DEVELOPMENT AND CHARACTERIZATION OF SELF-HEALING CAR PAINT USING CHITOSAN

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By

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NIGERIA

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DECLARATION

I declared that, the work in this thesis entitled DEVELOPMENT OF SELF-HEALING CARPAINT has been carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

…… ……
……...

Name of Student Signature Date

CERTIFICATION

This thesis entitled DEVELOPMENT OF SELF-HEALING CAR PAINT by ABDULLAHI BELLO meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

I dedicated this work to my late brother “Abdulmuluq”. May Almighty God have mercy upon him, forgive all his sins and grant him with Al-jannatulFirdaus.

ACKNOWLEDGEMENT

I thank God for life, for His all sufficient grace and for bringing me this far. My gratitude and sincere appreciation goes to my supervisors - Dr. A.O. Ameh, Dr. M.T. Isa and Dr. M.S. Galadima for their commitment and guidance that has enabled me to accomplish this work. How could I have executed this work without daily prayers and other supports from my mum and dad, I am most grateful for all and will forever appreciate you two. My sincere appreciations go to my - bigger bross, mentor, role model, Lecturer for his good heart. I am very much indebted to him not only for his profound pieces of advice, financial support, prayers and encouragement, which were very instrumental to the success of this project, but also for his personal concern and provision of relevant materials and ideas throughout the period of its execution. This journey began with an encouragement from him and with his endless support all through made it a success. Sir, I had continued to look unto you all the way and words are too limited to express my profound gratitude for your ever willingness to mentor me in every part of my life. I want to also appreciate his wife "mama mariam" for her good heart, support, prayers and encouragement all through. I thank my love for her patient, prayers, support, love, caring and indelible touches in my live both in character and learning. I will forever appreciate you for all. I want to appreciate my sister "Asma'u" for her endless support, love and prayers, may Allah reward you in not small way. I want to also appreciate my brothers and other sisters – Ibrahim, Raheem, Muhammed, Abdulmumeen, Musa, Lukman, Husseini, Rabi, Hassana, Rukaya, Amina and Hajara for their well wish. I shall never forget the support I got from my friends – Mr. Samuel, Engr. Hanan,Mr.Lawal, Mr.Jatman, Pham. Jamiu, Mr. Jamil, Mr.Zanna and all others I could not mention, may God Almighty bless you all in all your endeavours. My heartfelt thankfulness goes to my little angel "Mariam" and her brothers – Hamza (Prof), Mubarak (Massimo) and MuhammedTijani (Sheik) for their love, prayers, desires to always be with me which makes me happy to focus more. May Allah reward you guys abundantly. Finally, I want to thank the HOD and other staffs of Peugeot Automobile Nigeria's Industrial laboratory unit for their assistance in the physico-mechanical analysis part of this work. I thank my colleagues for their encouragement and belief in me as I made this endeavour a success.I want to also appreciate the encouragement and financial support I got from Dr. C.S Ajinomoh. I also want to thank Prof. A.S Ahmed and Dr. B.O. Aderemi for their support. Finally, I want appreciate all my lecturers for the knowledge and discipline they impacted on me.
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ABSTRACT

Car surfaces are vulnerable to scratches from environmental conditions, thereby prompting car users to visit car workshop for re-spray. This process does not usually bring permanent solution to scratches on car surfaces since they are often re-spray with non-self-healing paint. The aim of this work was to develop self-healing car paint. In doing this, response surface methodology (RSM) was used to obtain an optimum paint formulation which was then improved into a self-healing car paint by incorporating chitosan into the formulation, sprayed on substrates, allowed to dry, scratched with a pin, exposed with UV light from the sun and then investigated for self-healing using scanning electron microscope (SEM).

The model developed for drying time and coverage responses using (ANOVA) in the RSM study were significant as their respective "Prob > F" values were less than 0.0500 with R^2 values 0.8693 and 0.9204 respectively. The "lack of fit" in both cases were not significant which is desirable in statistical analysis of this nature. Physico-chemical analysis (viscosity, density and pH) were done on the 20-runs of formulated paint where runs 1, 3, 7, 8 and 13 had the best density values of 0.956 g/cm^3, 0.977g/cm^3, 0.875 g/cm^3, 0.896 g/cm^3 and 0.944 g/cm^{3}respectively as compared to other runs. Runs 1, 3, 7, 8 and 13 viscosity values fall within range of "30±5 cp",(ASTM, 2009; PAN, 2013) standard specification for car paint. The pH values of the twenty runs were in the range of 6.6 to 6.9.

The physico-chemical test performance of runs 1, 3, 7, 8 and 13 was a criteria for their selection to undergophysico-mechanical test, in which run 8 among the other runs selected had the optimum performance in terms of gloss, film thickness, cross-scratch, punch, chemical resistance, heat resistance and colour stability tests as its results agreed closely to ASTM/PAN car paint standard specifications.The SEM analysis done on the coated substrates showed that chitosan has self-healing effect.

TABLE OF CONTENTS

CONTENTS	PAGES
DECLARATION	i
CERTIFICATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	xiii
LIST OF TABLES	xv
LIST OF PLATES	xvii
ABBREVIATIONS	Xviii

CHAPTER ONE

1.0 INTRODUCTION	1
1.1 Problem Statements	4
1.2 Justifications	4
1.3 Aim and Objectives	4
1.4 Research Scopes	5

CHAPTER TWO

2.0 LITERATURE REVIEW 6

2.1 Classification of Paints 6

2.1.1 Emulsion paint 6

2.1.2 Gloss paint 7

2.2 Composition of Paints 7

2.2.1 Binders 8

2.2.1.1 Convertible binders 8

2.2.1.2 Non-Convertible binders 9

2.2.1.3 Alkyd resin 10

2.2.2 Pigments 11

2.2.2.1 Classification of pigments 12

2.2.3 Solvents 14

2.2.3.1 Hydrocarbon Solvents 15

2.2.3.2 Oxygenated solvents 15

2.2.3.3 Chlorinated solvents 16

2.2.4 Additives 16

2.3 Paint Formulation Process 16

2.4 Hazards Associated with Paint Formulations and it Preventive 17

Measures

2.4.1 Preventive measures 19

2.5Physico-Chemical Analysis of Paint 21

2.5.1 Viscosity measurement 21

2.5.2 Density test 21

2.5.3 pH test 21

2.5.4 Drying time 22

2.5.4.1 ASTM test method of drying time 22

2.6Physico-Mechanical Analysis 23

2.6.1 Film thickness 23

2.6.2 Gloss (Opacity) analysis 24

2.6.3 Chemical resistance 24

2.6.4 Punch test 25

2.6.5 Cross-scratch test 25

2.6.6 Colour stability 26

2.7 Modelling of Experimental Formulation 26

2.7.1 Response surface methodology (RSM) 27

2.7.1.1 Fitting of model analysis 27

2.8 Self-Healing Coating Polymers 29

2.8.1 Benefit of self-healing coatings 30

2.8.1.1 Intrinsic self-healing 31

2.8.1.1.1 Self-healing based on physical interactions 31

2.8.1.1.2 Self-healing based on chemical interactions 32

2.8.2 Extrinsic self-healing 34

CHAPTER THREE

3.0 MATERIALS AND METHOD 35

3.1 Materials and Equipment 35

3.2 Methodology 37

3.2.1 Source of raw materials 37

3.2.2 Experimental design 37

3.2.3 Paint formulation procedure 39

3.2.4 Paint viscosity measurement 39

3.2.5 Density test 40

3.2.6 pH measurement 40

3.2.7 Preparation of plates for spray 40

3.2.8 Drying time and coverage responses determination 41

3.2.9. Analysis of the applied paints on substrates 41

3.2.10 Spraying of the substrates 41

3.2.10.1 Gloss test 42

3.2.10.2 Film thickness test 42

3.2.10.3 Cross-scratch test 43

3.2.10.4 Punch test 43

3.2.10.5 Chemical resistance test 43

3.2.10.6 Heat resistance test 44

3.3 Self-Healing Car Paint Formulation 44

3.3.1 Investigation of self-healing property of the paint on coated substrates 45

3.3.2 Fourier transform infrared analysis 45

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS 46

4.1 Effect of Component Proportioning on Viscosity of Formulated Paint 46

4.2 Effect of Component Proportioning on Density of Formulated Paint 48

4.3 Effect of Component Proportioning on pH of Formulated Paint 48

4.4 Physico-Mechanical Analysis 48

4.4.1 Gloss (opacity) test 49

4.4.2Film thickness test 50

4.4.3Cross-scratch test 51

4.4.4Punch test 52

4.4.5Chemical resistance test 53

4.4.6 Heat resistance/colour stability test 54

4.5 Drying Time and Coverage Responses 56

4.6 Drying Time and Coverage Mathematical Models 58

4.7 Statistical Analysis for Drying Time and Coverage 59

4.7.1Drying time response 59

4.7.2 Coverage response 61

4.8 Predicted and Actual Drying Time and Coverage Relationship 62

4.9 3D-Surface Plots of Variable Parameters and Responses Studied (Drying Time and Coverage) 64

4.10 Optimized Solutions from the Simulated Responses 66

4.11 Self-Healing Property of Chitosan Investigation on the Formulated Paint 67

4.12 Fourier Transform Infrared Spectroscopy (FTIR) 71

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS 74

5.1 CONCLUSIONS 74

5.2RECOMMENDATIONS 75

REFERENCES 76

APPENDIX A 82

APPENDIX B 88

LIST OF FIGURES

Figure 2.1: Classification of pigments 13

Figure 2.2: Parity plot of experimental and predicted values 28

Figure 2.3: Three dimensional plot of temperature-pH against yield 28

Figure 4.1a: Actual (experimental) and predicted drying time relationship of the formulated paint 62

Figure 4.1b: Actual (experimental) and predicted coverage relationship of the formulated paint 63

Figure 4.2a: 3D plot of drying time against solvent versus binder 64

Figure 4.2b: 3D plot of coverage against solvent versus binder 65

Figure 4.3 a and b: 0% chitosan concentration (control sample) at 0 minute and 60 minutes respectively 68

Figure 4.3 c and d: 0.5% chitosan concentration at 0 minute and 60 minutes respectively 68

Figure 4.3 e and f: 1.0% chitosan concentration at 0 minute and 60 minutes respectively 68

Figure 4.3 g and h: 1.5% chitosan concentration at 0 minute and 60 minutes respectively 69

Figure 4.3 i and j: 2.0% chitosan concentration 0 minute and 60 minutes respectively 69

Figure 4.4a: FTIR graph of raw chitosan used in the paint formulation 71

Figure 4.4b: FTIR graph of the formulated car paint without chitosan 72

Figure 4.4c: FTIR graph of the formulated self-healing car chitosan 72

Figure A_1: Three dimensional relationship between binder-pigment (coverage agent) interactions against drying time response of the formulated paint 85

Figure A_2: Three dimensional relationship between solvent-pigment (coverage agent) interactions against drying time. 86

Figure A_3: Three dimensional relationships between binder-pigment (coverage agent) interactions against coverage response 86

Figure A_4: Three dimensional relationships between solvent-pigment (coverage agent) interactions against coverage response 86

Figure A_5: Optimization of drying time and coverage responses simulation interface 87

LIST OF TABLES

Table 2.1: Binders and their properties 9

Table 2.2: Oil modified alkyd resin with their properties 11

Table 3.1: List of materials and their sources used in this work 35

Table 3.2: List of equipment used 36

Table 3.3: Design of experimental status 37

Table 3.4. Design of experiment data 38

Table 4.1: Density, Viscosity and pH results of the formulated auto base paint 47

Table 4.2: Gloss (opacity) of the formulated paint 49

Table 4.3: Film thickness test result of the formulated paint 50

Table 4.4: Cross-scratch test of the formulated paint 51

Table 4.5: Punch test analysis of the formulated paint 52

Table 4.6: Chemical resistance analysis of the formulated paint on substrates 53

Table 4.7: Heat resistance analysis of the formulated paint 54

Table 4.8: Drying time and coverage responses analysis of the formulated auto base paint 57

