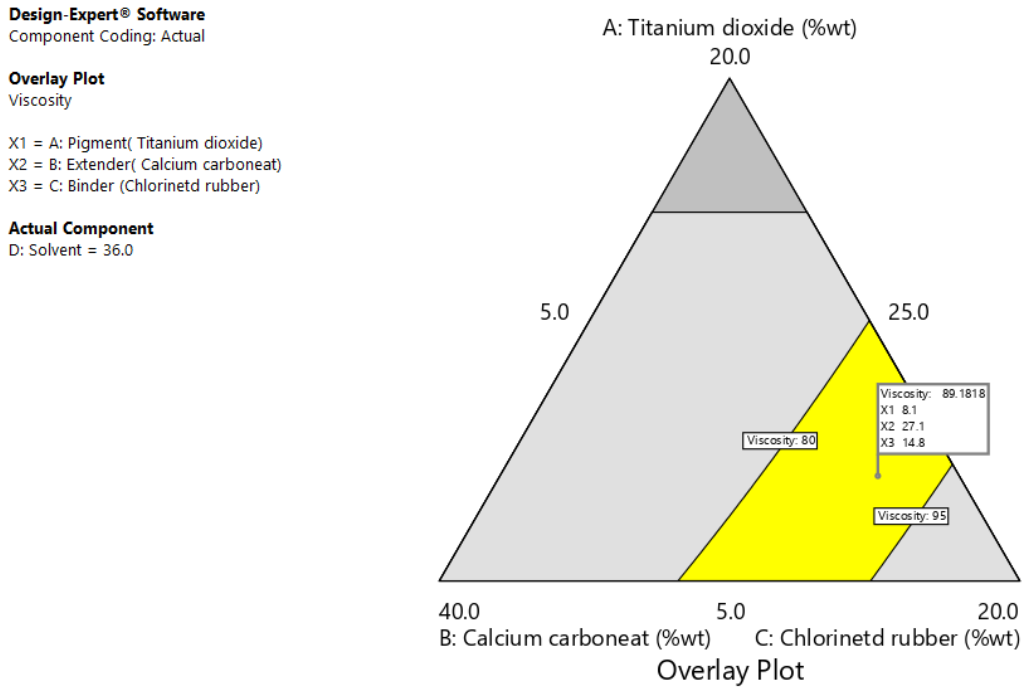


Figure 4. 4.optimum paint formulation zone (yellow area).

The response equation for viscosity (dependent variable) in terms of the four components(pigment, extender, binder and solvent) of the traffic marking paint is as below;

$$\mathbf{Viscosity} = \mathbf{62.27} * \mathbf{A} + \mathbf{68.93} * \mathbf{B} + \mathbf{119.28} * \mathbf{C} + \mathbf{56.42} * \mathbf{D} - \mathbf{5.11} * \mathbf{A} * \mathbf{B} - \mathbf{18.54} * \mathbf{A} * \mathbf{C} - \mathbf{19.15} * \mathbf{A} * \mathbf{D} - \mathbf{18.60} * \mathbf{B} * \mathbf{C} - \mathbf{29.68} * \mathbf{B} * \mathbf{D} - \mathbf{106.82} * \mathbf{C} * \mathbf{D} \quad \text{Eq 4. 1}$$

Different end-user properties were checked for the traffic marking paint formulated sample that had viscosity in the 80-95 KU range. From 24 DoE experimental runs with a viscosity of between 80-95 KU, four traffic marking paint samples of run 4, 7, 10, and 20 were found. Then, to evaluate paint formulation with better results, wet-based tests such as density, wet film thickness test, and dry-based tests such as adhesion, hardness, water immersion, and thermal resistance test were performed.

The chosen traffic marking paint is coated for dry-based testing on an aluminum plate. Then, depending on the test process, all the paint films fully dry at atmospheric temperature for various durations. Since pigment volume concentration highly affects the paint property, the pigment volume concentration (PVC), critical pigment volume concentration (CPVC) of the selected traffic marking paint were calculated using Eq (1) and Eq (2). Table 4.4 shows pigment volume concentration and critical pigment concentration value of the selected traffic marking paint.

Table 4. 4. PVC and CPVC of traffic marking paint.

Run	4	7	10	20
PVC	43.89	37.5	37.5	41.7
CPVC	46.66	46.66	46.76	46.54

Figure 4.5 demonstrates the surface appearance of the four selected traffic marking paint films. As shown in Figures 4.5(a) and 4.6(b), the metal plate coated with run 4, and 20 paint samples had a poor appearance with the creation of cracks. This is due to the absence of sufficient binder to fill the void between the pigment and filler particles. The PVC of the paint formulation of run 4 and 20 is 43.89 and 41.7 respectively and it is high as compared to that of the other two. Traffic marking paint sample of run 4 and run 20 has high PVC and the increasing of PVC in paint formulation reduces the resistance of the paint film to crate crack. According to (Singh, Tambe et al. 2004), the presence of a high amount of pigment (i.e. high PVC) causes for reduction of the resistance of the coating for the creation of crack. This is due to the presence of an air pocket between the pigment and extender particles instead of polymer.

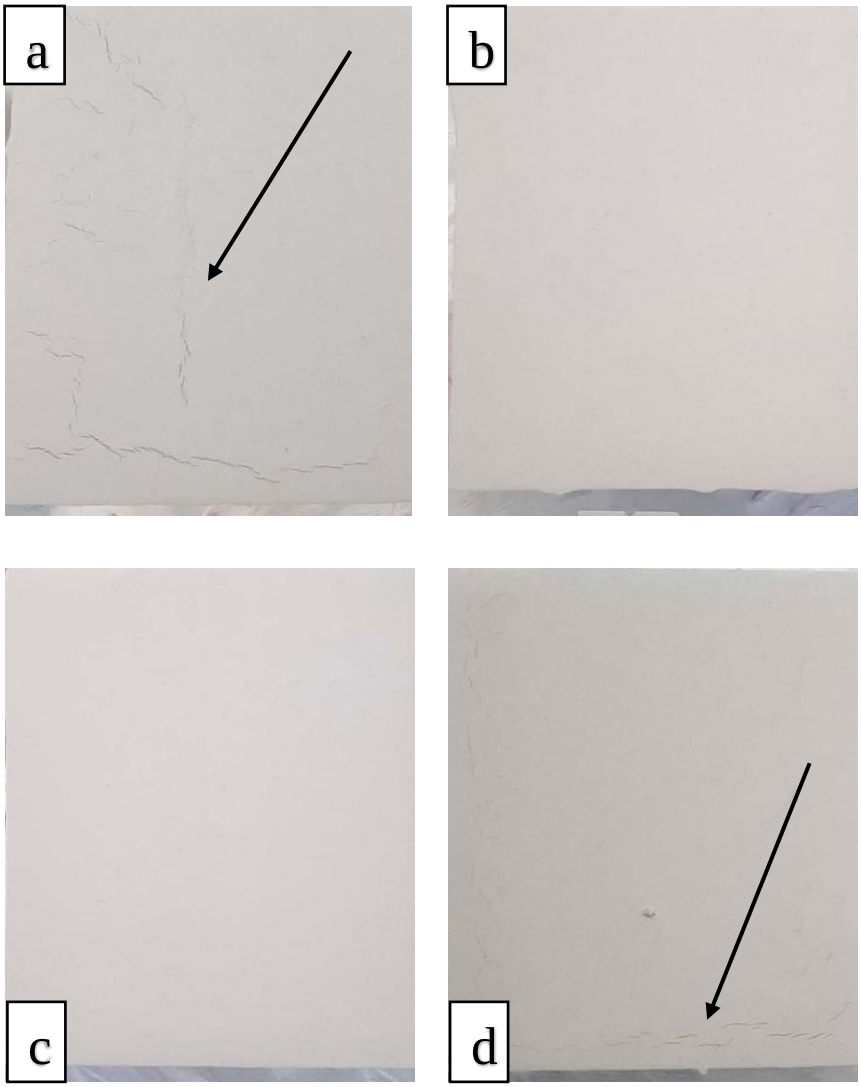


Figure 4. 5. The surface appearance of the four paint samples.

Paint film of traffic marking sample run 7 and 10 display best surface appearance without the creation of crack as shown in figure 4.5(b) and (c). Run 7 and 10 had PVC of 37.5. The better appearance of the film is due to the presence of sufficient binder to hold the ingredient of paint and to fill the void between the pigment and extender particles. The uniform distribution of pigment and extender particles on continuously connected binder matrix results in the better appearance of the paint with good mechanical property.

4.3.1. The density of traffic marking paint

Weight per volume (density) of the formulated traffic marking paint was determined based on the ISO 2811 standard test method using a metal pycnometer at a temperature of 21.8 ^{o}C. The density value of the four traffic marking paint formulations listed in Table 4.5. As shown in the table the density value in the range of 1.304 to 1.311 g/ml. However, most commercially available chlorinated rubber-based traffic marking paint has a density in the range of 1.43 to 1.56 g/ml (Brand name Ef serious High VOC Chlorinated Rubber Traffic Paint and TTP-115F) which is higher than the formulated traffic marking paint. The difference in density is due to the difference in materials used such as additives, plasticizers.

Table 4. 5. The density of traffic marking paint sample.

Run	4	7	10	20
Density (g/ml)	1.304	1.309	1.311	1.306

4.3.2. Film thickness measurement

Traffic marking paint needs to be thicker as compared to other paint used in different application areas such as interior and exterior house paint to withstand erosion effect due to high traffic volume and adverse weather condition. The wet film thickness of formulated traffic marking paint was determined according to ASTM D4414 standard test method. The wet film thickness of the paint was measured immediately after application of the traffic marking paint to the aluminum plate to avoid much loss of solvent by evaporation. The thickness measurement was held in three different locations and the average value was taken as the thickness of the paint. Figure 4.6 shows the wet film thickness measurement of traffic marking paint.

The wet film thickness measurement of the formulated traffic marking paint test result is summarized in Table 4.6. As shown in the table the traffic marking paint had a wet film thickness of 466.6 µm. This value indicates the thickness of the formulated traffic marking paint is within the range of commercially available ones. Commercially available traffic marking paint has wet film thickness within the range of 304-508 µm (Miller and Wolfe 1980).

Table 4. 6. The wet and dry film thickness of the formulated traffic marking paint.

Run	4	7	10	20
Wet film thickness (µm)	466.66	466.66	466.66	466.66

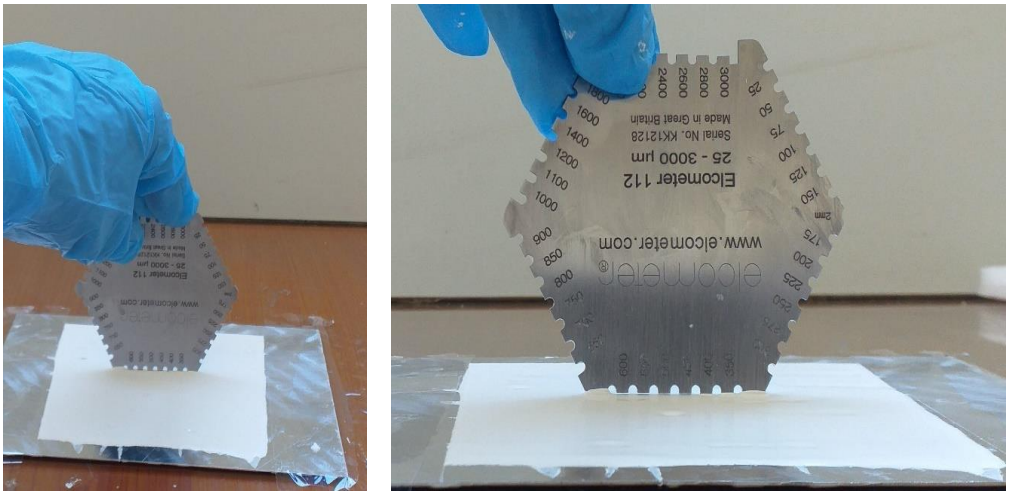


Figure 4. 6. Wet film thickness measurement of traffic marking paint using comp wet film thickness gauge.