Table 4.9a: Analysis of variance (ANOVA) for drying time response 60

Table 4.9b: Analysis of variance (ANOVA) for coverage response 61

Table 4.10: Optimized auto base paint formulation solutions 67

Table A_1: Density of the formulated auto base paint 82

Table A_2: Drying time and coverage 83

Table A_3: Design of experimental status 84

Table A_4: Statistical diagnostic of predicted actual time in minutes for each run 84

Table A_5: Statistical diagnostic of predicted actual time in minutes for each run 85

Table A_6: Optimization solutions of the auto base paint 87

Table B_1: ASTM auto base standard specifications (ASTM, 2009) 88

Table B_2: PAN auto base paint standard specifications (PAN, 2013) 89

Table B_3: Gloss value of the formulated auto base paint on coated substrates (Raw results from PAN industrial laboratory) 89

Table B_4: Film thickness analysis on the coated substrates (Raw results from PAN industrial laboratory) 90

Table B_5: Infrared absorption band characteristics of some functional groups 91

Table B_6: Infrared correlation chart 92

Table B_7: Comparative FTIR analysis of fluoroquinlones 93

Table B_8: Saturated aliphatic and olefinic frequencies 93

LIST OF PLATES

Plate I: Coated panels with the formulated paints 41

Plate II: Coated panels after subjected for film thickness test, gloss test, cross scratch test, punch test, chemical resistance test and heat resistance test. 56

LIST OF ABBREVIATIONS AND SYMBOLS/UNITS

RSM	Response Surface Methodology
DOE	Design of Experiment
SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
ASTM	American Society for Testing and Materials
PAN	Peugeot Automobile Nigeria
cp	Centipoise
µm	Micrometre
VOC	Volatile organic compound
PEL	Permissible exposure level
CCD	Central composite design

CHAPTER ONE

1.0 INTRODUCTION

The surfaces of any object is vulnerable as it often makes continual contact with the corroding (or oxidizing) air, most especially**when left in an open place, thereby bear the brunt of the sun, rain,**fug, dew and snow (Rodger, 2008). Thus, under these conditions, the surfaces tend to rust, disintegrate, corrode and crackresulting to wear of daily use.However, these effects can be prevented or managed with various surface coating medium such as wallpapers, plastic sheet, chrome, silver plating and paint which have being identified and applied to decorate and smooth out any surface roughness or irregularities (Jonathan, 2009). Paint is commonly used as compared to other surface coating due to its ease of application, maintenance and versatility (Jonathan, 2009).

Paint is defined as an engineered material made of several ingredients such as resin, solvent, pigments and additives that are mixed together to create a specific product with its own unique properties (Rodger, 2008). It is classified based on purposes and area of applications. A paint whose diluent of formulation and medium of cleanliness is solvent is refers to as ‘gloss paint. This type of paint can be formulated for car surface coating, refinery equipment coating, road marking purposes, varnishes and so on (Rodger, 2008; Alireza*et al*., 2009). While a water base paint is term as an emulsion paint which can be applied for architectural building (Michael, 2005; Rodger, 2008). It can be formulated from four major components, be it solvent base or water base type(Michael, 2005). These components are resin (binder), pigments (sometimes in conjunction with extenders), solvent and additives (Rodger,2008).

Paint has been in existence for decades and there are standard formulation for its high quality, though there are no much published work on its detail experimental apart from the general knowledge of its product, this may be due to the products being mostly

patented. However, it has been established that, mixing binder, solvent, pigments and additives in random proportion will result to paint product, but its certified quality depends on its ability to meet standard specification test, where its best performance after application tells and differentiate it from low quality product (Turner, 1999;DuPont, 2010;Shawn, 2011; PAN, 2013). Thus, having knowledge of the appropriate proportions of each component of the paint to be added during formulation will give rise to a desired quality product as may be proved from analysis of its physico-chemical/physico-mechanical test before and after application (Alireza*et al*., 2009).

Oragwu (2013), used castor seed oil as plasticizer in 23.65wt% titanium dioxide, 70ml of white spirit and 90ml of alkyd resin in car paint formulation. But there was no justification to why these ranges or proportions of raw materials for the paint formulation were chosen and there was no physico-mechanical test done on substrate where such paint was applied to ascertain its quality.

However, design of experiment technique incorporated with response surface methodology (RSM) can be used to generate runs of experiment by inputting desirable variable conditions that will result to optimum paint formulation from expected responses. The technique (RSM), is a dynamic tool in which set of statistical design of experiment (DOE) are used, which aids the relationship between output variables with process input decision variables to accomplish the objective of maximization or minimization of the responses (Ali *et al.*, 2011;Li *et al*, 2012; Ali, 2014).

Ali *et al.,* (2013) use RSM to evaluate the compositional variations and interactions of glycerylbehenate and poloxamer 188 as lipid carrier and surfactant respectively in developing theophylline. Also, Ali (2014) optimized the process variables for fluoride

ion removal with the aid of maghenite nanoparticles using RSM. Keshani*et al*., (2010) also applied RSM in the optimization of concentration process on pomelo fruit juice. Moreover, optimization of process conditions for tomato foam development was done by Balasubramanian*et al*., in 2012, using RSM. RSM was used by Yamin*et al*., (2013) for lead ion removal from aqueous solution with the aid of intercalated tartrate-Mg.Al layered double hydroxides. Xinyue*et al*., (2014) also applied RSM in the optimization of process parameters for litopenaceusvannmei seafood sauce. Bulent *et al*., (2007) determined the effects of drying air velocity and pepper size on drying time, drying product's ascorbic acid level and colour using RSM. Therefore, it can be assumed that RSM is suited for the optimization of car paint formulation.

Due to daily technology development most especially on polymer modification, satisfied quality car paint can as well be improved on as it has been done to other polymer materials that exhibit self-healing property. Self-healing car paint differs from ordinary car paint in that, it contains an autonomic healing materials capable of responding to harsh environmental effects which subsequently repair damages incurred on coating where it is been applied without external intervention (Chris *et al*., 2011).

Kousouraki and Mouritz (2010), worked on the effect of self-healing hollow fibres on the mechanical properties of polymer composites. Kessler *et al*., (2003), used microencapsulated healing agent on self-healing fibre reinforced polymer matrix composite material. Also, in (2011), Yan *et al*., used epoxy-mercaptan as self-healing agent in self-healing of low-velocity impact damage in glass fabric/epoxy composites study. A scandium (iii) triflate catalysed self-healing system in an epoxy based fibre reinforced polymer composite material was investigated in (2011) by Tim *et al*. Also, Biswajit*et al*., (2011), studied self-healing ability of oxetane-substituted chitosan in

polyurethane resin coating. While, Hüsnügül*et al*., (2013) investigated self-healing property of chitosan in an epoxy dye.

While RSM has been used extensively in studies of several processes, it use in paint formulation has not been investigated. More so, scanty literature source is available on the use of chitosan on self-healing application in car paint formulation.

The present investigation is on the production of self-healing car paint, where attempt was made to fill research gap that exist in previous works.

1.1 Problem Statements

The standard formulation of auto base paint is hidden as there is no published work that has stated clearly the right proportions of each component that make up the formulation with optimum properties.Also, lot of human hours/resources are wasted by car owners visiting auto shops frequently. Finally, researches on self-healing car paint and use of RSM in paint production are scanty.

1.2 Justifications

The research will establish optimum car paint formulation using Design of Experiment (DOE) incorporated with Response Surface Methodology (RSM). More so, improved quality special car paint will be formulated (self-healing car paint), thereby reducing constant visit of car owners to car spray workshop. More so, there is availability of raw materials for chitosan synthesis in Nigeria which will create employment and market value for the sources of chitosan.

1.3 Aim and Objectives

The aim of this work is to develop a self-healing car paint; with the objectives of:

- ✓ Developing empirical model for paint formulation using response surface methodology (RSM) technique
- ✓ Optimization for optimal formulation
- ✓ Incorporation of chitosan in the optimum formulation and analyze for self-healing property.

1.4 Research Scopes

The scope of this work involved

- ✓ The design of experiment(DOE) using RSM.
- ✓ Use of medium oil alkyd resin for the formulation of car paint with the help of experimental design.
- ✓ Physico-chemical/physico-mechanical characterization of the formulated paint
- ✓ Incorporation of chitosan in the formulation for self-healing verification of the paint.

CHAPTER TWO

2.0 LITERATURE REVIEW

It has been established that paints have been manufactured since the prehistoric times, which were mainly used for artworks (Craig, 2009). Since 19th Century till date, paints are not only used for colouring but also used as a medium of protecting many surfaces such as houses, cars, road marking, industrial equipment and underground vessels (Craig, 2009). However, eachof these different applications requires different sort of paint, whose composition may differ (Craig, 2009).

2.1 Classification of Paints

Basically, paints are classified according to area and purpose of application. They are classified as emulsion (water base) and gloss (oil base) paints.

2.1.1 Emulsion paint

Emulsion paints are water based which are made up of synthetic polymer, pigment and water (Aymane*t al*., 2013). This type of paint is generally used for interior decoration most especially walls of an architectural building and ceilings (Aymane*t al*., 2013). They work so well on walls and ceilings because they are easier to apply than many other paints. An emulsion paint on wall or ceiling can easily be cleaned with water since it is water based, without any damage done to its surface of application (Aymane*t al*., 2013).Emulsion paint give a matt finish effect and are often used to cover large area unlike gloss paint that give glossy finish.

The advantage of emulsion paint over gloss paint is that, it can be painted on to just about any surface from brick to cement to lining papered walls. It is less toxic but can last less long than that of gloss paint due to its in-ability to withstand harsh environmental conditions (Shawn, 2011). Polyvinyl acetate (PVA) resin is probably the best known emulsion polymer binder mostly used in water base paint. This is commonly used in both paints industry and the adhesives industry. In the paints industry they form the basis of water-thinnable paints, and they are used in the adhesives industry for wood and cardboard glues (Shawn, 2011).

2.1.2 Gloss paint

Gloss paints are sometime referred to as high-solids coatings or oil. They are solvent-based paints, whichcontain greater amounts of pigment and binder than traditional water-based paint(Rodger, 2008).Solvent such as mineral spirit and mineral turpentine are the major dispersant. This type of paints are commonly applicable in exterior surfaces,they are formulated to meet more hostileatmospheric conditions such as rain, dew, temperature extremes, UV radiation and other pollutants (Aymane*t al*., 2013). Gloss paints have good and inherent potentials which make them last longer than traditional water based paint (Alireza*et al*., 2009). The application of this type of paints are mainly found in an industrial coatings products such as automobiles, refinery equipment, road marking paint, varnish (non-pigmented paint) and special purpose paints (formulated from special pigment like copper) for the purpose of anti-fouling in ship application.

2.2 Composition of Paints

Paints are formulated using four major components, these are binders (resins), solvents, pigments (which sometimes include extenders) and additives (Rodgers, 2008). The selection ofthese components for any type of paint formulations will affect its stability (shelf life), application,characteristics, handling, clean-up, disposal, and most importantly, the performance of the product on which it is applied (Rodgers, 2008).

2.2.1 Binders

Binders are the film-forming component that identifies the paint (Rodgers, 2008). It is the most important component in determining the properties of a paint. The major functions of binders are to provide adhesion to a substrate, form a continuous film and bind the pigments and additives into the paint (Turner, 1999). Solvent-borne binders are oftenreferred to as resins and water-borne paint binders as a latex (Rodger, 2008).

The important of binders in paint formulation cannot be over-emphasized because it determines the quality of paint or its suitability in its area of application (Alireza*et al*., 2009). Though, the other components of paint can affect the performance (particularly in the case of highly specialised paints such as anti-corrosive paints) but the binder is much more important (Alireza*et al*., 2009). Binders exist in form of convertible and non-convertible type as discussed in the next sub-sections.