4.3.3. Adhesion test

A significant necessity for all paints, including traffic marking paint, is the adhesion of paint to the substrate. The adhesion test is an important test method for determining the resistance of the paint film (including paint marking) to separation from the substrate on which it is applied. The adhesion strength test of the formulated traffic marking paint to the aluminum metal plate was performed in accordance with the ISO 2409 standard test method by cross-cut test and the result is shown in Figure 4.7. The ISO 2409 cross-cut adhesion test result classification can be seen in table 4.7. According to the standard, the first three classifications are acceptable for general purposes, namely 0, 1, and 2.

The adhesion of the paint to the aluminum plate increase with the increase of the amount of chlorinated rubber. This means at low PVC the adhesion of paint to the substrate increase due to the presence of sufficient binder. Figure 4.7 shows the cross-cut adhesion test of the four formulated traffic marking paint. As shown in figure a, and d of figure 4.7, most of the dry film of the formulated traffic paint of run 4 and 20 detached from the cross-cut pattern. This test result corresponds to classification 5 of the ISO 2409 test result which means greater than 65% of the dry paint film separate from the aluminum plate. This is attributed to the lack of enough binder to cover the pigment surface. Binder used as a glue in paint, it holds all paint ingredient together as well as it controls the adhesion of the paint to the substrate. Lack of binder in paint system results in the creation of void between pigment particle which causes for loss of adhesion.

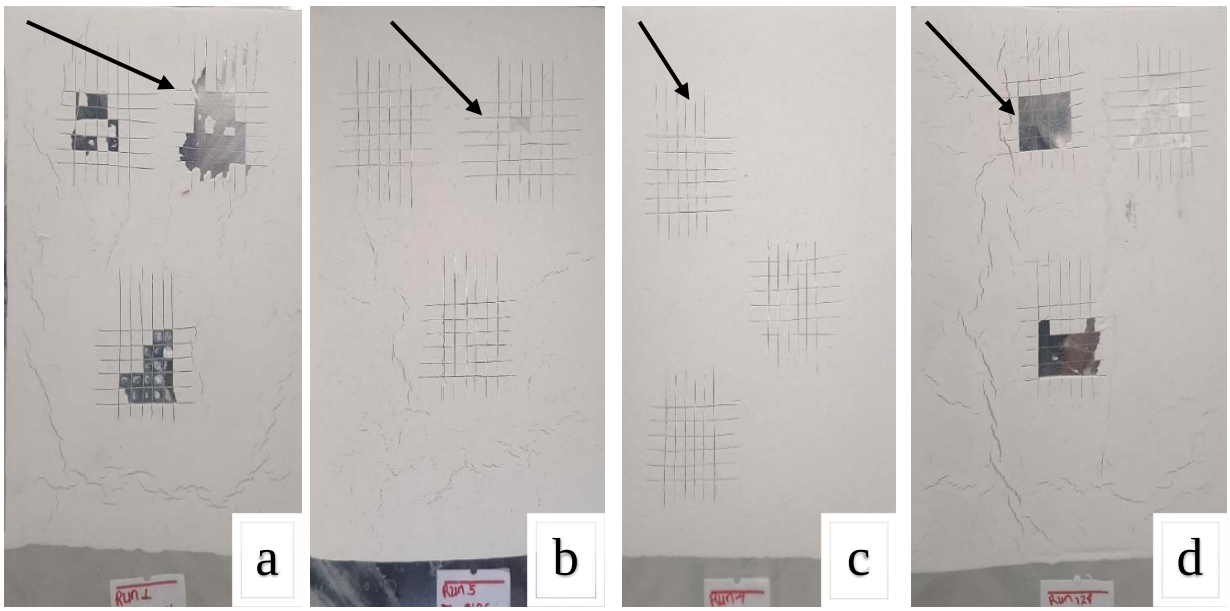


Figure 4. 7.A) photograph of traffic marking paint film after cross-cut adhesion test. a) run 4, b) run 7, c) run 10, and d) run 20.

As shown by the arrow in Figure b of figure 4.7, a small fragment of dry paint film of the formulated traffic paint of run 7 detached from the aluminum plate. This test result corresponds to classification 1 of the ISO 2409 test result which means that less than 5% of the dry paint film separate from the aluminum plate. Figure c in figure 4.7 shows that the dry paint film of the formulated traffic paint of run 10 did not separate from the aluminum plate. This corresponds to classification 0 of the ISO 2409 test result which means that noting is detached from the surface

of the coated aluminum plat. This result is attributed to the formation of the continuous dry paint film due to the uniform distribution of pigment particles in a continuously connected matrix of the polymer. Table 4.8 shows the summarized result of the cross-cut adhesion test result of the four formulated traffic marking paint.

Table 4. 7. ISO 2409 cross-cut adhesion test result classification.

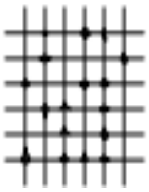
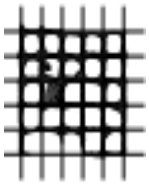
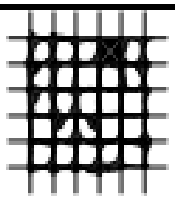
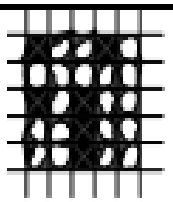
Classification	**0**	**1**	**2**	**3**	**4**	**5**
Dscribtion	0% detacment	<5% detacment	5-15% detacment	>35% detacment	35-65% detacment	>65% detacment
The appearance of the surface of the cross-cut area	-					-

Table 4. 8. Cross-cut adhesion test result of formulated traffic marking paint.

Run	4	7	10	20
Result of cross-cut adhesion	5	1	0	5

4.3.4. Pencil hardness test

The hardness of the paint film is defined as the resistance of the film to mechanical forces such as pressure, scratching, and rubbing (Alvarez and Paulis 2017). The hardness of the paint is an important property of paint which is affected by the flexibility and crosslinking density of the network (İşeri-Çağlar, Baştürk et al. 2014). The hardness of the formulated traffic marking paint was determined using a pencil hardness test method. The pencil hardness test is a constant-load scratch test. It uses pencil leads of different hardness grades (6B–6H) as the scratch stylus. The same normal load with indenters of different hardness is applied to the samples. The hardest pencil grade that does not cause damage to the coated specimen is considered as the pencil hardness of the coating.

By using the Wolff-Wilborn pencil hardness tester, the hardness of traffic marking paint coated on the aluminum metal plate was tested according to the ISO 15184 standard test process. The 10N force on the paint film surface was applied by the tester. In accordance with the ISO 15184 standard test method, the degree of hardness of the set of pencils is as shown in Table 4.9. Based on this, on the aluminum metal plate coated with traffic marking paint, the pencil hardness test was carried out beginning with the soft (6B) pencil up to the hardest pencil that causes a cohesive fracture.

Table 4. 9. Degree of hardness of pencil used in pencil hardness tester.

Pencil hardness test scale													
Paincil name	**6B**	**5B**	**4B**	**3B**	**2B**	**B**	**HB**	**H**	**2H**	**3H**	**4H**	**5H**	**6H**
Hardness range	Soft →												Hard

The test result of the pencil hardness test is summarized in Table 4.10. As shown in the table "×" indicate that the pencil grade that did not cause a cohesive fracture. These pencils are soft, they just slip over the paint film without scratching it. The symbol "✓" indicates that the pencil causes cohesive fracture on the surface of the paint.

Table 4. 10. Pencil hardness test result.

Run	**Pencil hardness test scale**												
	6B	**5B**	**4B**	**3B**	**2B**	**B**	**HB**	**H**	**2H**	**3H**	**4H**	**5H**	**6H**
1	×	×	×	×	×	×	×	×	×	×	✓	✓	✓
2	×	×	×	×	×	×	×	×	×	×	✓	✓	✓
3	×	×	×	×	×	×	×	×	×	×	✓	✓	✓
4	×	×	×	×	×	×	×	×	×	×	✓	✓	✓

The photographic image of a pencil hardness test result of traffic marking paint coated on an aluminum metal plate is shown in Figure 4.8. As shown in the figure, at a pencil hardness of 4H, cohesive fracture begins and 3H was the hardest pencil grade that did not cause damage to the paint film. Therefore pencil hardness of 3H was recorded as the hardness of the traffic marking paint. The high hardness (3H) of the traffic marking paint is due to the formation of a strong cross-linking network between paint ingredients. The presence of driers in the paint composition promotes the hardening of the film's former binder. They enhance the oxidation cross-linking of the binder after the evaporation of the solvent and result in a strong paint film (Bielman 1993).

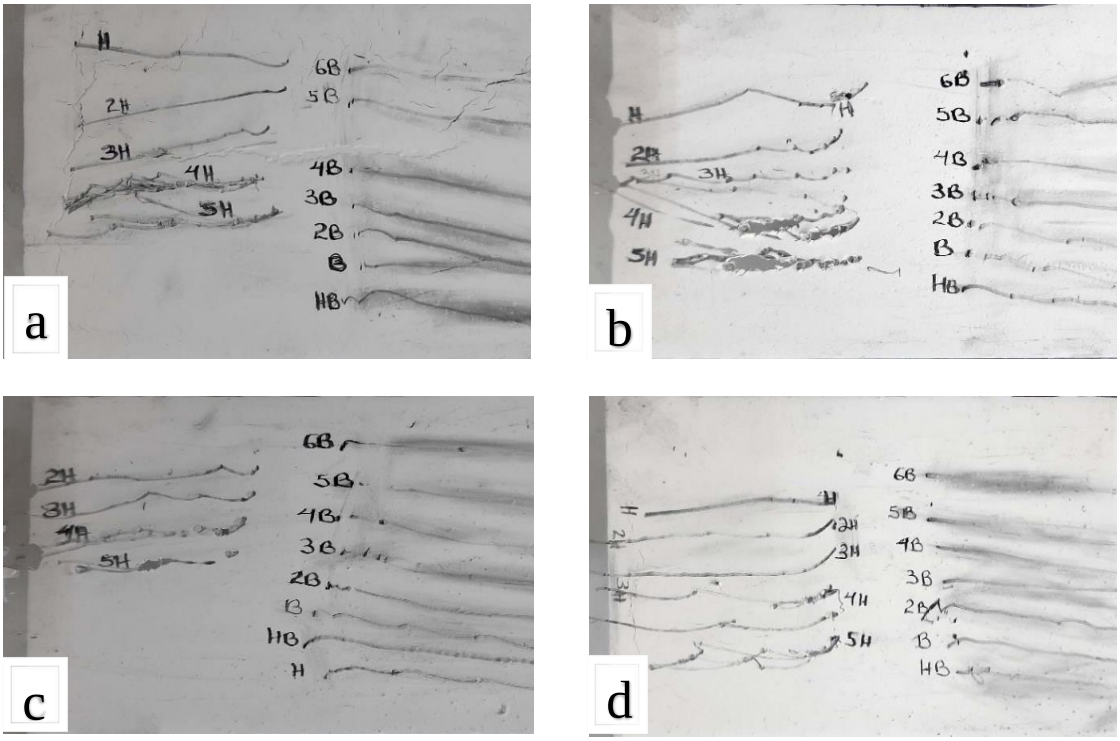


Figure 4. 8. The photographic image of traffic marking paint film after the pencil hardness test. a) run 4, b) run 7, c) run 10, and d) run 20.

4.3.5. Determination of Volatile matter contains road marking paint

Volatile matter contains traffic marking paint sample was determined according to ASTM D2369 standard test method. The test result of the volatile matter content of traffic marking paint is shown in table 4. 11. As shown in the table the paint sample of run 7 has a high content of volatile

matter contents this is due to a high amount of solvent content of the paint. The weight percent solids content (nonvolatile matter) of traffic marking paint was also determined by subtracting the volatile content of the paint from the total and the result is as shown in Table 4.11. The weight percent solids (non-volatile matter) indicate the amount of materials remaining in the dry film after the volatile matter (solvent) evaporates and is a measure of the film solid present during film formation. Most commercially available chlorinated rubber traffic marking paint has weight percent solids content in the range between 70-80% (Brand name Ef serious High VOC Chlorinated Rubber Traffic Paint and TTP-115F). The non-volatile matter of formulated traffic paint has a slight difference from the commercially available traffic marking paint which indicates the amount of solid film present after the solvent evaporates from the film.

Table 4. 11. Volatile matter and non-volatile matter content of the four selected traffic marking paints.

Run	**Volatile matter content of traffic marking paint (%)**	**Weight percent solids content (nonvolatile matter)**
1	34.8	65.2
7	37.4	62.6
10	35.9	64.1
20	35.0	65

4.3.6. Water resistance of traffic marking paint by water immersion test

Water absorption into the paint film can cause damage (Dileep, Jacob et al. 2020). The service life of the paint for traffic marking was determined by a water immersion test. By conducting a water immersion test as per ASTM D870, the resistance of four traffic marking paint coated on the aluminum metal plate to water was analyzed. The sample of paint was immersed in a water bath at 38 ^{o}C for 8 days to determine the influence of water on the surface of traffic marking paint-coated film and any change on the surface of paint film such as blistering, loss of adhesion, softening, and color change was recorded. The photographic image of the four samples before and after the water immersion test is as shown in Figures 4.9 A and B.

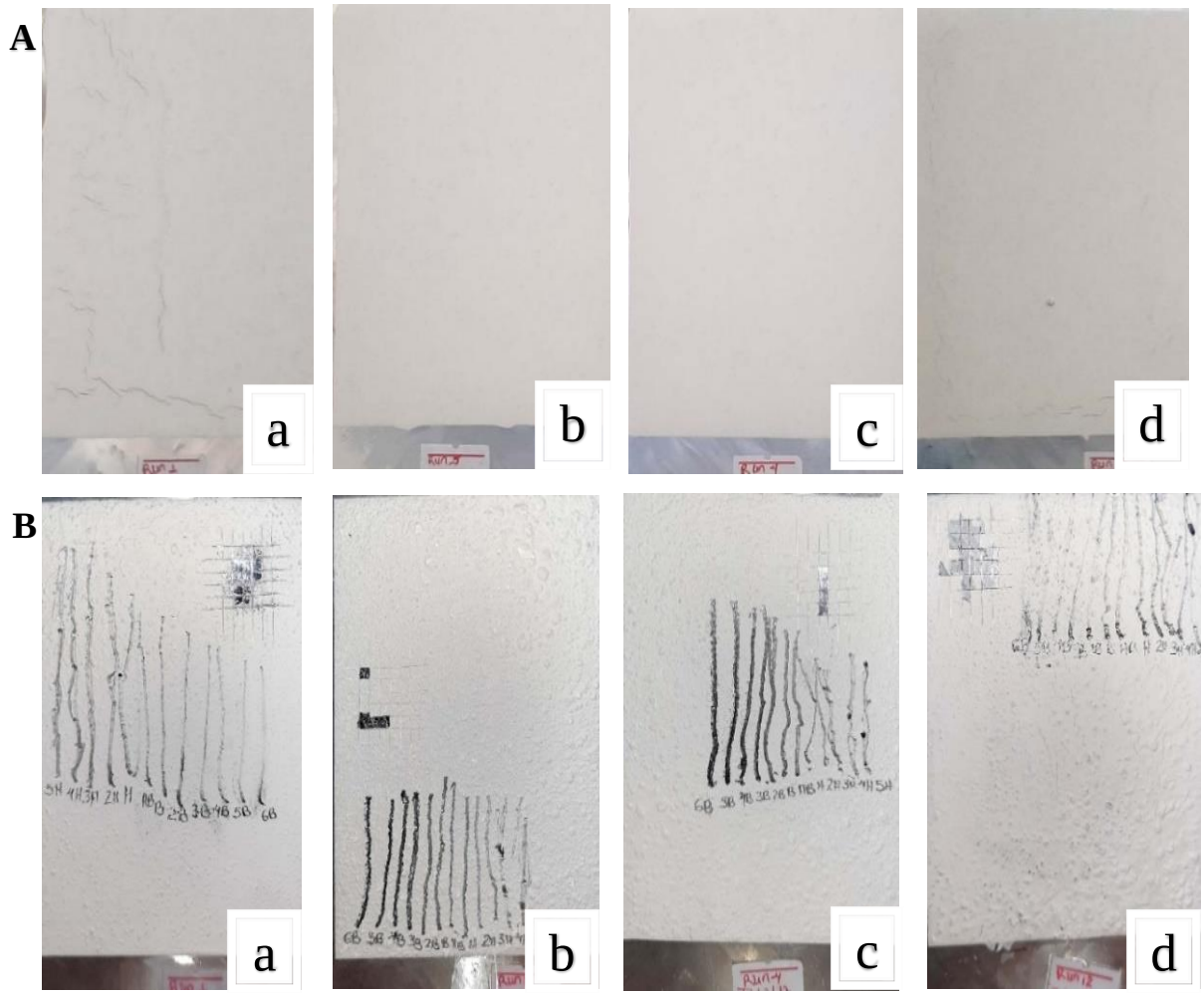


Figure 4. 9. A) a photographic image of traffic marking paint film before the water immersion test. a) run 4, b) run 7, c) run 10, and d) run 20. B) a photographic image of traffic marking paint film after water immersion test.

As shown in figure 4.9 the four traffic marking paint film had a smooth surface before the water immersion test, but after immersion of the film in the water at 38 ^{o}C for 8 days, the paint film had an irregular surface due to the formation of blistering. The formation of blistering on the surface of the paint film is due to the presence of a bubble. Bubble on the surface of paint film may form due to different reasons such as the presence of foam in the paint, the presence of rust, and water on the surface of the substrate (Dietrich 2014). For our case, the formation of a bubble could most

probably due to the presence of foam in the paint, because the aluminum substrate used was carefully cleaned and dry before usage.

Foam is an undesirable phenomenon that may cause optical defects in the coating surface, and also foam formation diminishes the protective function of the coating (Brock, Groteklaes et al. 2000). Foam in the paint may form during production, packaging, and application and this foam stabilized due to the addition of a surface-active agent within the paint. The surface-active agent is a dispersing agent added to the paint formulation to improve the wetting and stabilization of TiO_2 pigment and $CaCO_3$ extender in liquid media.

Such surface-active agents also stabilize air introduce in paint composition during production, packaging, and application in the form of foam (Brock, Groteklaes et al. 2000). Stabilization of foam begins when the surface-active substance (e.g. wetting and dispersing agent) accumulate on the surface of the air/ liquid interface. We incorporate dispersing agent (BYK 104s) to our traffic marking paint formulation to enhance wetting and stabilization of pigment and extender. But the presence of such surface-active agent also stabilizes the foam formed during the production of paint.

Studies have shown that some of the air bubbles (foam) rise to the surface of a paint film during application of the paint to the substrate and they disappear. But the air bubbles either burst for quick curing paint composition, as they rich the paint film surface and make tiny craters, or they can't reach the paint surface and they're stuck within the paint film. As the curing or hardening of the paint film increase, the trapped bubble remains fixed within the film.

Since the traffic marking paint had stabilized air bubble some of the bubbles becomes fixed within the paint and some of the bubbles create a crater. Such defect becomes more visible after long exposure (i.e. 8 days) of the paint film to water at 38 ^{o}C as shown in figure 9B. The adhesion property and hardness of the traffic marking paint coated on the aluminum metal plate after water immersion for 8 days at 38 ^{o}C were evaluated to investigate the effect of water immersion on the property of the paint. The cross-cut adhesion test result is shown in figure 4.10.

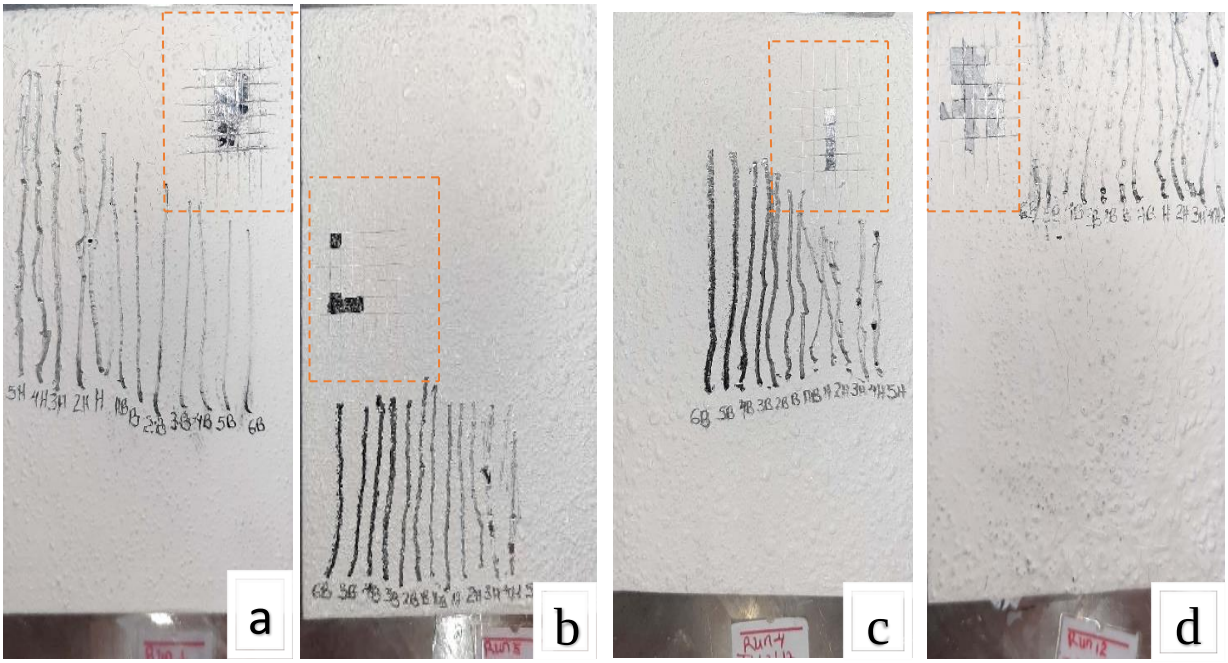


Figure 4. 10. Photographic image of cross-cut and pencil hardness test on traffic marking paint. a) run 4, b) run 7, c) run 10, d) run 20.