2.2.1.1 Convertible binders

Convertible binders are binder that when dry, tend to chemically react with a hardener, moisture, or oxygen from the air to form a completely new chemical compound that has quite different chemical and physical properties to the starting binder or resin (Rodger, 2008). These types of resins often become very hard and as a consequence are difficult to recoat (Rodger, 2008). Examples of convertible binders are acrylic epoxy,acrylic urethane, epoxy resins,ethyl silicate, linseed oil,moisture cured urethane,polyester

urethane, special acrylic latex, oleoresinous varnishes, amino resins, polyurethane resins and urethane alkyd.

Table 2.1: Binders and their properties

	Alkyd	Alkyd Amino	Baking Polyester	Modified Alkyd	Acrylic	Cellulose	Catalysed Epoxy	Urethane
Exterior durability	E	E	E	G	E	E	G	E
Salt spray	E	G	G	G	E	E	E	E
Alkali resistance	P	F	G	G	G	P	E	F
Solvent aliphatic	G	E	E	F	F	F	E	E
Solvent ketone	P	P	G	P	P	P	G	E
Flexibility	E	G	E	G	E	E	F	E
Impact	G	E	E	G	E	E	G	E
Heat resistance	G	G	E	G	G	P	G	G
Colour retention	G	G	E	G	E	E	F	E
Gloss retention	E	G	E	F	E	G	P	E

E = Excellent, G = Good, F = Fair and P = Poor

Source: Rodgers, 2008.

The properties of some binders are depicted in Table 2.1. The table shows various resins type with their performance or suitability in area of application. Thus, alkyd resin was

chosen in this work due to its availability, less cost effectiveness and excellent performance.

2.2.1.2 Non-Convertible binders

These are category of binders that do not change chemically as they dry (Rodger, 2008). Lacquers and latex paints dominate this category (Rodger, 2008).Generally the better performing non-convertible binders are of high molecular weight, which gives them good toughness and durability without them having to chemically react further as convertible coatings do (Turner, 1999; Rodger, 2008). The advantages of this category of binders are that, their physical properties will not change over time and they will always be easy to recoat (Rodger, 2008).Examples of non-convertible binders are acrylic latex,acrylic urethane latex, alkyd resin, bitumen, chlorinated rubber, solution acrylic,cellulose, nitrocellulose, vinyl acrylic and vinyl butyral. Table 2.1 shows some example of binders with their properties in area of applications.

2.2.1.3 Alkyd resin

Alkyd resins are high molecular weight esters formed when polyhydric alcohols react with polybasic and monobasic acid (Alireza*et al.*, 2009). Alkyd resin are characterized by their good adhesion and drying properties for organic coating (Alireza, *et al*., 2009).It can be modified with a number of oils which include soya, linseed, dehydratedcastor, and coconut. They in turn can be combined with such resins as acrylics, vinyltoluene, silicones, and amino-resins (Rodgers, 2008). The latitude of compatibility of the oil-modified resins makes them popular for use in industrial coatings (Rodgers, 2008; Alireza*et al.*, 2009). They are fairly inexpensive and have a variety of properties (Rodgers, 2008). Alkyds can be prepared directly from oil

(triglyceride), a polyol, or an acid and the percentage of oil contained in an alkyd classifies its end use, which affects its properties as speed of drying, flexibility, durability, and so forth (Rodgers, 2008). Thus, the oil modified alkyd resins are classified into long oil, medium oil and short oil alkyd resins (Aymane*t al*., 2013).

The long oil alkyd resin is applicable in exterior trim paints, wall paint, marine paint and metal maintenance paint. The medium oil type is used in standard vehicle industrial applications such as primer, undercoat and metal surface finishes. While the short oil alkyd type is used in baking primer and enamel (Rodgers, 2008; Alireza*et al*., 2009). Table 2.2 shows the oil modified alkyd resin with their oil length and properties.

Table 2.2: Oil modified alkyd resin with their properties

Alkyd	Oil length	Characteristics	Uses
Short	20-25	Non-oxidative. Soluble in aromatic hydrocarbon solvents. Hard brittle film	As modifying remains in baking system for interior use
Medium	45-60	Air drying or baking cure. Soluble in aliphatic-aromatic solvent blend. More flexible film	As above for interior and exterior. Also used in fast drying system
Long	60-80	Air drying (oxidative), soluble in aliphatic solvent. Very flexible film	Exterior drying system

Rodgers, 2008.

2.2.2 Pigments

Pigments are particulate solids that are dispersed in paints to provide certain characteristicssuch as colour, opacity, durability, mechanical strength, and corrosion protection for metallic substrates (Rodger, 2008). Pigments may be inorganic and organic materials. Organic pigments are used primarily for decorative purposes, while inorganic types have traditionally been added for protective properties (Khanna, 2008). Sometimes, extenders are used in conjunction with pigments to modify the properties of the paint (Khanna, 2008).

The size and shape of the pigment particles are important considerations, since they affect the agglomeration or packing within the paint binder or matrix (Manouchehr*et al*., 2005). Most pigments are crystalline and the crystal form often affects the characteristics of the pigment. Particle size also affects the finished gloss, settling of the pigment during storage, and wetting by the binder. Pigments usually have particle size of about 0.5 to 5 μms in standard paints but can beas small as 0.01 μms in the case of some bright organic pigments (Manouchehr*et al*., 2005).

Other factors such as colour, tint strength, colour fastness, and opacity are inherent characteristics of the pigment. Density is another important factor affecting not only settling, but also the volume of pigment for a given weight addition (Manouchehr*et al*., 2005).Pigments have to be uniformly dispersed in the binder to provide a consistent appearance. They have to remain in suspension or be easy to disperse if settling occurs (Rodgers, 2008).

2.2.2.1 Classification of pigments

Pigments, whether synthetic or naturalcome in form of white, coloured, metallic and extenders. Generally, white pigments are present inalmost all paint formulation (Manouchehr*et al*., 2005). Its function is to adjust the lightness darkness of the final

colour and enhance its high opacity (Rodger, 2008). Some common examples of white pigments are depicted in Figure 2.1

White	Coloured	Metallic	Extenders
Titanium	Iron oxide	Aluminium	Blanc fixe
Zinc oxide	Red lead	Zinc	Paris white
Antimony oxide	Cadmium oxide	Lead	Barytes whiting
White lead	Lead silicochromate		China clay
Lead sulphate	Lead chromate		Mica
	Zinc chromate		Talc
	Cadmium yellow		
	Calcium plumbate		
	Chroium oxide		
	Prussian blue		
	Ultramarine blue		

Figure 2.1: Classification of pigments (Rodger, 2008)

As it can be seen from Figure 2.1, the most widely used type of white pigment is titanium dioxide (Manouchehr*et al*., 2005; Rodger, 2008). This is mostly used among others because of its high refractive index which is a function of high degree of opacity

in paint films. Titanium dioxide comes in two different crystalline forms, the rutile and anatase. The rutile crystalline type is more compact, has a higher specific gravity and greater refractive index. It enhances paint product stability and durability, it is photo-chemically inert and it protect paint films from degrading unlike the anatase crystalline type that is photo-chemically active and paints formulated with such pigment are subject to heavy chalking, this is only used for interior application due to its cleaner white colour (Rodgers, 2008).

Colour pigments can be divided into inorganic and organic products. The inorganic pigments are chemically inert, very light-fastproducts based on oxides and sulphides of the elements iron and chromium in particular, and of zinc, molybdenum and cadmium to a smaller level. The colour pigments either be of natural or synthetic origin (Manouchehr*et al*., 2005). Synthetic pigments are preferred by the paint formulators because they fulfilrequirements for colour consistency and uniformity (Rodger, 2008). Figure 2.1 shows some examples of coloured pigments.

Metallic pigments are very popular for paints that will be used on products such asautomobiles, motorcycles, metal office furniture, and other products that requireexceptional appearance characteristics (Rodger, 2008). While aluminium is the most commonlyused metallic pigment, stainless steel, lead, and zinc have also been used in paint formulation. Some of the examples of metallic pigments are showed in Figure 2.1.

The last part of this classification is extender pigments which are usually naturally occurring minerals such as clay, mica, talc, limestone. These are often used as a cheap way of reducing the cost of producing paint as it is cheaper and can be incorporated into paint formulation to reduce the quantity of pigment (which is more expensive than extenders) present in the total formulation (Rodger, 2008).

2.2.3 Solvents

Solvents are chemical substances that can dissolve, suspend,or extract other materials, usually without chemically changing either the solvents or the other materials (Rodgers, 2008). Solvents make it possible to process, apply, clean or separate materials. It works on the principle of "like dissolves like." Thus, for a solvent to work, it needs to have similar chemical characteristics to the substance that it is trying to dissolve (Joseph, 2012). The most powerful known solvent is water because it can dissolve more materials than any other liquid in existence (Craig, 2009).

Organic solvents are best known for their role as thinners for paints but also playimportant roles in a wide range of other industries such as plastics, footwear, dry cleaning, building, photographic, adhesives, printing inks and even hair-care products. Their most basic job is to make the paint easy to apply(Joseph, 2012).

Organic solvents can be divided into hydrocarbon, oxygenated and chlorinated solvents. Solvents have a wide variety of roles to play in wet paint.

2.2.3.1 Hydrocarbon Solvents

Hydrocarbon solvents are either aromatic or aliphatic compounds made from the chemical elements of carbon and hydrogen alone. This include: kerosene, turpentine, mineral spirit, acetone, butyl acetate, butyl alcohol, ether, methyl ethyl ketone, toluene and xylene (Rodger, 2008). Typically these types of solvents are relatively cheap compared to the oxygenated types and find use in thinners for the common alkyd enamel or solvent-borne paints (Rodger, 2008).

The preferred type of solvent is an odourless aliphatichydrocarbon such as mineral spirits, which can be used in all areas including the home (Manouchehr*et al*.,

2005;Rodger, 2008;Udeozo, 2013).However, aromatic solvents such as toluene, xylene and naphtha provide stronger solvency, but with a greater odour (Rodger, 2008).

2.2.3.2 Oxygenated solvents

Oxygenated solvents include ethyl alcohols, glycol ethers, ketones, esters, and glycol etheresters that are synthesized from other chemicals to form a desired solvent that is typically 99% pure (Turner, 1999). They are often very similar in composition to hydrocarbon solvents but always contain oxygen. These solvents are typically used in nitro-cellulose paints and nail lacquer remover (Turner, 1999). They can mostly be distinguished from hydrocarbon solvents because of their distinctive, often fruity, smells. This can range from very sweet (acetates) to quite foul (butyl alcohol) (Turner, 1999; Rodger, 2008).

2.2.3.3 Chlorinated solvents

An example of chlorinated solvent is methylene chloride which is highly carcinogenic, it is therefore now seldom in used (Rodger, 2008).

2.2.4 Additives

Additives are substances that are added in small quantities during paint formulation to improve or modify certain properties of the finished product during its manufacture, storage, transport, or application (Manouchehr*et al*., 2005; Rodger, 2008).

Additives can affect the paint material characteristics and the finished film properties.Examples of such properties that can be adjusted with paint additives include viscosity, foaming, skinning, pigment dispersion, stability, flexibility/hardness, gloss, UV resistance, fire resistance, bacteria resistance, and many more (Rodgers, 2008).

Examples of additives are: anti-skinning agents, deodorants, driers, fungicides, moisture scavengers, silicones/waxes for mar resistance and slipperiness and UV Absorbers.

2.3 Paint Formulation Process

Basically, production of solvent-based paint begins by mixing resins, dry pigment, and pigment extenders with the aid of high speed mixer (Aymane*t al*., 2013). During this operation, solvents and additives are also added. Following the mixing operation, the batch frequently is transferred to a mill for additional grinding and mixing, and the type of mill is dependent on the types of pigments being handled, so that no one style is universal (Aymane*t al*., 2013). The paint concentrate is then transferred to an agitated tank where tints and thinner (usually a volatile naphtha or blend of solvents) and the balance of the resin are added (Aymane*t al*., 2013). Upon reaching the proper consistency, the paint is filtered to remove any non-dispersed pigment and transferred to a loading hopper (Aymane*t al*., 2013). Then, at this stage, the paint is poured into cans, labelled, packed, and moved to storage (Aymane*t al*., 2013).