Most of the dry film of the formulated traffic paint of run 4 and 20 was detached from the cross-cut pattern, as shown in figure a, and d in figure 10. This test result corresponds to ISO 2409 test result classification 5, which means more than 65 percent of the dry paint film is removed from the aluminum plate. Figure 10b shows a small fragment of dry paint film of traffic marking of run 7 detached from the aluminum metal plate. This test result corresponds to ISO 2409 test result classification 2, which indicates 5% to 15% of the dry paint film is removed from the aluminum plate. Figure 10c shows a small fragment of dry paint film of traffic marking of run 10 detached from the aluminum metal plate. This corresponds to classification 2 of the ISO 2409 test result which means that 5% to 15% of the dry paint film detached from the surface of the coated aluminum plat. Cross-cut adhesion results of the four traffic marking paint films show a slight change in comparison with the traffic marking paint film before the water immersion test. The cross-cut result of the traffic marking paint film before and after the water immersion test is summarized in Table 4.12.

Table 4. 12. Cross-cut result of the traffic marking paint film before and after the water immersion.

Run	Cross-cut adhesion before a test	Percentage of removal	Cross-cut adhesion after a test	Percentage of removal
4	5	>65%	5	>65%
7	1	<5%	2	5-5%
10	0	5-15%	2	5-15%
20	5	>65%	5	>65%

The pencil hardness test result of traffic marking paint after the water immersion test shows no change as shown in Figure 4.11. This is due to the strong crosslinking of the binder (chlorinated rubber) in the paint. Pencil hardness test result of traffic marking paint before and after water immersion test summarized in table 4.13.

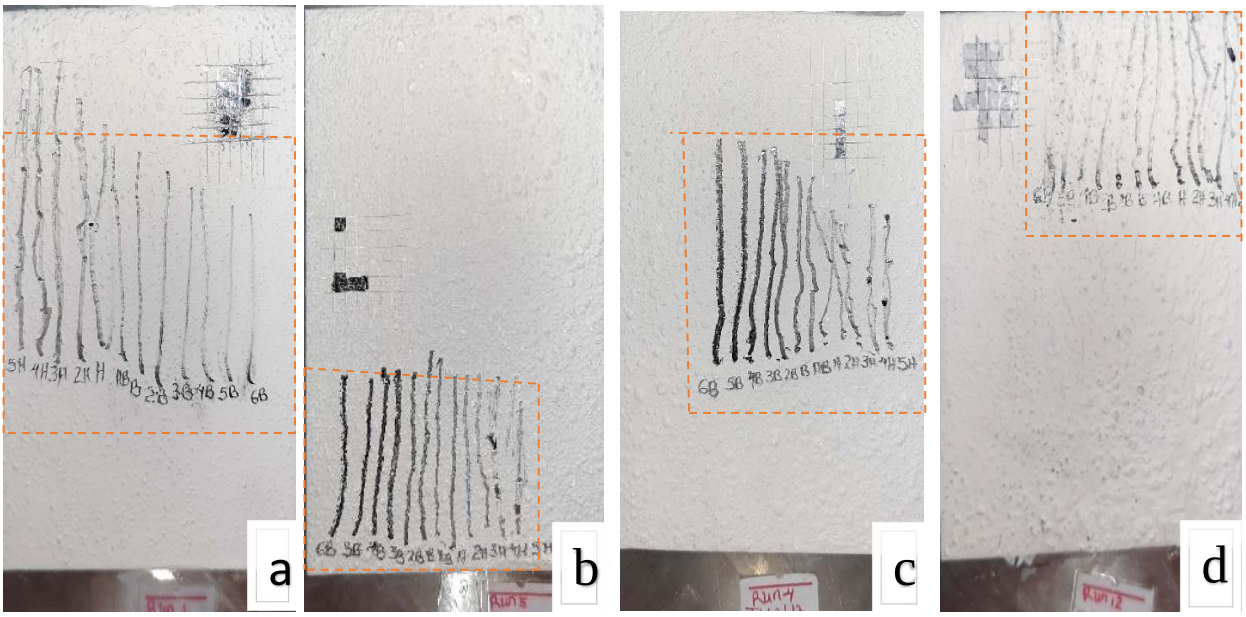


Figure 4. 11. Photographic image of pencil hardness test on traffic marking paint. a) run 4, b) run 7, c) run 10, d) run 20.

Table 4. 13. Pencil hardness test result of traffic marking paint film before and after water immersion test.

Run	4	7	10	20
Pencil hardness before test	3H	3H	3H	3H
Pencil hardness test after test	3H	3H	3H	3H

4.3.7. The thermal resistance of paint film

The temperature difference in the paint film can lead to expansion and contraction stresses. This stress allows the paint film itself to expand and contract (Koleske 1995).). During the service period, traffic marking paint was exposed to high temperatures. In Ethiopia, the surface temperature of the pavement exceeds 60 ^{o}C.

By exposing the coated plate to a high temperature, quantification of the thermal resistance of the formulated traffic marking paint sample painted on an aluminum metal plate was performed. Even though the pavement surface temperature in Ethiopia reaches 60 ^{o}C, we choose high temperatures (100 ^{o}C) to see the effect of such temperatures on the traffic marking paint film.
The test was performed every day at 100 ^{o}C for 10 hr and thermal expansion or contraction was quantified by measuring the area defined on the paint film surface. The test lasted for a total of 3 days. During the test period, the formulated traffic marking paint did not show any softening (i.e. expansion or contraction), which means that the paint film can withstand temperatures of up to 100 ^{o}C. This is due to the high thermal resistance property of chlorinated rubber. Chlorinated rubber is used in traffic marking paint and other application areas, due to its thermal resistance, acid and base resistance (Zhong, Li et al. 1999).

4.4. Modification of road marking paint using industrial waste silica/ Nano TiO2 composite as photo-catalyst

4.4.1. Thermogravimetric analysis of Awash Melkassa S.C byproduct silica

Clay material consist of physisorbed water bounded water and other chemicals and impurities. Such impurities may affect the pore volume and effective surface area of supporting material. These impurities can also reduce the internal reaction during the preparation of photocatalysts. Consequently, this phenomenon affects the photocatalytic property of the composite (Chong, Vimonses et al. 2009). Appropriate treatment to remove such impurities from the high silica contain kaolin is required to avoid the negative impact of impurities.

Awash Melkassa residue silica was subjected to thermogravimetric analysis(DTA-TG) to obtain the weight loss profile against the temperature gradient. Thermogravimetric analysis of the sample can be useful to determine the appropriate outgassing temperature to remove water and other impurities from the silica. Figure 4.12 illustrates the TGA and DTA analysis of Awash Melkassa residue silica.

The first 11.74 % mass loss in the TGA curve and endothermic peak in the DTA curve at 96.6 ^{o}C is due to the release of physically adsorbed water on the surface silica. The second mass loss in the TGA curve of 9.91% and the endothermic peak in the DTA curve at 623 ^{o}C was attributed to the release of structural water and organic matter. Living organisms and non-living organisms in the soil can contribute to the presence of organic matter in clay. Bacteria, fungi, and new undecomposed plant and animal debris are living organisms that are a potential source of organic matter in the soil. Another source of organic matter in the soil is non-living substances such as fulvic acid, humic acid, and humus derived from decaying plants and animals (Yeo, Ling et al. 2017). Since the Awash Melkassa residue silica damped to the environment there is a high probability of mixing of the byproduct with such organic matter present in the soil.

The third mass loss of the TGA curve is 9.01%, and there is an endothermic peak at 764.9 ^{o}C. This is due to the removal of residual aluminum sulfate presented in the by-product. Previous studies have shown that sulfate will degrade in the temperature range of 719-844 ℃ (Sangita, Nayak et al. 2017). The presence of sulfate in the residual silica was also confirmed by FT-IR

analysis. The remaining amount of residual silica which accounts for 69% of the total mass shows high thermal stability within the temperature range of 800 ^{o}C to 1000 ^{o}C. Depending on the observed thermal stability of the residual silica, 900 ^{o}C was selected for the preparation of anatase nano-TiO_2 /Awash Melkassa residue silica composite.

The result of TGA-DTA is supported by EDX analysis, before the thermal treatment, the EDX result shows that the silica contains 6.08 wt. % accounts for the organic compound. However, after the treatment, the organic contain removed totally. The EDX of Awash Melkassa residue silica before and after the thermal treatment is shown in Figure 4.13.

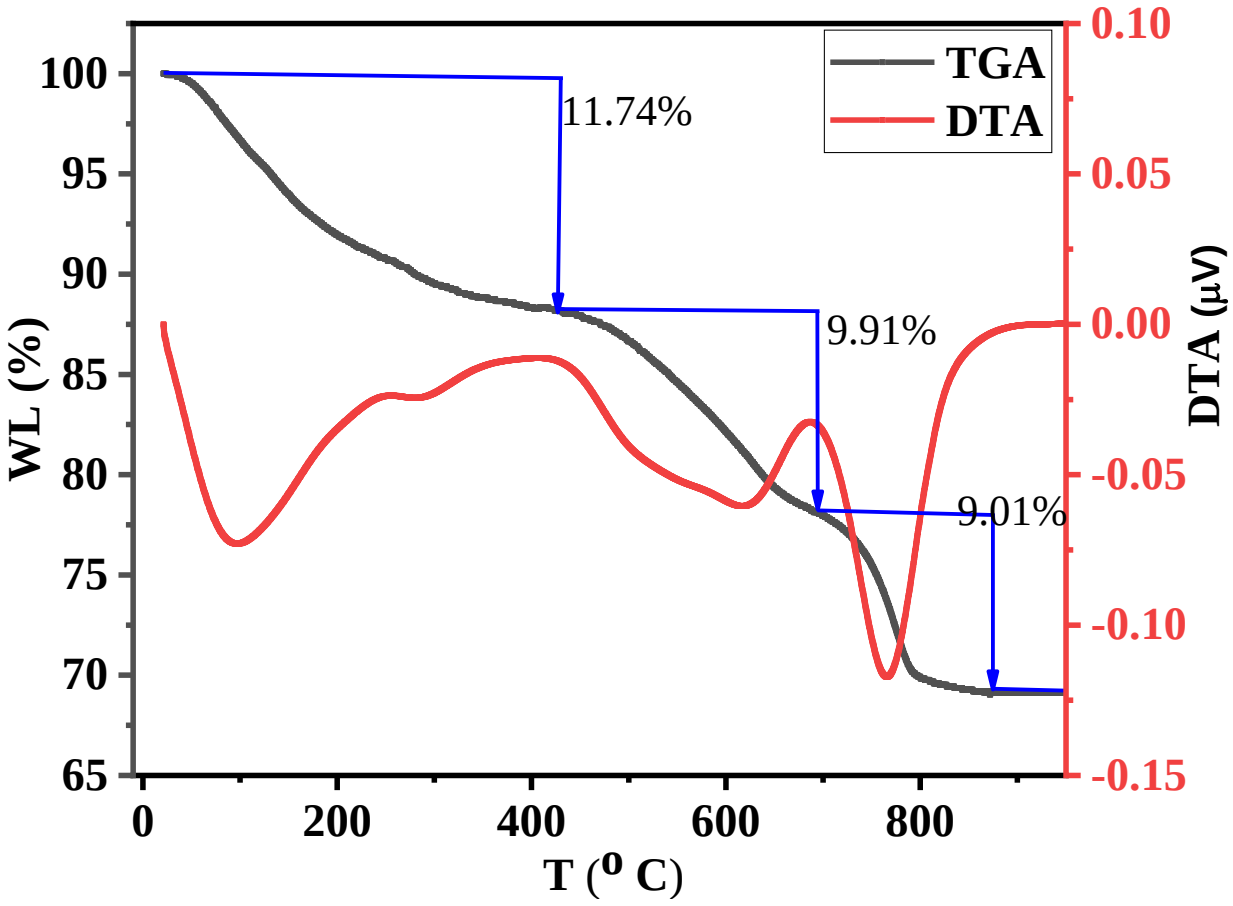


Figure 4. 12. TGA and DTA of Awash Melkassa residue silica.

4.4.2. Characterization of Nano TiO_2/ SiO_2 composite

i. EDX analysis

EDX analysis was performed to determine the composition of Awash Melkassa residue silica before and after heat treatment. Figure 4.13 shows the EDX- SEM image of Awash Melkassa residue silica before and after heat treatment and their corresponding spectra. The major element that is detected in silica before heat treatment is oxygen, silicon, aluminum and carbon and sulfate and less amount of potassium, iron, and magnesium. The EDX analysis display seven elements namely O_2, Si, Al, K, Mg, Fe, C, and the content is 54.13, 26.13, 12.87, 0.35, 0.17, 0.27,6.08 wt.% respectively. After heat treatment, the major element that is detected in silica is oxygen, silicon, aluminum and less amount of sulfate, potassium, iron, and magnesium. The EDX analysis shows that the Awash Melkasa residue silica after heat treatment contains six elements namely O_2, Si, Al, K, Fe, Mg and less amount of sulfate and the content is 43.81, 35.73, 19.4, 0.45, 0.43, 0.127 wt. % respectively.

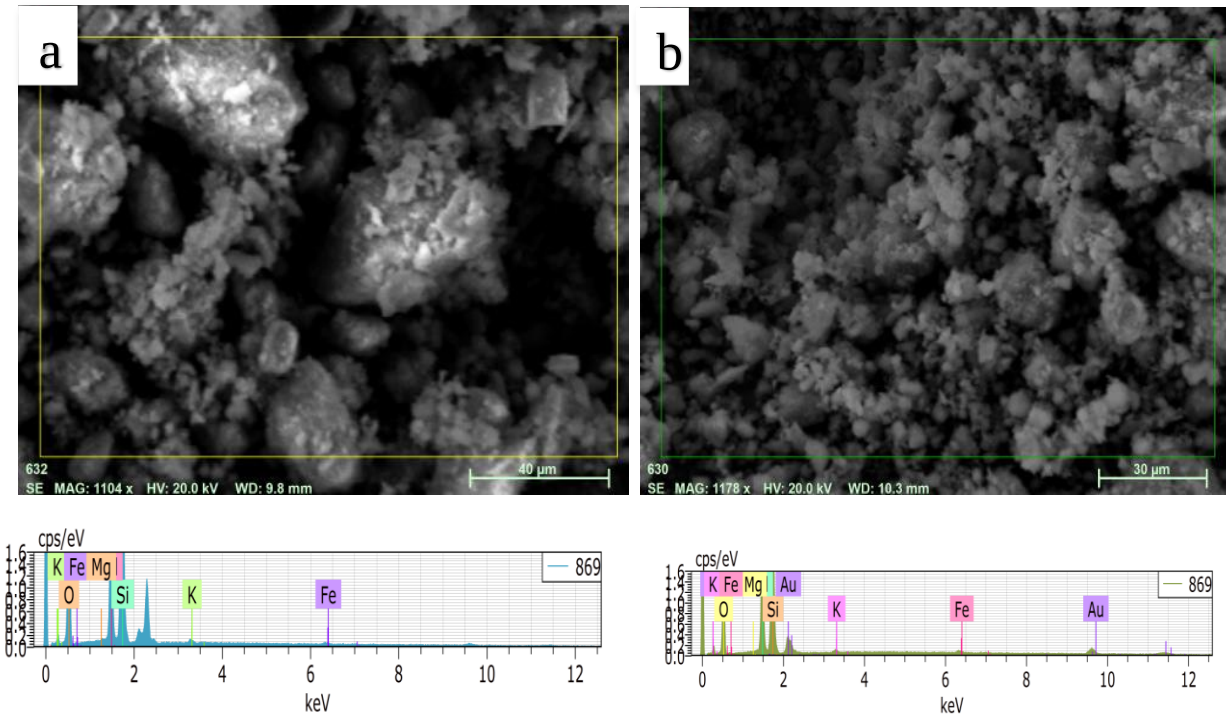
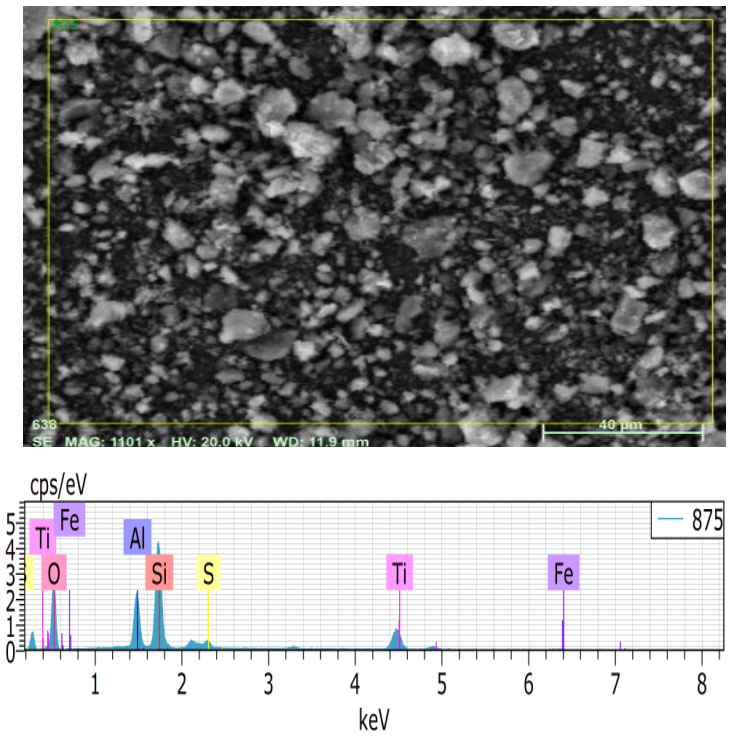


Figure 4. 13. EDX-SEM of Awash Melkassa residue silica; a)before heat treatment,b) after heat treatment.

Table 4. 14. EDX of Awash Malkasa residue silica before and after heat treatment.

Silica	**Composition (Wt.%)**						
	O	**Si**	**Al**	**C**	**K**	**Fe**	**Mg**
Befor heat treatment	54.13	26.13	12.87	6.07	0.35	0.27	0.17
After heat treatment	43.81	35.73	19.40		0.45	0.43	0.127

EDX analysis was also performed to determine the composition of Nano-TiO_2/ Awash Melkassa residue silica composite. Figure 4.14 shows the EDX- SEM image of Nano TiO_2/ Awash Melkassa residue silica composite and their corresponding spectra. The major element that is detected in a composite is oxygen, silicon, aluminum and titanium and less amount of, iron and sulfur. The EDX analysis display eight elements namely O_2, Si, Al,Ti, S and Fe, and the content is 51.93, 20.68, 12.88, 11.91, 0.17, 2.33,0.26 % respectively.



Element	**Wt.%**
O_2	51.93
Si	20.68
Al	12.88
Ti	11.91
S	2.33
Fe	0.26

Figure 4. 14. EDX- SEM of Nano-TiO_2/ Awash Melkassa residue silica composite.

ii. XRD analysis

The XRD spectra of Awash Melkasa residue silica calcinated at 900 ^{o}C, Nano-TiO_2, and Nano TiO_2/SiO_2 composite are shown in figure 4.15. The X-ray diffraction peak of Awash Melkasa residue silica shows broad characteristics diffraction peak between 20^{o} and 30^{o} centered at a 2θ angle of 23^{o}. This indicates that the presence of amorphous phase silica. Previous research shows that acid leaching of kaolin results in an amorphous phase due to the disintegration of the layered structure of the kaolin by acid (Panda, Mishra et al. 2010, Foo, Mahmood et al. 2011). In addition to the diffraction peak of the amorphous phase of silica, the crystal phase also appeared in the x-ray diffraction pattern of residue silica. The broad peak in the Awash Melkassa residue silica annealed at 900 ^{O}C with 2θ of 20.14 and 26.6^{o} corresponds to quartz. This result is in line with the previous work (Jiang, Duanmu et al. 2014). Awash Melkassa residue silica annealed at 900 ^{O}C is a byproduct during the formation of aluminum sulfate after the treatment of kaolin by sulfuric acid. Treatment of kaolin with acid leads to the formation of residual quartz and high amorphous silica (Ahmed, Tantawy et al. 2015). The other broad peak at 2θ of 15.18 and, 21.01, 25.39, 26.6, 27.47, 30.66, 33.72, 34.15 indicate the presence of crystalline silica and other types of clay minerals such as potassium aluminum silicate according to X'pert high scholar.

The X-ray diffraction pattern of synthesized Nano-TiO_2 particles calcinated at 500 ^{o}C is also illustrated in figure 4.16. The diffraction pattern of Nano-TiO_2 has a broad peak at 2θ of 25.3, 37.8,48.1, 54, 55.15, 62.8, 68.70. 70.4 and 75.1 which corresponds to the anatase phase. This result has a good agreement with Wang, H., et al. (Wang, Chao et al. 2019). During the synthesize of the composite, titanium sol-liquid was converted to anatase phase after calcination of the sol-liquid at 500 ^{o}C for 2hr. This result is in agreement with the result reported by Sun, S., et al., (Sun, Deng et al. 2017). Annealing temperature plays a great role in the formation of the crystalline phase of TiO_2. The anatase phase of TiO_2 formed at a temperature below 600 ^{o}C and further heat treatment at a higher temperature (900 ^{o}C) may result in a rutile phase (Win Myint, Moe et al. 2019). From the XRD result, it can be seen that only the anatase phase of TiO_2 is present, while the rutile phase did not appear for the heat treatment of TiO_2 sol-liquid at 500 ^{o}C

Previous reports indicate that the crystal phase of TiO_2 has a significant effect on photocatalytic performance. Among the three crystalline phases of TiO_2 (i.e anatase, rutile, and brookite), the

anatase phase exhibits the highest photocatalytic activity under UV radiation (Sun, Deng et al. 2017). Therefore the existence of Nano- TiO_2 in the anatase phase will enhance the photocatalysis property of the composite.