Similarly, the water-based paintformulation process is very similar to that ofsolvent-based type (Aymane*t al*., 2013). The major difference is the substitution of water for solvent and the sequencing of material additions (Aymane*t al*., 2013). Preparation of water-based paint begins by mixing together water, ammonia, and a dispersant in a mixer. To this mixture, dry pigment and pigment extenders are added. After mixing, the material is ground in a mill and then transferred to an agitated mix tank (Aymane*t al*., 2013). Four additions of materials occur in this tank. First, resin and plasticizers are added to the mixture; second, a preservative and an antifoaming agent are added; third, a polyvinyl acetate emulsion is added; and fourth, water is added as athinner (Aymane*t al*., 2013). Following this mixing operation, the handling ofthe paint is similar to that

for solvent-based paints. At many facilities the grinding and the mixing and grinding operation may be by-passed with all the dispersion operations occurring in a single high-speed mixer (Aymane*t al*., 2013).

2.4 Hazards Associated with Paint Formulations and it Preventive Measures

Basically paints are a mixture of pigments, solvents and other additives to enhanceits performance, like dryers and hardeners (Manouchehr*et al*., 2005). Pigments and additives inpaint do not dissolve completely but rather remain suspended throughout the systems to form emulsions and other paint mixtures (Agnes, 2011). As most substances in paints are toxic to humans, they are as well constitute ahealth hazard to the users (Akzo, 2012). Therefore, the spraying activities of paint create paint mists that spread the volatile matters to the surrounding air (Manouchehr*et al*., 2005; Agnes, 2011).

Depending on the type of the spray gun used and its pressure, a high concentration of airborne contaminants is produced in vapours and is harmful to human health when inhaled (Agnes, 2011). The solvent's hazards are compounded by the fact that paints contain additives such as disocyanates, lead and other heavy metals, which are highly carcinogenic and require a supply of clean air to the painter to disperse or minimize their contact (Agnes, 2011).

Individuals have different sensitivity, reactivity and irritationlevels to the chemicals, even at low concentrations, many solvents and solids in paints have specific threshold limit values (NIOSH, 2004). Thus different exposure values and guidelines require controlled exposure monitoring to establish the appropriate and effective protection methods (NIOSH, 2004). This calls for use of protective devices when handling paints.

Paint may also come into contact with the skin if not properly protected. Although skin contact may not be a major route of exposure, it may enhance the overall body

exposure. When the chemicals in the paint effectively permeate the skin, theharmful pigments and other additives may be dangerous, and present adverse health effects to the painter as well (Agnes, 2011).

Many disease symptoms may be caused by spray painting, but the two primary occupational diseases associated with spray painting are painter's asthma and dermatitis (DuPont, 2010). While neither of these two have significant data to determine their risk, there is enough evidence to warrant concern (Anna *et al*., 2004).

The potential health effects of volatile organic compounds (VOC) emission is a major concern in paint manufacturing and applications (Anna *et al*., 2004). This is because it is a precursor of ozone depletion in the troposphere and it is this pollutant which most frequently approaches or exceeds levels at which deleterious (hazardous) effects on human health may be observed (Anna *et al*., 2004).Solvents are commonly used in manufacturing and laboratory processes. They areindispensable for many applications such as coatings (paints) and other chemicalprocesses. Most solvents are known to upset the ecosystems and notably thevolatile organic compounds (VOC). Some solvents are known to cause cancer,are neurotoxins or can cause sterility in those individuals frequently exposed tothem (NAOSH, 2004; NAUSEA, 2010). While contained use of these solvents would beacceptable from both an environmental and a health perspective, such operationsare difficult to achieve and alternative solvents are currently being sought tominimize the problems inherent in their release to the environment (NAOSH, 2004; Agnes, 2011).

2.4.1 Preventive measures

The European Commission has seen the need to move further on the issue of VOC and are in the process of drafting guidelines concerning air emission of solvents fromindustries (Agnes, 2011).

The draft directive envisages two routes to compliance. The first one is based on abatement and the other on coating re-formulation (Agnes, 2011). Currently many countries of the world have taken the second option of re-formulation of paint systems (Agnes, 2011).

Also, the European Commission has recently adopted a proposal for a framework directive on ambient air quality assessment and management (Jelena, 2012). This willseek to set health based limit values and alerts for a range of pollutants. Its aim is to attain ambient air concentrations that are under putative with no-adverse effect levels and provide information to the public (Jelena, 2012). Some of the legislation made by the commission are:

I. The control of emission should be done
II. The coating formulation should reduce the amount of solvents, which is the most potentially hazardous component of paint
III. Improve on transfer effectiveness ofcoating i.e. reduce over spray.
IV. As the awareness and understanding of how solvents and driers affect the environment and human health grow, the regulations that govern the use of these chemicals should be strictly adhere to (Jelena, 2012).One good example is the implementation of the Montreal Protocol, the Clean AirAct (CAA), and the Pollution Prevention Act (PPA) of 1990, which is a clearindication that many countries are becoming aware of increased use of organicsolvents in chemical processes (PPG, 2009; DuPont, 2010). The advances made in thesearch for ‘green’ replacements for traditional solvents are reviewed withreference to

solvent alternatives for cleaning, coatings, and chemical reaction andseparation processes (DuPont, 2010). Government agencies such as theOccupation Safety and Health Administrative of United States of Americahave installed measures to protect workers from solvent exposure (DuPont, 2010). The bodyhas implemented strict regulations called permissible exposure levels (PEL) forchemical concentrations for which one may be exposed without detrimental healtheffects. The conventional polyurethane resins usually contain a highproportion of volatile organic solvents, normally between 40% and 60% by weight(Bittner and Ziegler, 2000; DuPont, 2004).

2.5 Physico-Chemical Analysis of Paint

Generally, the final paint product is expected to undergo physico-chemical test such as viscosity, density, pH, drying time and so on. These are commonly known as quality controltest in paint industries before packaging for applications (Joseph, 2012).

2.5.1 Viscosity test

The viscosity test is the property of paint that checkitsfree flow.It is done and compare with international standard, which is 30±5 cp (ASTM, 2009; PAN 3013) for auto base paint. This will give car paint sprayers idea how to thin the paint before its application on car substrate (PAN, 2013).

2.5.2 Density test

The essence of density test is to determine the volume of the paint produced per batch by the manufacturer, as he/she combined paint's raw materials during formulation on a weight basis (Joseph, 2012). The relationship between these parameters is shown in equation 2.1

$$\text{Density} = \frac{mass}{volume} \quad \text{.....2.1}$$

2.5.3 pH test

Alkaline conditions can be very devastating to many paints. Therefore, it is important to measure the pH of the surface of applications before paint can be applied to such surface (Joseph, 2012). pH is a measure of the acidity or alkalinity of a substance. A pH of 7 indicates neutrality. pH readings decreasing from 7 indicate increasingly acidic conditions. Likewise, pH readings increasing up from 7 indicate increasingly alkaline conditions.However, most manufacturers would recommend that traditional paint products not be applied to surfaces having greater alkalinity.

2.5.4 Drying time

The process of drying involves severalphysical and/or chemical changes, such as solvent evaporation,oxidation, and polymerization, all of which aretime dependent (Uzoh*et al*., 2013). The various stages of drying that occurin organic films may be subjective, difficult to measurereproducibly, and are influenced by many factors such asfilm thickness, substrate, temperature, humidity, light, andair circulation (Joseph, 2012). Therefore, it is essential that most of thesevariables must be minimized in order to make drying timedeterminations more quantitative (Joseph, 2012;Uzoh*et al*., 2013).

2.5.4.1 ASTM test method of drying time

ASTM D1640, test method for drying,curing, or film formation of organic coatings at room temperatureis the most commonly used method to determinethe various stages and rates of film formation in thedrying of organic coatings normally used under conditionsof ambient room temperature (Joseph, 2012). The testing methods are highlighted as follow (Joseph, 2012):

- ✓ Set-To-Touch Time: The test film is lightly touched with the tip of a cleanfinger, and the fingertip is immediately placed againsta piece of clean, clear glass to determine when the filmdid not adhere to the finger or transfer to the glass.
- ✓ Dust-Free Time: This test is generally performed to determine when dustor cotton fibres lightly dropped on the test film canbe removed by blowing over the test film. Individualabsorbent cotton fibres are dropped from a height of 1in. (25 mm). The film is considered to be dust free whenthe cotton fibres can be lightly blown off the test film.
- ✓ Dry-Hard Time: The test film is considered dry-hard after maximumdownward thumb pressure (without twisting) appliedto the test film leaves no mark when the contacted areais lightly polished with a soft cloth.
- ✓ Dry-To-Recoat Time: The test film meets this requirement when a secondcoat can be applied without causing any film irregularities,e.g., lifting, wrinkling.
- ✓ Print-Free Time: The test film meets this requirement when imprintingfabric under a pressure of 1/2 or 1 lb/in.2 (3.5 or 7.0kPa) shows the coating to be print free. This procedureis similar to ASTM D2091, Test Method for Lacquers.

2.6 Physico-Mechanical Analysis

After paint application on car substrate; it is required to be subjected to several analysis on the substrate been applied (PAN, 2013). Some of these analysis includes: Film thickness test, gloss test, punch test, cross-scratch test, heat resistance, chemical resistance, colour stability and so on (Joseph, 2012; PAN, 2013). The essence of these analysis on car coated substrate are discussed in the next subsections.

2.6.1 Film thickness

One of the major requirements of paint and coating testingis the measurement and control of film thickness (Joseph, 2012). The measurement of film thickness provides the opportunity in the coating application process to check the coating thickness, this offers an assessment of the spreading rate of paints. It is very important that wet film measurements are made as soon as the coating is applied to avoid error due to solvent loss during the curing process (James *et al*., 2011; Joseph, 2012). The ASTM standard test method for coating film thickness is D1212 and it standard specification is 7.2±0.8 µm or 1.8±0.2 mil (ASTM, 2009). While Peugeot Auto mobile Nigeria standard specification is 7.5-15 µm (PAN, 2013).

2.6.2 Gloss (opacity) analysis

Gloss is defined in ASTM E284, as an angular selectivity of reflectance, involving surface-reflected light, responsible for the degree to which reflected highlights or images ofobjects may be seen as superimposed on a surface (ASTM, 2009).This test measures the reflectiveness of the paint on the coated substrate. Gloss measurement is dependent on therefractive index of the material and the curvature of the sample. Therefore, the visual assessment of gloss requiresa multi-dimensional description (ASTM, 2009; Dulux, 2011; Viktor, 2012). The ASTM standard test code method for this test is E284 and its standard specification is ≥85 for high gloss (ASTM, 2009; PAN, 2013).

2.6.3 Chemical resistance

The ability of a coating to resist chemicaldeterioration or staining is an essential element in itsevaluation (Joseph, 2012). This test provides a thorough method of determiningthe ability of a coating to resist discoloration from chemical reagents and other materials

common in today's environment. The tests generally expose the coating surface to a spot of the reagent on the coating surface or by immersion of a coated test panel in the reagent for a specified period with timed checkpoints (DuPont, 2010; Joseph, 2012).

2.6.4 Punch test

For a coating to meet its service requirements, it must exhibit appropriate properties of flexibility and toughness to withstand cracking when it is subjected to stresses produced by punching or deformation (James *et al*., 2011). Thus, for coating on substrate to satisfy this test, it must be able tobend or flexed with the substrate deformation effects without cracking or undergoing other failure (James *et al*., 2011). Generally, the bend, punch and impact tests used to evaluateflexibility and toughness are much more severe than actual service conditions. This is because the tests are usually performed on relatively fresh, un-aged coating films (DuPont, 2010; James *et al*., 2011; Joseph, 2012).