Based on the XRD data and Scherrer equation, the grain size of Nano-TiO2 present in the system was about 13nm. The X-ray diffraction pattern of synthesized Nano-TiO_2/ SiO_2 shows the presence of Nano-TiO_2 but the diffraction peak of anatase of titanium is low as compared to pure Nano TiO_2. Only diffraction peak at 2θ of 25.3^o is present in the Nano-TiO_2/ SiO_2 composite and the other peak present in the Nano-TiO_2 sample disappear, this phenomenon is attributed to the high composition of silica in the synthesized composite. Based on the report of Sun, S., et al., (Sun, Deng et al. 2017) as a concentration of Nano-TiO_2 increases in the Nano-TiO_2/ SiO_2 composite, their diffraction pattern can be clearly indicated in the x-ray diffraction peaks of the composite.

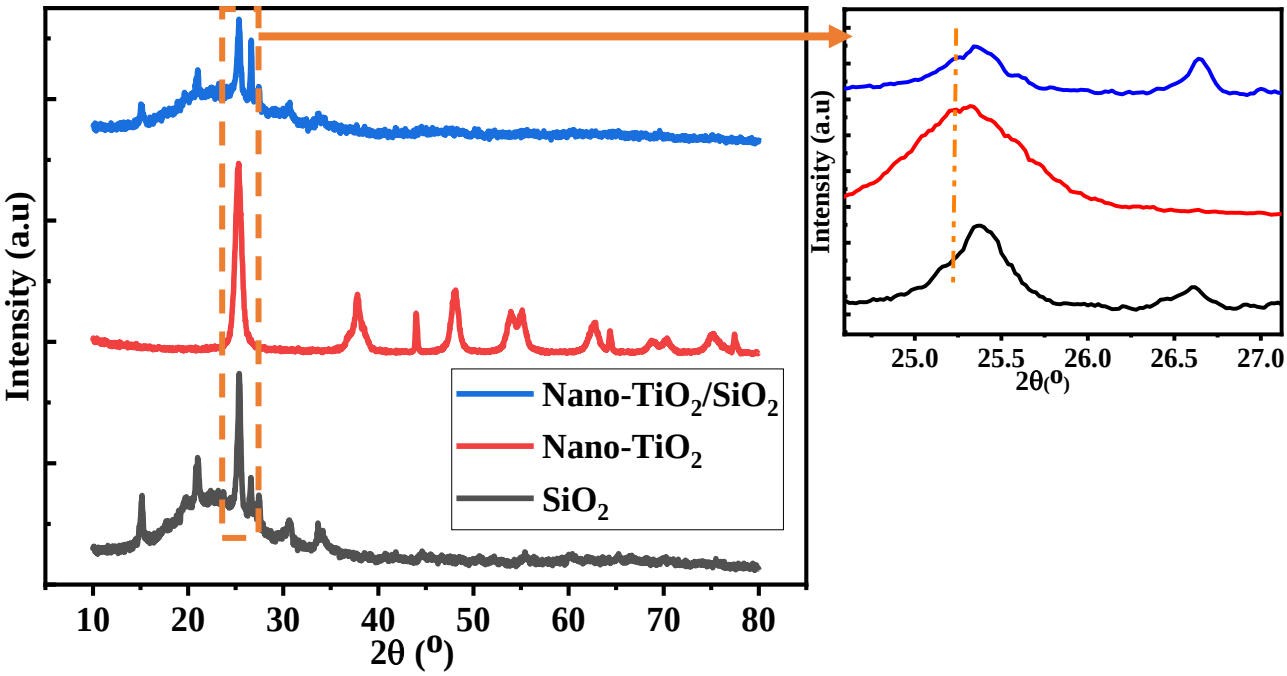


Figure 4. 15. XRD pattern of Awash Melkasa residue silica, Nano-TiO2, and Nano TiO2/SiO2 composite.

The X-ray pattern of Awash Melkassa residual silica has a characteristic diffraction peak at 25.39^o and the d-spacing was calculated to be 3.5 Å by using Bragg's equation Eq 3.8. After the addition of Nano-TiO_2, the diffraction peak for the residue silica had slightly shifted to a lower angle

(25.36 ^{o}) and also the d-spacing increased slightly as shown in Table 4.15. A slight change in the diffraction peak of 20.14^{o}, 21.01^{o} and its interlayer distance causes the shift of the reflection peak and also it confirms the presence of Nano-TiO_2 between silicon atoms.

Table 4. 15. 2 theta value and d-spacing value of residue silica calcined at 900 ^{O}C, Nano-TiO_2, and composite.

2 theta of residue silica calcinated at 900 ^{o}C	**d-spacing**	**2 theta of Nano-TiO_2**	**d-spacing**	**2 theta of composite**	**d-spacing**
15.18	5.83	25.3	3.52	15.17	5.83
20.14	4.4	37.83	2.38	20.98	4.23
21.01	4.22	48.1	1.89	22.03	4.03
25.39	3.5	54	1.69	25.32	3.51
26.6	3.34	55.15	1.66	25.36	3.508
27.47	3.24	62.8	1.48	26.63	3.34
30.73	2.91	68.7	1.44	27.369	3.256
33.449	2.67	70.4	1.349	30.62	2.91
34.183	2.62	75.1	1.26	33.749	2.65
				34.23	2.61

iii. FT-IR analysis

The FTIR spectra of Awash Melkassa residue silica before and after calcination is shown in Figure 4.16. The band at 3698 and 3620 cm^{-1} came from stretching vibration of the outer and inner (Al-O-H) hydroxyl group bonded to aluminum ions. This band disappears in the FTIR spectra of Awash Melkasa residue silica calcinated at 900 ^{o}C due to thermal destruction of the kaolinite phase. The disappearance of alumina sheet hydroxyl (Al-O-H) starching band after calcination 900 ^{o}C indicates strong dehydroxylation of the kaolinite structure. Similar results were found by (Volzone and Ortiga 2011, Torres-Luna and Carriazo 2019) after they calcinate the acid-treated kaolin at 900 ^{0}C the band at 3698 and 3620 cm^{-1} disappear due to thermal destruction of the kaolinite phase.

The strong broad band at 3450 cm^{-1} is attributed to stretching vibration hydroxyl group and interlayer water. This indicates a high amount of water physisorbed on the surface of the silica. The band observed at 1635 cm^{-1} is attributed to the bending vibration mode of physisorbed water on the surface of residue silica due to leaching. The silica used here is the byproduct which is produced by acid leaching of kaolin clay by sulfuric acid to produce aluminum sulfate as the main product. Acid leaching of kaolin results in an increase in the surface area that allows the silica surface to absorb a high volume of water. Previous research indicates that the sulfuric acid treatment of kaolin results in an increased surface area that allows the silica surface to absorb a significant amount of water (Panda, Mishra et al. 2010). A similar band at 3450 cm^{-1} and 1635 cm^{-1} was also found in awash Melkassa residue silica calcinated at 900 ^{o}C. Even though, the residue silica was calcined at 900 ^{o}C high amount of water absorbed on its surface which is due to its hygroscopic property. The hygroscopic property of the residue silica calcinated at 900 ^{o}C came from its high surface area result from acid leaching.

Asymmetric stretching vibration of Si-O-Si is responsible for the band at 1102 cm^{-1}. The band at 1102 cm^{-1} was also observed in awash Melkassa residue silica calcinated at 900 ^{o}C which indicates the presence of amorphous silica. A similar result was also found by (Volzone and Ortiga 2011). The band at 1030 cm^{-1} corresponds to SO^{-2}_{4} vibration (China, Hilonga et al. 2019). The presence of sulfate anion indicates the existence of aluminum sulfate (the main product of the factory) with the byproduct. The shoulder peak at 939 cm^{-1} attribute to OH deformation of the inner-surface hydroxyl group and the band at 911 cm^{-1} corresponds to Al-OH deformation. For Awash Melkassa residue silica calcinated at 900 ^{o}C peak at 939 cm^{-1} and 911 cm^{-1} is disappeared due to dehydroxylation of kaolinite structure because of the thermal treatment. Previous research also shows that after calcination of acid leached kaolinite peak at 939 cm^{-1} and 911 cm^{-1} disappear due to dehydroxylation (Torres-Luna and Carriazo 2019).

The FTIR spectra of the Awash Melkassa residue silica at band 796 cm^{-1} is related to Si-O vibration which is the characteristics peak of quartz (Daneluz, Favero et al. 2020). This peak is shifted to the higher frequency of 807 cm^{-1} after calcination of residue silica. The band at 696 cm^{-1} corresponds to Si-O perpendicular vibration which indicates the presence of quartz in the residual silica (Daneluz, Favero et al. 2020). This peak is shifted to a low frequency of 684 cm^{-1} after calcination of the residue silica. The 536 cm^{-1} band is associated with Al-O-Si deformation

and this peak disappears after the calcination process in the FTIR spectrum of residue silica, which is caused by Al-O-Si bond distraction. This finding is consistent with the previous analysis of the disappearance of the band at 536 cm-1 after the calcination at 700 and 900 ^{O}C due to the distraction of the Al-O-Si bond (Torres-Luna and Carriazo 2019). The band at 468 cm^{-1} in the FTIR spectra of residue silica before calcination corresponding to Si-O-Si deformation which conforms to the presence of silica (Torres-Luna and Carriazo 2019).

After calcination of the residue silica, the band observed at 445, and 480 cm^{-1} caused by Si-O-Si deformation confirms the presence of silicate species. The band at 420 cm^{-1} in the FTIR spectra of residue silica caused by Si-O deformation (Rahmalia, Fabre et al. 2018). The increasing of Si-O-Si deformation peak after calcination of the residue silica confirms the formation of silica. Previous research also shows an increase in Si-O-Si deformation after heat treatment conform formation of silica (Torres-Luna and Carriazo 2019).

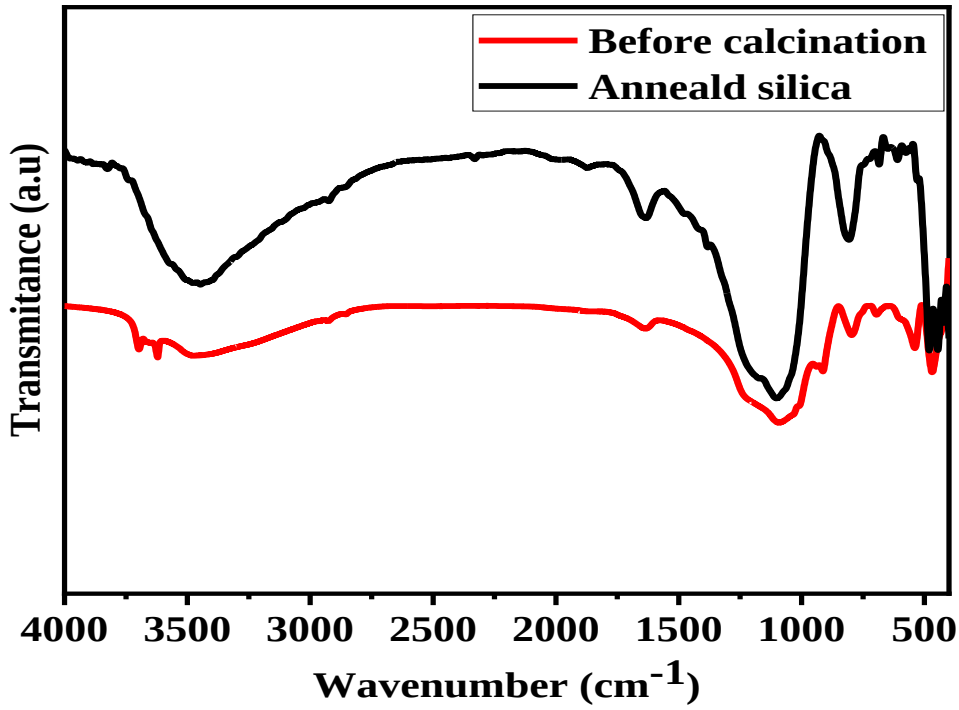


Figure 4. 16. FTIR spectra of Awash Melkasa residue silica before calcination and after calcination at 900 ^{o}C.