2.6.5 Cross-scratch test

Organic coatings are applied to a variety of substrate for decorative,protective, and functional applications (James *et al*., 2011). In each case, it is imperative that the coating adheres well to the substrate (James *et al*., 2011).

Cross-scratch test for auto base paint coating testtells the cohesive adhesion of the paint on coated surfaces when a scratch is incurred on it (Joseph, 2012). The ASTM "D5178″test method involves cleaning the coated substrate with cotton wool, cross-scratching it with multi-blade cutting tool and then covering the scratched region with adhesive tape (ASTM, 2009). The adhesive tape is then pulled off rapidly from the scratched surface for observation (ASTM, 2009). Ifno paint comes off with the adhesive

taped area, the coating is acceptable and graded A or B, but if the paint peel off with the adhesive tape topcoat, then the coating has failed the test, which will be graded as C or D (ASTM, 2009). The ASTM grading system are A and B for adherence of paint to the substrate without fall off and expose the metal while C and D are both classified as failed as the paint fall off after is similar to Pan auto mobile Nigeria (PAN, 2013) auto base standard paint grading system.

2.6.6 Colour stability

Colour is a significant factor in the appearance of an object and an important characteristic of any paint (Joseph, 2012). Appearance, of which colour is a part, is one quality of a product that every customer can judge for himself (Joseph, 2012). No matter how good the physical properties of a paint, if its colour does not meet the expectation of the customer, the finished product will be rated as unsatisfactory (Joseph, 2012). Thus, a high quality paint is expected to maintain its colour stability on substrate for ten (10) years under harsh environmental condition (PAN, 2013).

2.7 Modelling of Experimental Formulation

Mathematicalmodel of a process is done to control and maintain its optimal level, as well as to provide maximal yield of the product (Zivorad, 2004). Statistical methods in mathematical modelling of a process is efficient in the experimental formulations (Zivorad, 2004). The common statistical method for this is design of experiment (DOE). To design an experiment, the optimal experiment design to be used simultaneously for varying all the analysed factorsare selected (Tatsuyuki, 2004). By designing an experiment one gets more precise data and more complete information on a studied phenomenon with a minimal number of experiments and the lowest possible material costs (Tatsuyuki, 2004;Arunachalam and Annadurai, 2010). The development of

statistical methods for data analysis, combined with development of computers, has revolutionized the research and development work in all domains of human activities (Tatsuyuki, 2004;Zivorad, 2004). This technique is incorporated with response surface methodology for statistical analysis of the responses.

2.7.1 Response surface methodology (RSM)

Response surface methodology is an important subject in the statistical design of experiments that involves the collection of mathematical and statistical techniques useful for themodelling and analysis of problems in which response of interest is influenced by several variables whose objective is to optimize this response (Nuran, 2007;Evaristo*et al*., 2009). A simple example can be seen from the growth of plant which is affected by certain amount of water say $x_1$and sunshine x_2. The plant can therefore grow under any combination of x_1 and x_2 treatment (Nuran, 2007). Based on this, water and sunshine can be vary continuously. Thus, response surface methodology is useful for developing, improving and optimizing the response variable if treatments are from a continuous range of values (Montgomery, 2005; Nuran, 2007). If x_1 and x_2 are the independent variable in this case, lets y represents the response which depends on the independent variables. It can then be expressed that:

$$y = f(x_1, x_2) + e \quad \text{.....2.2}$$

Where *e* is the experimental error as *y* is a function of x_1 and x_2.

This statistical technique is capable of carrying out analysis of variance (ANOVA) by screening of factors present according to the significances of their effects on system responses (Sidhu *et al*., 2007), developing a model for responses to be studied, comparing the experimental and predicted data studied and optimized response if they are more than one (Montgomery, 2005;Andre and Siuli, 2010; Li*et al*., 2012).

2.7.1.1 Fitting of model analysis

The analysis of variance for the independent variables and responses can be represented graphically, normally refers to as parity plot that shows the relationship between predicted and experimental data generated (Yamin*et al*., 2013). A good model fitting can easily be identified from if the data points are well distributed close to a regression line (straight line), which suggested an excellent relationship between the experimental and predicted values of the response (Yamin*et al*., 2013). Typical illustration of such plot is shown in Figure 2.2

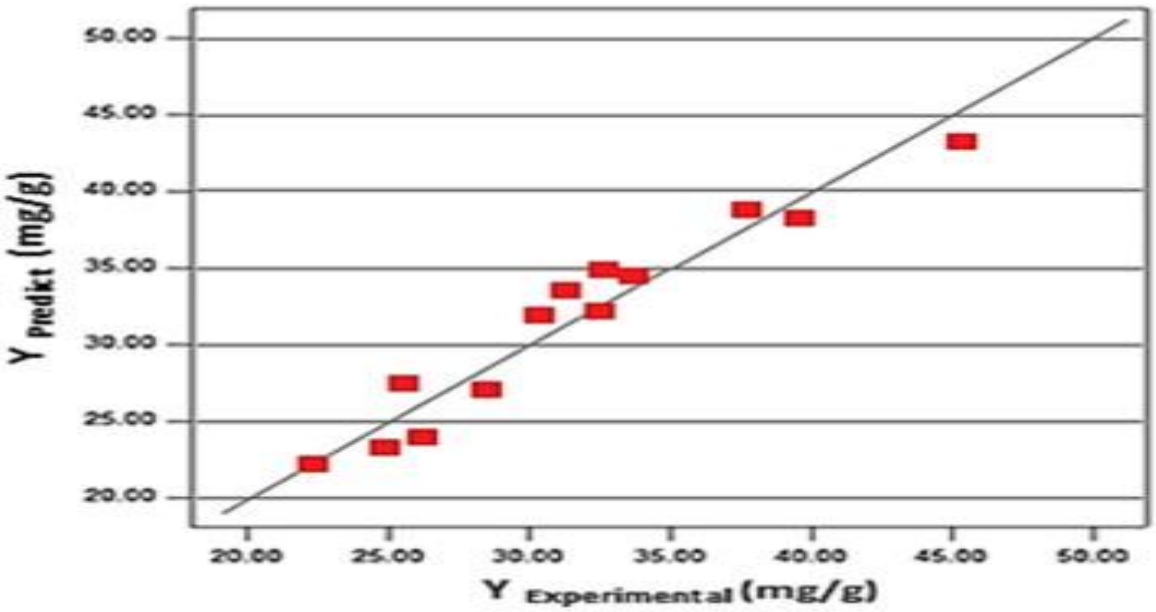


Figure 2.2: Parity plot of experimental and predicted values (Yamin*et al*., 2013)

3-D surface plot is another graphical way of showing the responses and other variable factors relationships in the process (Ali, 2013). Figure 2.3 depicted typical example of 3-D surface plot for dependent variable ‘y’ against pH and temperature of a process.

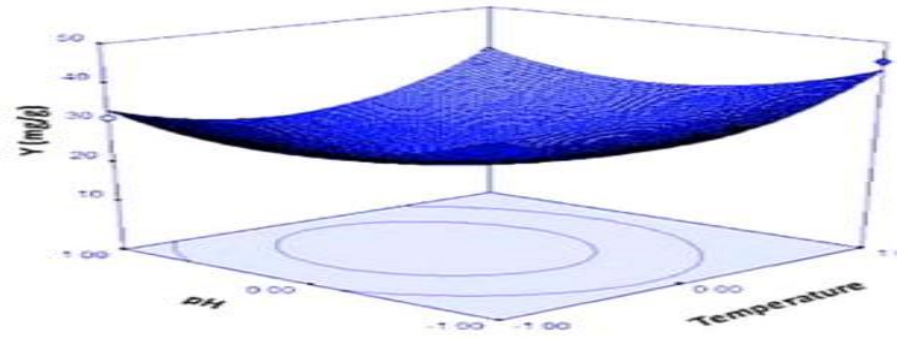


Figure 2.3: Three dimensional plot of temperature-pH against yield (Ali, 2013)

As the pH vary with temperature, it affects the response. The nature of the surface plot indicate if the model is significant or not. The elliptical nature of 3-D surface plot indicates its significance (Galadima*et al*., 2012;Ali, 2013;Xinyue*et al*., 2014).

2.8 Self-Healing Coating Polymers

Polymers and polymer composites have beenwidely used in tremendous engineering fields because of their advantages which include light weight, good processibility, chemical stability in any atmospheric conditions and so on (Robert, 2000;Yuan *et al*., 2008). However, long-term durability and reliability of polymeric materials are still problematic when they serve for structural application (Carneiro*et al*., 2012). Thus, frequent exposure to harsh environment would easily lead to degradations of polymeric components (Carneiro*et al*., 2012). Comparatively, micro-cracking is one of the fatal deteriorations generated in service, which would bring about catastrophic failure of the materials and hence significantly shorten lifetimes of the structures (Carneiro*et al*., 2012 and Chao *et al*., 2013).Since the damages deep inside materials are difficult to be perceived and to repair in particular, thematerials had better to have the ability of self-healing (Yuan *et al*., 2008).

It has been established biologically that, the natural healing in living bodies depends on rapid transportation of repair substance to the injured part and reconstruction of the tissues (Nathalic*et al*., 2011). Having been inspired by these findings, continuous efforts are now being made to mimic natural materials and to integrate self-healing capability into polymers and polymer composites (Yuan *et al*., 2008; Nathalic*et al*., 2011). The progress has opened an era of new intelligent materials. On the whole, researches in this field are still at itsinfancy (Soo*et al*., 2008; Christopher *et al*., 2012). Thus, more scientists and companies are interested in different aspects of the topic. Innovative measures and new knowledge of the related mechanisms are constantly emerging (Soo*et al*., 2008). Therefore, it might be the right time to review the attempts carried out so far in different laboratories in the world. According to the ways of healing, self-healing polymers and polymer composites can be classified into two categories: The intrinsic ones that are able to heal cracks by the polymers themselves and theextrinsic type in which healing agent has to be pre-embedded (Yuan *et al*., 2008).

2.8.1 Benefit of self-healing coatings

Generally, polymer composite structures are prone to delaminationcracking caused by impact, through-thickness loads, edge stresses, environmental degradation and other damaging events (Cliff, 2009;Kousourakis and Mouritz, 2010). Delamination cracks between the ply layers can severely reduce the structural properties of composite materials, such as reduced compression strength and fatigue life (Soo*et al*., 2008).Various techniques have been developed to suppress the initiation and/or growth of delamination cracks in composite panels and bonded joints, including toughened resin systems, thermoplastic interleaving, and through-thickness reinforcement by three-dimensional weaving, stitching or pinning (Dong *et al*., 2008). While these techniques

are effective at resisting delamination cracking, any damage growth must remain unrepaired until the component is taken out-of-service (Kousourakis and Mouritz, 2010).

A solution to delamination damage is the autonomic repair process of self-healing (David, 2009), which is achieved by dispersing small vessels containing a low viscosity healing fluid and catalyst within the polymer matrix (Kousourakis and Mouritz, 2010). Self-healing basically works by the growing delamination rupturing the vessels and thereby releasing liquid healing agent into the crack. The healing agent is polymerized inside the crack by reacting with the ultraviolet (UV) light form the sun to trigger the healing process (Yuan *et al*., 2008).

2.8.1.1 Intrinsic self-healing

These materials contain chemical bonds that have the ability to reformafter having sustained damage (Yuan *et al*., 2008). This reformation can be triggered by an external stimulus such as heat, light, and oxygen (Yuan *et al*., 2008; Jonathan, 2009) and a division of these materials will be made basedon the healing mechanism used. First the systems based on molecular diffusion will be addressed, followed by the largest group of materials, making use of reversible bonds in the crosslinking of the matrix.

Intrinsic self-healing polymer composites are based on specific performance of the polymers and polymeric matrices that enables crack healing under certain stimulation (mostly heating) (Yuan *et al*., 2008). Autonomic healing without external intervention is not available in these materials for the time being. As viewed from the predominant

molecular mechanisms involved in the healingprocesses (Yuan *et al*., 2008), this is consist of two modes: (i) physical interactions, and (ii) chemical interactions.

2.8.1.1.1 Self-healing based on physical interactions

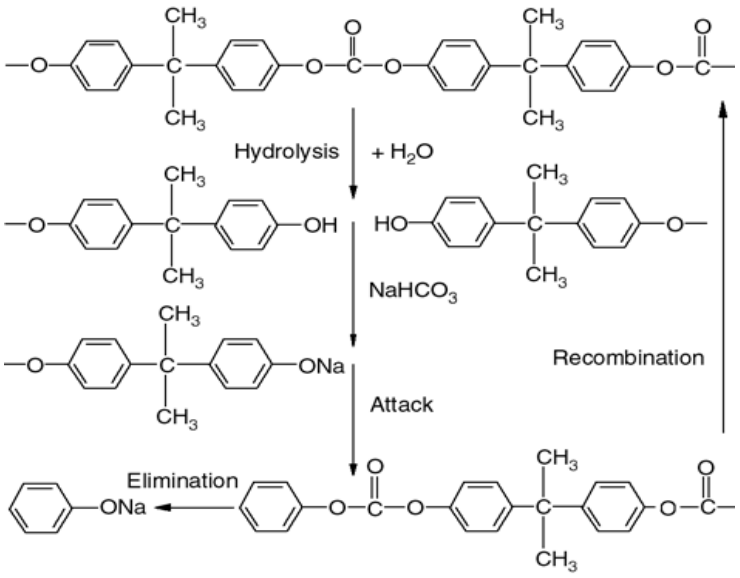
The theory involved in self-healing process was studied by 'Wool and O'Connor' (Kousourakis and Mouritz, 2010), where it was established that, healing process goes through five phases. These are: (i) surface rearrangement, which affects initial diffusion function and topological feature; (ii) surface approach, related to healing patterns; (iii) wetting, (iv) diffusion, the main factor that controls recovery of mechanical properties, and (v) randomization, ensuring disappearanceof cracking interface.

2.8.1.1.2 Self-healing based on chemical interactions

Cracks and strength decay might be caused by structural changes of atoms or molecules, likechain scission (Yuan *et al*., 2008; Stijin*et al*., 2009). Therefore, inverse reaction, i.e.recombination of the broken molecules, should be one of the repairing strategies (Yuan *et al*., 2008;Soo*et al*, 2009). Such method does not focus on cracks healing but on 'nanoscopic' deterioration (Yuan *et al*., 2008). One example is polycarbonate (PC) synthesized by ester exchange method. The PCs were treated in a steam pressure cabin at 120°C prior to the repair (Yuan *et al*., 2008). As a result, molecular weight of the PCs dropped by about 88 to 90% as reported from the work (Yuan *et al*., 2008).

After drying them in a vacuum cabin, the repairing treatment was done in an oven at 130°C with N_2atmosphere under reduced pressure (Yuan *et al*., 2008). The reduced tensile strength due to the deterioration treatment can thus be gradually recovered (Yun *et al*., 2008). The repairing mechanism was considered as the following procedures.

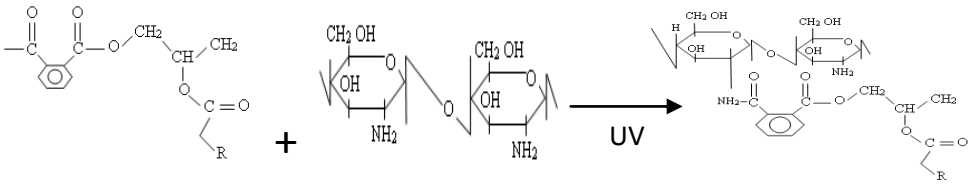
Firstly, the carbonate bond was cut by hydrolysis, and then the concentration of the phenoxyend increased after deterioration. The (–OH)end-group on the chain was substituted by sodium ion. The (–ONa) end might attack a carbonate bond at the end of one of the other chains, leading to recombination of these two chains with the elimination of the phenol from PC Equation 2.3. The repairing reaction was accelerated by weak alkaline, such as sodium carbonate. It suggested that two conditions are required for the PC to re-combine the polymer chains. One is the chemical structure of the chain end and the other is the catalyst (Na_2CO_3) for acceleration of the reaction (Yun *et al*., 2008). The process is showed in Equation 2.3.



…… 2.3

Yuan *et al*., 2008

Equation 2.4 also depicted typical cross-linking reaction between alkyd resin and chitosan.



…..….2.4

Alkyd resin or binder Chitosan Paint polymer

Equation 2.4 shows the cross-linking reaction of chitosan with alkyd resin paint structure into self-healing paint composite. The monoglyceride structure of alkyd constituting CH_2 (methylene group) and CH (methyne group) combined with chitosan containing OH group and NH_2 that is responsible for self-healing process during the cross-linking reaction.

2.8.2 Extrinsic self-healing

In the case of extrinsic self-healing, the matrix resin itself is not a healable one. Healing agent has to be encapsulated and embedded into the materials in advance (Tim *et al*., 2011). As soon as the cracks destroy the fragile capsules, the healing agent would be released into the crack planes due to capillary effect and heals the cracks (Yuan *et al*., 2008; Tim *et al*., 2011). In accordance with types of the containers, there are two modes of the repair activity: (i) self-healing in terms of healant loaded pipelines, and (ii) self-healing in terms of healant loaded microcapsules. Taking the advantages of crack triggered delivery of healing agent, manual intervention(e.g. heating that used to be applied for intrinsic self-healing) might be no longer necessary.

CHAPTER THREE

3.0 MATERIALS AND METHOD

This chapter entails the materials, instrumentations/equipment and detailed methodology of this work.

3.1 Materials and Equipment

The list of materials and equipment used in this work, where they were obtained and models are listed in Table 3.1 and 3.2 respectively.

Table 3.1: List of materials and their source used in this work

Materials	Sources
Alkyd resin, pigments and drier	Shekina paint, Kaduna
Mineral spirit (white spirit), nose mask	Hadis Chemical store, Zaria
Electric hand spraying gun	PAN, Kaduna

Car panels	PAN, Kaduna
Methyl ethyl ketoxime (MEKO)	Shekina paint, Kaduna
Chitosan	Green world, Zaria branch
Density bottle	Chem. Engn. A.B.U, Zaria
Measuring cylinder, nose mask	Hadis Chemical store, Zaria
Demineralize water	PAN, Kaduna
Acetone, adhesive tape, brush	PAN, Kaduna

Table 3.2: List of equipment used

EQUIPMENT	MODEL	MANUFACTURER
Heavy duty mixer	L2R 3577	Silverson Ltd, England
Digital weighing balance	AV-264 Adventurer pro	OHAUS, U.S.A
Viscometer	Synchro-Lectric-RVT-43329	Brookfield engineering inc
Gloss machine	Micro-Tri-gloss (kat.Nr 4430)	Qualitest, Germany
Thickness guage	Dualscope 259	FISCHEL,

		Germany
Multi-blade cutting tool	Scotch 2525,	Scotch, Germany
ERICHEN Punching machine	3mm-D-5870. (Fabr.Nr.96)	ERICHEN Hemer-sundwig, Germany
Oven	SR2000 thermosi	ZOETERMER, Holland

3.2 Methodology

This sub-section contains the detailed experiment that was done in this work.

3.2.1 Source of raw materials

Medium oil alkyd resin, iron (ii) oxide (pigment), titanium (iv) oxide, and additives were obtained from Shekina paint shop, Kaduna. The solvent (Mineral spirit) used was purchased from Hadis chemical store, Zaria.

3.2.2 Experimental design

Central composite design (CCD) employed resulting in a total number of 20 experiments using the design expert 6.0.6 version to optimize the chosen key factors namely: Binder (A), solvent (B) and pigment (C), in relation to drying and coverage time response studied. These variables at two levels, low and high: A (10g – 160g), B (10g – 70g) and C (10g – 30g) were selected and inputted respectively on the design of

experiment interface tool as depicted in Table A_3Appendix Afor experimental optimization. Table 3.3 shows the summary of the specifications.

Table 3.3: Design of experiment status

Factors	Name	Units	Low Actual	High Actual	Low Coded	High Coded
A	Binder	G	10	160	-1	1
B	Solvent	G	10	70	-1	1
C	Pigment	G	10	30	-1	1

The tool came out with 20-runs of experiment based on the parameters specified and number of responses to be studied as showed in Table 3.4

Table 3.4: Design of experiment data

Runs	A	B	C	Drying Time (mins)	Coverage (m^2)
1	160.00	70.00	30.00	-	-
2	10.00	10.00	10.00	-	-
3	85.00	40.00	20.00	-	-
4	10.00	10.00	30.00	-	-
5	10.00	70.00	30.00	-	-
6	41.13	40.00	20.00	-	-
7	160.00	70.00	10.00	-	-
8	85.00	40.00	3.18	-	-
9	160.00	10.00	30.00	-	-

10	85.00	40.00	20.00	-	-
11	85.00	40.00	20.00	-	-
12	85.00	40.00	36.82	-	-
13	160.00	10.00	10.00	-	-
14	10.00	70.00	10.00	-	-
15	85.00	40.00	20.00	-	-
16	85.00	40.00	20.00	-	-
17	85.00	10.45	20.00	-	-
18	85.00	40.00	20.00	-	-
19	85.00	90.45	20.00	-	-
20	211.13	40	20.00	-	-

3.2.3 Paint formulation procedure

The major paint components varied as shown in Table 3.4 from experimental design were binder, solvent and pigment while the additives such as anti-settling agent, anti-skinning agent, dryer and preservative were kept constant during the formulation.

In run one, 70g (90 ml) of mineral spirit was measured and transferred to the mixing unit while the mixer was powered on for stirring the raw materials coming in. This was followed by addition of anti-settling agent into the mixing unit to ensure that other solid components coming into the mixing unit were kept in suspension for proper and uniform mixing without settling down. As the mixing was continued, 30g of pigments (70% of red (ii) oxide and 30% of titanium (iv) oxide) were added and mixed until a consistence product without lumps was achieved, after which the solution was binded with 160g of medium oil alkyd resin as the mixing continued. This was followed by addition of cobalt dryer to enhance quick drying process after application.Anti-skinning

agent and preservative were then added to prevent the paint from sticking to its container and prevent it from microorganisms attack. Each additive added was 1.5% of the total formulation as specified (Ali, 2005). The paint product obtained was filtered to remove undissolved pigment. This procedure was repeated for the other 19 runs as scheduled in Table 3.4.

3.2.4 Paint viscosity measurement

20 ml of the paint product was measured out into 50 ml beaker while Brookfield RVT-43329 viscometer was powered on. After the machine stabilized, the paint sample measured was taken closed to the spindle of the machine until it touched its tip. The spindle was allowed to rotate at 360^0on the paint product according to ASTM testing standard, and the displayed viscosity value at that point was recorded for run 1. This procedure was repeated for other 19-runs of experiment, while their respective viscosity values were taken and recorded.

3.2.5 Density test

This test was carried out by weighing an empty density bottle of 50 ml capacity, the weight was assigned W_1. The empty density bottle was now filled with run-1 paint product and then weighed which was labelled as W_2. The density bottle capacity used was 50 ml, which was represented as V. Thus, the density of run-1 paint product was determined by ASTM D16.

$$\text{Density} = \frac{W_2 - W_1}{V} \quad \text{.....3.1}$$

Where: W_1 = weight of empty density bottle, W_2 = weight of empty bottle + weight of paint product and V = Density bottle capacity = 50 ml.