The FT-IR spectra of Awash Melkasa residue silica calcinated at 900 ^{o}C, Nano-TiO_2, and Nano TiO_2/SiO_2 composite are shown in Figure 4.17. The FT-IR spectra of Awash Melkasa residue show the strong broad band at 3450 cm^{-1} which is attributed to stretching vibration hydroxyl group and interlayer water. This indicates high a high amount of water physisorbed on the surface of the silica. The band observed at 1635 cm^{-1} is attributed to the bending vibration mode of physisorbed water on the surface of residue silica annealed at 900 ^{0}C due to leaching. Even though, the residue silica was calcined at 900 due to its hygroscopic property high amount of water absorbed on its surface. The hygroscopic property of the residue silica calcinated at 900 ^{0}C is due to the high surface area results from acid leaching. Previous research shows that treatment of kaolin with sulfuric acid results in increased surface area which causes a large amount of water to be absorbed on the surface of silica (Panda, Mishra et al. 2010).

Asymmetric stretching vibration of Si-O-Si is responsible for the band at 1102 cm^{-1} and it indicates that the presence of amorphous silica (Volzone and Ortiga 2011). The peak observed at 807 cm^{-1} is attribute to Si-O vibration and it is the characteristic peak of quartz (Daneluz, Favero et al. 2020). The band at 684 cm^{-1} is a characteristic for quartz and attributed to the symmetric stretching vibration of Si-O-Si. A similar result was also found (Tantawy and Alomari 2019). The band was observed at 445, and 480 cm^{-1} caused by Si-O-Si deformation and it confirms the presence of silicate species (Torres-Luna and Carriazo 2019). The band at 420 cm^{-1} in the FTIR spectra of residue silica calcinated at 900 ^{O}C is caused by Si-O deformation (Rahmalia, Fabre et al. 2018).

In FT-IR spectra of Nano-TiO_2, a band at 3431 and 1626 cm^{-1} is a characteristic of surface water and bending vibration of physisorbed water. The peak at 475 cm^{-1} indicated the presence of O-Ti-O bonding in the anatase Nano-TiO_2 (Bagheri, Shameli et al. 2013). The FTIR spectra Nano-TiO_2/SiO_2 composite also shows a band at 1102 and 807 cm^{-1} which is attributed to asymmetric stretching of Si-O-Si and the formation of amorphous silica. This indicates that silica is the main component of the composite. The FTIR spectra of the composite are similar to that of the spectra for Awash Melkassa residue silica but a new peak was observed at 468 and 433 cm^{-1} which is attributed to the Ti-O bond. This implies that the presence of TiO_2 in the composite (Licciulli, Nisi et al. 2016).

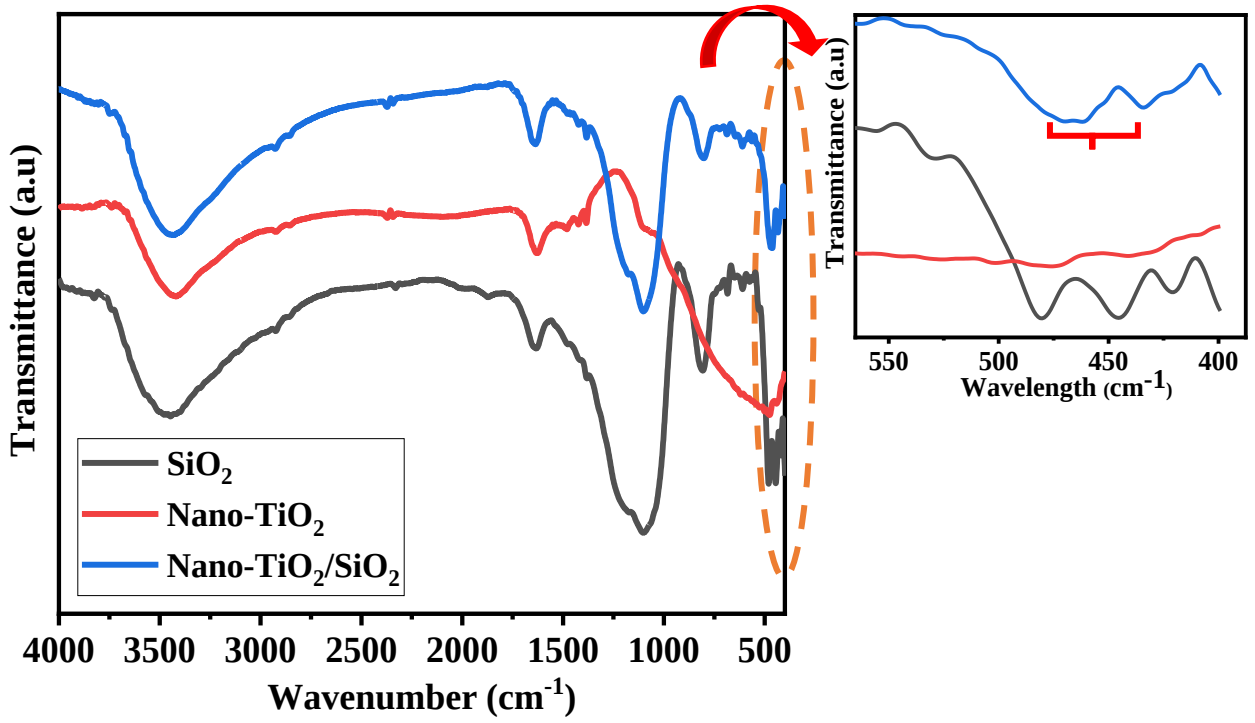


Figure 4. 17. FTIR spectra of Awash Melkasa residue silica, Nano-TiO_2, and Nano TiO_2/SiO_2 composite. The magnified view on the right side shows the presence of a new peak in the FTIR spectra of the composite which indicates the formation of Nano-TiO_2/SiO_2 composite.

4.4.3. Formulation of modified traffic marking paint with a self-cleaning performance

The optimum formulation of traffic marking paint that has better end-user property was selected to prepare self-cleaning traffic marking paint. Formulation of traffic marking paint sample of run 10 was selected as optimum because it shows better performances in each test path. The test result of run 10 is summarized in Table 4.16. Then the self-cleaning paint was prepared by using Nano-TiO_2/ Awash Melkass residue silica composite as a photocatalyst.

Table 4. 16. Summary of the test result of traffic marking paint sample of run 10.

Test	Result
Viscosity	93.65
Density	1.31
Film thickness	466.66
Adhesion	0 (No detachment from the surface)
Hardness	3H
Percent weight of solid	64.1
Water resistance	Show blistering
Thermal resistance at 100 ^{o} C	Can resist

4.4.4. Evaluation of Self-cleaning performance of road marking paint:

i. Photocatalytic degradation

The photographic image of the self-cleaning test performed on the paint sample stained with methyl blue dye with the concentration of 10ppm and 20ppm is shown in Figures 4.18. The degradation of methyl blue stain on the paint sample over irradiation time was observed by the naked eye. The photographic image of the self-cleaning test on the paint film shows that the modified traffic marking paint using Nano-TiO_2/ Awash Melkass residue silica composite has fast decolorization of methyl blue dye as compared to the paint synthesized using anatase TiO_2 pigment (micro size). With the increase of exposing time of the paint film stained with methyl blue to the sunlight, the modified traffic marking paint show better degradation of a stain than that of paint synthesized using TiO_2 pigment. The degradation of methyl blue dye on the paint film synthesized using TiO_2 pigment after 12hr exposing the film to sunlight was relatively slow.

The degradation of the stain is a good indication of the self-cleaning ability of the traffic marking paint. Better self-cleaning property of modified traffic marking paint is due to the presence of Nano-TiO_2/ Awash Melkass residue silica composite in the paint composition. The photocatalytic degradation property of the composite rise due to the presence of anatase nano-TiO_2 in the

composite. among the three phases of TiO_2, the anatase phase has high photocatalytic and photoinduced hydrophilic properties.

According to the photocatalytic mechanism of Nano-TiO_2 (Liu, Zhao et al. 2020), the electron-hole pair is generated when Nano-TiO_2 is exposed to sunlight and the following reaction happens:

$$light + TiO_2 \rightarrow e^- + h^+$$

$$e^- + O_{2\rightarrow} \bullet O^+$$

$$h^+ + OH\text{-}/HO_2 \rightarrow \bullet OH$$

This superoxide anion ($^{\bullet}O^+$) and the hydroxide radical ($^{\bullet}OH$) are oxidizing and reductive which degrade easily nearby organic pollutants such as methyl blue. The photocatalytic behavior of the Nano-TiO_2/ Awash Melkass residue silica is also related to the presence of silica in the composite. Usage of silica as supporting material to Nano-TiO_2 enhance its photocatalytic efficiency in two way. The first one, silica improves the dispersibility of Nano-TiO_2 in the paint system by avoiding the agglomeration tendency of Nano-TiO_2. The second one due to its high adsorption capacity, it increases the adsorption of pollutant on the surface of the Nano-TiO_2.