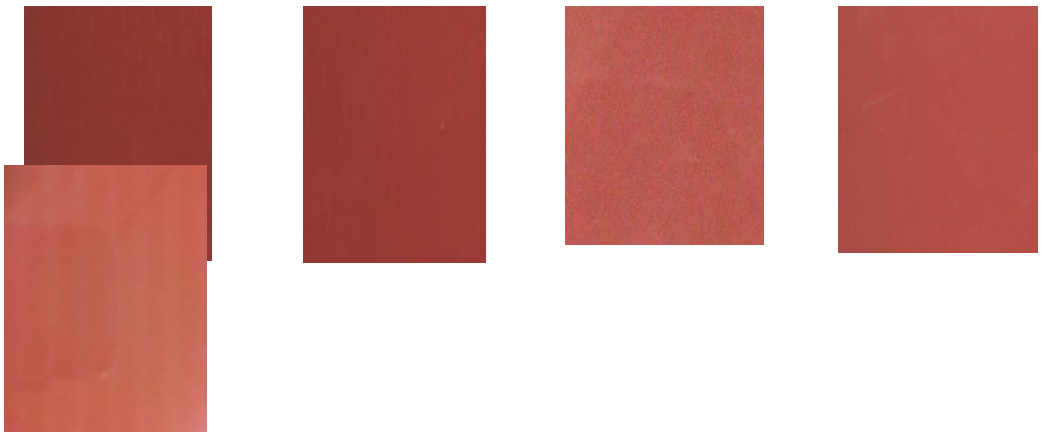
This method was repeated for the other 19-runs of the paint produced.

3.2.6 pH measurement

The pH value of each run of the formulated was determined by immersing pH spindle from buffer solution into the paint sample, where the reading was allowed to stabilised and then recorded against each run.

3.2.7 Preparation of plates for spray

The stainless steel plates sprayed for physic-mechanical test were de-scaled at 60^0C (PAN, 2013). This was followed by sanding with a smooth sand paper after which the surfaces were cleaned with cotton wool. The clean surface was then coated with cater, body-white and primer respectively. These were allowed to dry under normal air drying and smoothen again with sand paper, which were left for 24-hours before top coat was added. Plates 1 represent the coated substrates.



Plates 1: Coated panels with the formulated paints

3.2.8 Drying time and coverage responses determination

These were determined by measuring 2 ml each of 20-runs of paint products and sprayed on substrates to test for drying time and coverage in each case. The drying time was determined using ASTM D1640 (set-to-touch time) testing method, while the

coverage was determined using ASTM D4214 testing method.The area covered in square meter and the dying time in minute were determined for each run. Analysis of variance was conducted for the obtained data.

3.2.9 Analysis of the applied paints on substrates

Based on the result of control test such as viscosity and density obtained from the 20-runs of experiment, run 1, 3, 7, 8 and 13 products were selected due to their outstanding performance as compared with standard specifications, for further physico-mechanical analysis which include: gloss test, punch test, cross-scratch test, film thickness, chemical resistance test, heat resistance test and colour stability tests were conducted. All these analysis were done by adopting ASTM, 2009 and PAN, 2013 standards testing methods.

3.2.10 Spraying of the substrates

The substrates labelled run: 1, 3, 7, 8 and 13, after undergoing cater, white body and priming process; were treated by descaling, sanding with smooth sand paper and cleaned with clean dry cotton wool. These were then sprayed with the paint samples 1, 3, 7, 8 and 13 as top coat respectively which were allowed to dry at room temperature and then kept for 24-hours before subjected to the analysis listed in Subsection 3.2.9. After which physico-mechical test were conducted for the formulated paints.

3.2.10.1 Gloss test

This test was conducted by contacting the sensitive digital gloss meter at an angle of 60^0 with the coated substrate surface for four different points, while gloss values at each point were taken and recorded. The average value from the four different readings from

the coated substrate surface gave the actual gloss value for run 1. The procedures were repeated for runs: 3, 7, 8 and 13 whose gloss values were tabulated and compared with ASTM and PAN standard specifications in Table 4.2

3.2.10.2 Film thickness test

The film thickness of the top coat for run-1 was determined by measuring the cater, the white body, the primer and the top coat with the aid of Dualscope-259 thickness gauge. This was performed three times randomly on the coated substrate to obtain the average film thickness value. The difference between top coat film thickness and that of primer gives the film thickness value of run-1. This was also repeated for runs: 3, 7, 8 and 13 respectively and the results obtained were recorded and compared with ASTM and PAN standard specifications in Table 4.3

3.2.10.3 Cross-scratch test

Run-1 coated substrate was cleaned with cotton wool wetted with thinner, this was allowed to dry and then cross-scratched with a multi-blade cutting tool which was then covered with an adhesive tape. The adhesive tape was then forcefully pulled out of the scratched area and examined whether the coated paint peeled off along with it (i.e., if there was a paint stain in the adhesive tape). This procedure was repeated for runs: 3, 7, 8 and 13. The result of this test was used to classify the paint using ASTM and PAN standard auto base specifications.

3.2.10.4 Punch test

Erichen punching machine with 3mm deep maximum punch was used in this test. The first sample (coated run-1) was placed under the punch, it was then subjected to punch

test by raising the anvil and dropping on the coated substrate at first for 1mm deep deformation. The sample was removed from the punching machine and viewed with low powered magnification for any damage. As no damage to the substrate was established, it was then placed back into the punching machine and increased the punch deformation test to 2mm and subsequently 3mm respectively. The sample was removed in each case to check for damage with the aid of low powered magnification, it was checked to establish pass/fail specifications in accordance with ASTM D2794 test method. These procedures were repeated with runs: 3, 7, 8 and 13 respectively.

3.2.10.5 Chemical resistance test

A mixture of acetone, demineralized water and alcohol (isopropyl) were dropped randomly on the substrates labelled run 1, 3, 7, 8 and 13 and kept at room temperature for 24-hours according to ASTM D1308 test method. The samples were then examined to ascertain whether there were stains that can result to corrosion or reducing the life span of the coated substrates. Thus, based on the observation and the results obtained, they were rated and compared with ASTM and PAN standard specifications.

3.2.10.6 Heat resistance test

The coated plates labelled as run: 1, 3, 7, 8 and 13 were immersed into a container with solution of acetic acid, ethanol and demineralized water. This was heated in an oven at temperature of 180^0C for three days. The samples were removed from the solution and allowed to cool after which they were examined for the heat effects/colour stability. ASTM D2485 standard test method/specification was used to grade the samples. This procedure was repeated until instability was observed on the samples. It took 10 days to

observe instability on the samples. The test was used to establish the paint life span based on PAN standard.

3.3 Self-Healing Car Paint Formulation

The selected optimized paint formulation out of ten solutions obtained from response surface methodology as it combines drying time and coverage responses optimum values was used to formulate self-healing paint. The optimized formulation contains 160g of binder (short oil alkyd resin), 38.30g of solvent (mineral spirit) and 10g of pigment (iron (ii) oxide and titanium (iv) oxide). This was mixed together in a mixer with 1.5% each of anti-settling agent, anti-skinning agent, dryer and preservative of the total formulation. Five different paints of different chitosan content were formulated. The chitosan concentrations used were, 0.00% (which forms control paint), 0.5%, 1.0%, 1.5% and 2.0% respectively.

3.3.1 Investigation of self-healing property of the paint on coated substrates

Five 2mm by 2mm panels labelled 0.0%, 0.5%, 1.0%, 1.5% and 2.0% chitosan concentration were sprayed with the chitosan incorporated paint. These were allowed to dry, scratched with thin pin, and inserted inside a scanning electron microscope (SEM) machine to take their respective micrograph, which shows the extent of damages to the substrates. These were then exposed to ultra violet (UV) light from the sun for 60 minutes in each case and then taken back to the SEM machine to observe the extent of repair.

3.3.2 Fourier transform infrared analysis

1geach of the raw chitosan used, formulated paint without chitosan and self-healing formulated paint (i.e. the formulated paint with chitosan) were measured in each case and introduced into a cell of 10 cm length. These were transferred into potassium bromide disc, which then charged into FTIR spectrophotometer for spectral analysis of all the functional groups present in each sample charged into the machine.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This Chapter presents the results of various analyses done on the auto base paint produced and its related characterization on the substrates.

4.1 Effect of Component Proportioning on Viscosity of Formulated Paint

Table 4.1 depicted the auto base formulated paint's viscosity, density and pH values for each run.

The viscosity of paint is one of the quality control test that is required as part of product delivery specification. Thus, the viscosity for 20-runs of experiments with varied formulations were tested and presented in Table 4.1.

According to PAN (2013) auto base standard specification, the delivery viscosity of an auto base paint is expected to be (30±05) cp, (PAN, 2013). As presented in Table 4.1, runs 1, 3, 7, 8 and 13 fell within the range, which is an indication that the viscosity of the runs were balance (neither too thick nor too thin). The five runs fell in semi-viscous ranges which can easily be adjusted by car manufacturers to suit their ranges of applications so as to maintain a right applicable viscosity. Based on these, runs 1, 3, 7, 8 and 13 were selected from the experimental formulated paint for further car substrates application and analyses.

Table 4.1: Density, Viscosity and pH results of the formulated auto base paint

Run	Density (g/cm^3)	Viscosity (cp)	pH
1	0.956	25.7	6.8
2	1.111	2.53	6.6
3	0.977	28.20	6.9
4	1.147	1.73	6.9
5	1.056	16.37	6.8
6	1.007	3.44	6.7
7	0.875	29.61	6.8

8	0.896	31.22	6.9
9	1.18	1.30	6.6
10	1.085	14.90	6.8
11	1.086	41.60	6.7
12	1.018	97.80	6.9
13	0.944	34.0	6.9
14	1.222	24.92	6.7
15	1.085	15.92	6.8
16	1.023	6.22	6.7
17	1.056	19.00	6.9
18	1.046	23.50	6.6
19	1.044	20.10	6.9
20	1.042	17.68	6.8

Auto base standard viscosity specification = 30±5 Cp (PAN paint data sheet, 2013

4.2 Effect of Component Proportioning on Density of Formulated Paint

Table 4.1 presents the densities of the formulated paints. The density of each run was determined using Equation 2.1 from the raw data showed in Table $A_1$of appendix A.

The significance of paint volume-weight relationship is that, low density favours large volume production, which is a positive gain for the manufacturers/formulators. Thus, as it can be seen from the Table 4.1, run 7 has the lowest density, followed by run 8, 13, 1 and then 3 as compared to other runs.

4.3 Effect of Component Proportioning on pH of Formulated Paint

The pH values of the formulated paints as tabulated in Table 4.1 fall within 6.6 to 6.9, which are slightly acidic for all the 20-runs. Though, there is no reported literature on pH specification of car paint (which is an oil base paint) unlike water base paint where its pH value is expected to range between 8.5 and9.0 (Oragwu, 2013) due to alkaline nature of substrates where it is normally applied. However, the pre-treatment process (such as cata, primer and e-coat) on car substrate before top coat prevent corrosion on the substrate

4.4 Physico-Mechanical Analysis

Generally, physico-chemical analysis of formulated paint is not enough to ascertain a high quality of the product until it undergoes physico-mechanical test after being applied to a substrate (most especially, car panels) (PAN, 2013).

Thus, run 1, 3, 7, 8 and 13 were selected for punch test, cross-scratch test, gloss test, film thickness test, chemical resistance test, heat resistance test and colour stability test based on their physico-chemical performance. The results of the physico-mechanical test done on the formulated paint coated on substrates were presented in the next sub-sections.

4.4.1 Gloss (opacity) test

The recommended standard gloss value for auto base paint is ≥85 (ASTM, 2009 and PAN, 2013). Table 4.2 shows the gloss values of formulated coated substrates, labelled as run 1, 3, 7, 8 and 13 with their respective grades. The results obtained were compared with ASTM, (2009) and PAN, (2013)auto base standard specifications shown in Table B_1 and B_2 of Appendix B respectively.

Table 4.2: Gloss (opacity) of the formulated paint

RUNS	GLOSS VALUE	REMARKS
1	80.35	Semi-gloss
3	82.50	Semi-gloss
7	76.40	Semi-gloss
8	88.40	High-gloss (Accepted)
13	74.30	Semi-gloss
ASTM standard	85-95	High-gloss
PAN standard	≥85	Glossy finish

As shown in Table 4.2, run 1, 3, 7 and 13 had gloss value of 80.35, 82.50, 76.40 and 74.30 respectively, which are in the range of semi-gloss finishes while run 8 is in the range of high gloss finish recommended for auto base paint. Therefore, run 8 had the best gloss value as compared to others which also met the standard specification of auto base paint specified in PAN, (2013) auto base data standard specification sheet and ASTM, (2009) paint and related coating standard specifications.