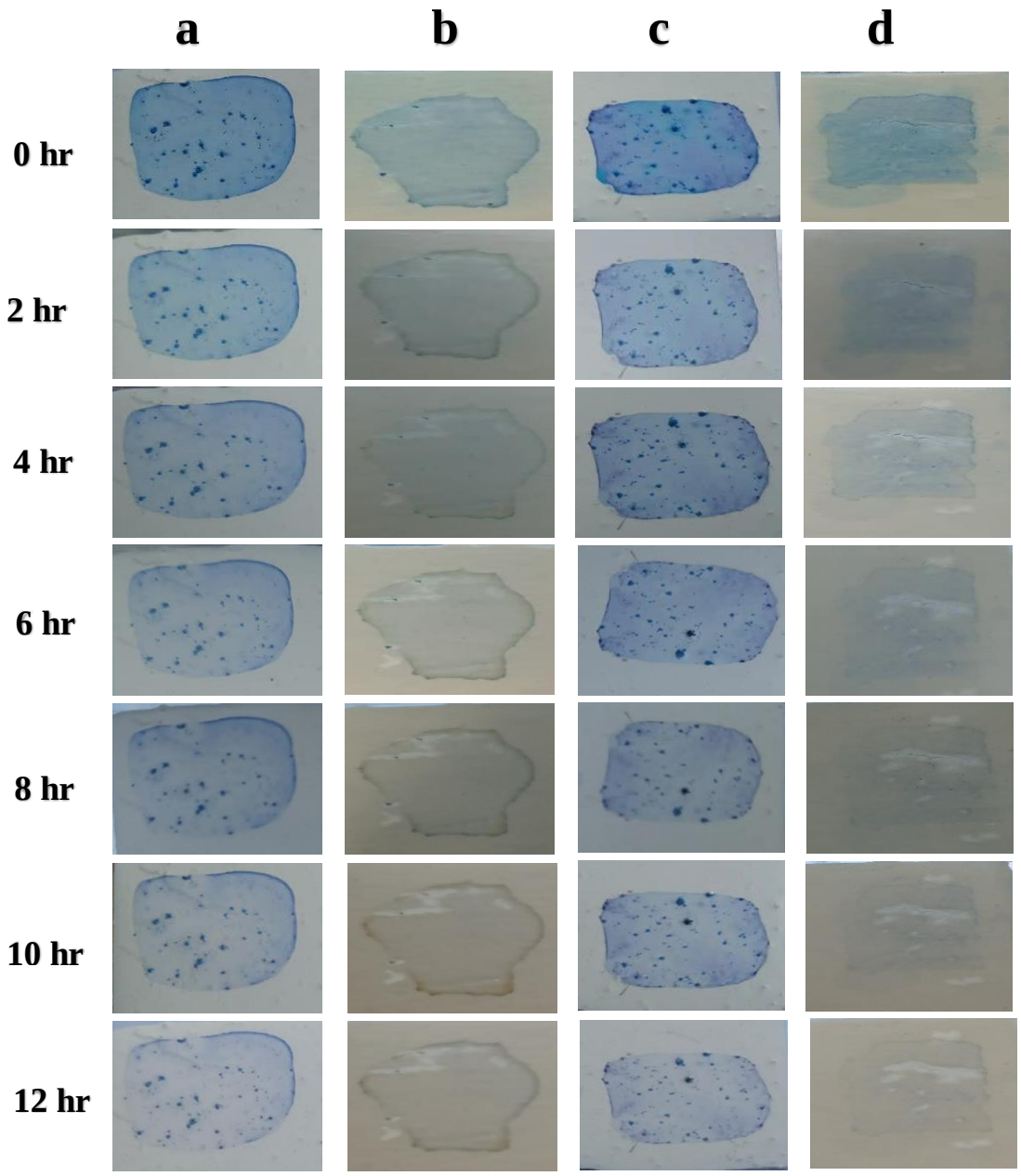


Figure 4. 18. Photographic image of the self-cleaning test. a) and c) paint film synthesized using TiO_2 stained with 10 and 20ppm MB respectively and b) and d) modified traffic paint film synthesized using composite stained with 10 and 20ppm MB respectively

.

ii. ***Wettability investigation of the modified road marking paint:***

To evaluate the hydrophilicity or the hydrophobicity of self-cleaning paint water contact angle was measured before and after sunlight exposure using ImageJ software. For comparison contact angle of paint prepared by using anatase TiO_2 pigment (micro size) was also measured. Figure 4.19 shows the photographic image of a water droplet on the surface of the paint before and after sunlight exposure. The result of water contact angle measurement before UV irradiation showed the paint film has a hydrophilic property with a contact angle of less than 90^o. The water contact angle of traffic marking paint synthesized using TiO_2 pigment show less change in water contact angle but the water contact angle of traffic marking paint modified using Nano-TiO_2/Awash Melkassa residue silica composite decreased from 67.56^o to 60.3^o after UV irradiation, which shows a strong photoinduced hydrophilic property of the traffic marking paint. The hydrophilicity property of the paint is due to the photoinduced hydrophilic nature of Nano-TiO_2. The contact angle measurement result of image J software before and after sunlight exposure is summarized in Table 4.17.

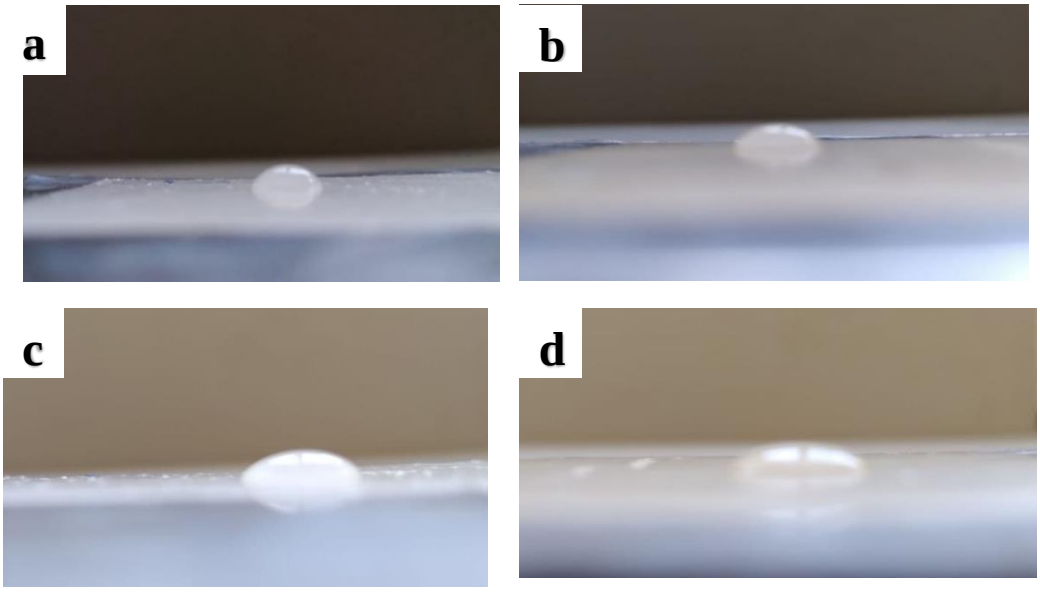


Figure 4. 19. Photographic image of water drop on the surface of paint, a) and c) paint using TiO_2 pigment before and after UV irradiation, b) and d) paint using composite before and after UV irradiation.

Table 4. 17. The contact angle of paint before and after UV irradiation.

Paint	**Contact angle before (^{o})**	**after (^{o})**
Paint using TiO_2 pigment	67.98	66.46
Paint using composite	67.56	60.3

From the result of both photocatalytic degradations of model pollutant methyl blue and water contact angle measurement, it can be concluded that traffic marking paint using Nano-TiO_2/Awash Melkassa residue silica composite as a photocatalyst shows a better self-cleaning property.

CHAPTER FIVE

5. CONCLUSION AND FUTURE WORK

5.1. Conclusion

In this study, the formulation of traffic marking paint started from the choice of solvent mixing ratio. The solubilization capability of benzene and toluene with mixing ratios 100/0, 85/15, 75/25, 65/35, 35/65, 25/75,15/85, and 0/100 were experimentally tested. Among the above mixing ratios, blending of benzene to toluene at 35/65 mixing ratio had a tendency of dissolving the chlorinated rubber as well as reduce the cost of 100% toluene solvent by 14.4%. Therefore, the solvent solution with a 35/65 mixing ratio was used to formulate traffic marking paint instead of using only toluene as a solvent as that of commercial traffic marking paints.

Mixture experimental design methodology was used to prepare traffic marking paint formulation. The validation of the model using ANOVA analysis verified that the quadratic models selected are accurate and consistent with a P-value of less than 0.05. Overall, the outcome clearly showed that each linear component of the paint namely titanium dioxide, calcium carbonate, chlorinated rubber, and solvent, had a major impact on the viscosity of the paint (P-value less than 0.05). The result also shows that the interaction of the paint ingredient calcium carbonate and binder, and calcium carbonate and solvent, and binder and solvent had a significant effect on the viscosity.

Based on the graphic optimization procedure, four optimal traffic paint formulation that has a viscosity in the range of 80-95 KU (8.09-13.5 poise) were selected. The test results of the wet and dry paint property of the optimum traffic paint formulation have relatively good agreement with a dry and wet film property of commercially available chlorinated rubber-based traffic paint. Based on this, among the four samples, the optimum one (i.e run 10) was selected and modified with the self-cleaning property using Nano-TiO_2/Awash Melkassa residue silica composite as a photocatalyst.

In this research Nano-TiO_2/residue silica composite was prepared and used to prepare the self-cleaning traffic marking paint. Before the usage of the Awash Melkasa residue silica, thermal treatment was done based on DTA-TGA analysis as a pretreatment to remove physisorbed water,

organic matter, and structural water and aluminum sulfate and based on DTA-TGA analysis the Awash Melkasa residue silica annealed at 900 ^{O}C.

The result from EDX analysis revealed information on the main content of the residue silica before thermal treatment which was as follows: O_2, Si, Al, C, SO^{-2}_4, Fe, K, and Mg. The content of the residue silica after thermal treatment was different from before which is due to the removal of organic matter and the same amount of aluminum sulfate. The EDX analysis of the Nano-TiO_2/Awash Melkassa residue silica composite indicates the presence of titanium (Ti). This indicates the presence of Nano-TiO_2 in the composite. FTIR analysis confirmed the existence of Ti-O-Si bonds in the composite, and XRD analysis also showed the presence of nano-TiO_2 in the composite in the anatase phase.

Nano-TiO_2/Awash Melkassa residue silica composite used to prepare self-cleaning traffic marking paint. The photocatalytic property of modified traffic marking paint shows better photocatalytic degradation of methyl blue dye stained on its surface than the traffic paint synthesized using TiO_2 pigment. This is due to the photocatalytic property of the anatase phase Nano-TiO_2 and the enhancement of its dispersibility and adsorption capacity by the silica.

The water contact angle of modified traffic marking paint and the paint synthesized using TiO_2 pigment before and after sunlight irradiation show hydrophilic property with a water contact angle less than 90^0. From both the photocatalytic test and water contact angle measurement result, it can be concluded that traffic marking paint modified with Nano-TiO_2/Awash Melkassa residue silica composite has self-cleaning property.

5.2. Future work

Present work formulated traffic marking paint using chlorinated rubber as a binder and evaluate different wet and dry film properties. The formulated traffic marking paint was modified with the self-cleaning property using Nano-TiO_2/Awash Melkassa residue silica composite as a photocatalyst. For continuing this work it is suggested to evaluate additional properties of paint such as drying time of the paint film, hiding power, wear resistance shall also be considered.

The drying time of the paint film should be carried out to obtain the No-Pick uptime of the paint and to know the time that the paint film dries completely without affecting traffic flow. Additionally, for future work, it is suggested to determine the hiding power of traffic marking paint to evaluate the ability of the paint to hide the road surface. Furthermore, the resistance of the paint film to wear should be carried out to evaluate the ability of the paint film to withstand wear from vehicles. Also, to increase the nighttime visibility of the traffic marking paint film glass bead can be used and measurement of retroreflection should be done.

Further studies on self-cleaning traffic marking paint are also suggested for future work. In this research, the residue silica obtained from Awash Melkassa Aluminium Sulphate & Sulphuric acid S.C factory was directly used to prepare the composite with only heat treatment. Further pretreatment, such as washing can be checked for future work to improve the white color of the silica, which helps in maintaining the white color of the traffic marking paint.

Finally, further studies on self-cleaning traffic marking paint can also be suggested including the checking of long-term atmospheric exposure test to determine the duration of the self-cleaning ability of the paint and to quantify the effect of the external environment on the paint film. Further optimization can also be done on the preparation of the Nano-TiO_2/Awash Melkassa residue silica composite to increase the self-cleaning ability of the paint.

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