4.4.2 Film thickness test

Film thickness is one of the physico-mechanical properties that play an important role in auto base paint product quality, which is a function of cost (Joseph, 2012). This is because, for instance spraying a 5ml to cover $4m^2$ square area in 1-coat is of cost effective, less energy utilization and better quality than spraying 10-ml of paint for the same square area in 2-coats. Table 4.3 shows the results of film thickness in

micrometres for run 1, 3, 7, 8 and 13 as compared with ASTM and PAN standard specifications shown in Table B_1 and B_2 of Appendix respectively.

Table 4.3: Film thickness test result of the formulated paint

Runs	Number of coat	Film thickness (µm)
1	2	35
3	2	40.4
7	2	29.6
8	2	7.5
13	2	43.9
ASTM standard	2	7.2±0.8µm (1.8±0.2mil)
PAN standard	2	7.5-15µm

As depicted in Table 4.3, only run 8 among others tested for this analysis agrees with the standard specifications. It gave a better performance in terms of film thickness. The summary results of the tested panels are shown in Table B_4 of Appendix B, where the average film thickness values were tabulated in Table 4.3.

4.4.3 Cross-scratch test

The ASTM grading system for adherence of paint to the substrate without fall off are A and B while C and D are both signified failed if the paint fall off from coated substrate after scratched. Table 4.4 showed the results obtained when run: 1, 3, 7,8 and 13 were subjected to cross-scratch test. As shown in the table, run 7 and 8 were graded B and A respectively as they are able to withstand the test which are acceptable according to

ASTM standard paint and coating standard specification. This signifies that, the paint coated on the substrates did not fell off by hard cross scratch test incurred on them. On the other hand, run 1, 3 and 13 coated paints failed to adhere to their respective substrates as they could not resist or withstand the cross-hatch test impact. Therefore, they were graded D, C and D respectively which are not acceptable for quality auto base paint.

Table 4.4: Cross-scratch test of the formulated paint

Runs	Remarks	Grade
1	Failed	D
3	Failed	C
7	Acceptable	B
8	Acceptable	A
13	Failed	D
ASTM specifications	Accepted Failed	1 & 2 3 & 4
PAN standard	Accepted Failed	A & B C & D

4.4.4 Punch test

Table 4.5 shows the result of the punch test on substrates coated with run 1, 3, 7, 8 and 13 auto base paint formulated.

Table 4.5: Punch test analysis of the formulated paint

Runs	Response	Grade	Remarks
1	Cracked	C	Failed
3	Cracked	D	Failed
7		B	Accepted
8	Did not crack	A	Accepted
13	Crack	C	Failed
ASTM	If there is no crack If cracked	1 and 2 3 and 4	
PAN	 If there is no crack If cracked	A and B C and D	

The results summarized in Table 4.5 shows that run 1, 3 and 13 failed to withstand punch test on the substrates which results to cracking of their respective coated panels. The panels were therefore, graded as C, D and C respectively according to PAN (2013) auto base paint technical data sheet. The grade C and D corresponds to ASTM grade ’3 and 4’, which is considered not good and unacceptable for auto base paint standard specification. Grade B and A were assigned to run 7 and 8 respectively because they resist cracks upon the 3mm deep punch test incurred on them. These grades (B and A) are equivalent to ASTM grade 2 and 1 which are classified as both accepted and recommended for quality auto base paint. However, grade ‘A’ (grade 1) is still better off than grade B (grade 2) in the sense that, it can still withstand further punch effect beyond 3mm deep or heat effect test at such state or condition, unlike run 7 that was assigned grade ‘B’, which mean that it was able to the test condition but may not be able to resist crack on undergoing further heat dependent test such as heat resistance

test. Therefore, based on these, it can be concluded that, though run 7 and 8 passed fit for this test but run 8 has the optimum property based on its grade.

4.4.5 Chemical resistance test

Table 4.6 depicted the chemical resistance analysis done on the selected runs coated on substrates.

Table 4.6: Chemical resistance analysis of the formulated paint on substrates

RUN	RESPONSE	REMARKS
1	0	Accepted
3	0	Accepted
7	0	Accepted
8	0	Accepted
13	0	Accepted

It was discovered after observation with watch glass, the morphology of the substrates tested for chemical resistance test did not change, i.e., they all remained unaffected by themixture of acetone, demineralized water and isopropyl drops on them. Therefore, based on their resilience to the treatment, they were graded zero (0) according to "PAN" laboratory technical data sheet grading system as no stains were recorded on the tested substrates. This result was compared with the ASTM and PAN auto base standard specifications as shown in Table B_1 and B_2 of Appendix B respectively.

4.4.6 Heat resistance/colour stability test

Table 4.7 shows the heat resistance test results on the coated substrates of run 1, 3, 7, 8 and 13 formulated paint with their respective responses.

Table 4.7: Heat resistance analysis of the formulated paint

1-3 DAYS DURATION OBSERVATION		
RUN	RESPONSE	COLOUR STABILITY
1	A	Stable
3	A	Stable
7	A	Stable
8	A	Stable
13	A	Stable
3-7 DAYS DURATION OBSERVATION		
1	A	Stable
3	A	Stable
7	A	Stable
8	A	Stable
13	A	Stable
7-10 DAYS DURATION OBSERVATION		
1	C	Not stable
3	C	Not stable
7	B	Fair
8	B	Fair
13	B	Fair

The grading system of "Peugeot Automobile Nigeria (PAN)"limited which is similar to that of ASTM D2485 standard specifications was adopted in this test as the analysis was carried out in PAN industrial laboratory, Kaduna.

As shown in Table 4.7, run 1, 3, 7, 8 and 13 coated substrates were graded “A” as all the substrates were not affected by the heat incurred on them inside a combined solution of acetone, isopropyl and demineralized water at a temperature of 180^0Cin an oven for the first three days. The colourof all the substrates also remains unchangedafter being subjected to these conditions. As the observation using watch glass under the same test conditions continues for another 4-7 days, the colour of all the substrates still remain stable and they were also graded “A” since the coated substrates were able to withstand the heat resistance conditions they were subjected to. As the testing period was increased from 7-10 days, run 1 and 3 were graded “C” as they were no longer able to withstand the heat resistance test. Thus, at this point, their colours were no more stable. But, run 7, 8 and 13 were graded “B” as the coated colours gradually faded uniformly. However, the grading system still showed that grade “B” assigned for run 7, 8 and 13 is “Ok” according to “PAN” paint data sheet, 2013 showed in TableB_2in Appendix B.

Plate I and II show the coated substrates by run 1, 3, 7, 8 and 13 formulated paint before and after subjected to series of analysis respectively.



Run 1 Run 3 Run 7 Run 8 Run 13

Plate II: Coated panels after subjected for film thickness test, gloss test, cross scratch test, punch test, chemical resistance test and heat resistance test.

4.5 Drying Time and Coverage Responses

Drying time and coverage were the two responses studied from three variable factorsvaried at two levels (i.e. low and high) as showed in the results (Table $A_3$of Appendix A). Table A_2 in Appendix A also show the raw data obtained for drying time and coverage for each run as 2-ml of paint produced were applied to substrates in each case. Table 4.8 shows the responses studied as a function of the varied parameters

Table 4.8: Drying time and coverage responses analysis of the formulated auto base paint

Run	A	B	C	Drying Time (mins)	Coverage (m^2)
1	160.00	70.00	30.00	62	1.1
2	10.00	10.00	10.00	67	1.1
3	85.00	40.00	20.00	64	0.7

4	10.00	10.00	30.00	48	0.1
5	10.00	70.00	30.00	50	0.2
6	41.13	40.00	20.00	53	0.2
7	160.00	70.00	10.00	42	1.3
8	85.00	40.00	3.18	37	1.5
9	160.00	10.00	30.00	96	0.4
10	85.00	40.00	20.00	67	0.6
11	85.00	40.00	20.00	69	0.6
12	85.00	40.00	36.82	72	0.4
13	160.00	10.00	10.00	45	1.4
14	10.00	70.00	10.00	68	0.1
15	85.00	40.00	20.00	60	0.5
16	85.00	40.00	20.00	60	0.6
17	85.00	10.45	20.00	71	0.4
18	85.00	40.00	20.00	63	0.4
19	85.00	90.45	20.00	73	0.4
20	211.13	40	20.00	66	0.7

Where: A, B and C are the variable factors while drying time and coverage are the two responses studied. Where A = binder, B = Solvent and C = Pigment.

The drying time and coverage responses were obtained using ASTM D1640 and D4417 standard specification methods respectively. As presented in Table 4.8, run 8 has the lowest and best drying time and coverage respectively among others. This may be attributed to the right combination of paint raw materials during the formulation process which is attributed to the significance nature of design of experiment. The optimum drying time obtained in this study was 37 minutes for run 8 which is lower than the

ASTM standard specifications. This showed that the drying is one of the good application property in this work.

4.6 Drying Time and Coverage Mathematical Models

Response surface methodology is a collection of mathematical and statistical techniques for developing, analysing, improving and optimizing processes (Montagometry, 2011). Equations 4.1 and 4.2 are the mathematical modelsin terms of actual factors developed for drying time and coverage responses respectively using the Response Surface Methodology (RSM).

$$\text{Drying Time} = \begin{pmatrix} 50.77621 - 0.18154(B) + 0.13748(S) + 1.10501(P) - 3.32412E \\ -003(B)^2 + 2.83289E - 003(P)^2 - 0.0363761(P)^2 - 2.22222E \\ -003(B)(S) + 0.018000(B)(P) - 0.012500(S)(P) \end{pmatrix} \quad \text{.....4.1}$$

$$Coverage = \begin{pmatrix} 1.68667 + 1.13239E - 033(B) - 0.012974(S) - 0.065304(P) \\ -4.48614E - 006(B)^2 - 4.01470E - 005(S)^2 + 6.85707E - \\ 004(P)^2 + 5.41616E - 005(B)(S) - 6.75529E - 006(B)(P) + \\ 5.51234E - 004(S)(P) \end{pmatrix}^2 \quad \text{.....4.2}$$

These models are capable of predicting the responses and checking their respective adequacy. In the two equations, the drying time and coverage are the response functions while B, S and P are the input variable parameters, where ‘B’ represents the binder, ‘S’ represents the solvent while ‘P’ the pigment. These models can be used to estimate and compare both the predicted and experimental data. These also show the relationship between the responses (drying time and coverage) and the variable parameters (binder, solvent and pigment).

4.7 Statistical Analysis for Drying Time and Coverage

The optimal conditions for the drying time and coverage of car paint were determined by means of design of experiment (DOE) under response surface methodology (RSM). The results are displayed in Table 4.9a and 4.9b respectively.

4.7.1 Drying time response

Tables 4.9a and 4.9b showed the analysis of variance (ANOVA) for drying time and coverage responses respectively. Generally, in statistical analysis if values of "prob> F" is less than 0.0500 this indicates that model terms are significant (Balasubramania*et al.*, 2012; Ali *et al.*, 2013;Li *et al.*, 2012; Yamin*et al.*, 2013; Xinyue*et a*l., 2014). Thus, as shown in Table 4.9a, F-value of 7.39 has a prob value of 0.0022. This implies that, the model is significant with prob value less than 0.0500. As also shown on the same Table, A, B and C represent the model terms, where A, B and C stand for binder, solvent and pigment respectively. Therefore, from the ANOVA results obtained, "C and AC" are the significant model terms depicted in Table 4.9a.

Table 4.9a: Analysis of variance (ANOVA) for drying time response

Source of model	Sum squares	DF	Mean square	F-Value	Prob> F	
	2914.70	9	323.86	7.39	0.0022*	Significant
A	83.97	1	83.97	1.92	0.1964	
B	68.73	1	68.73	1.57	0.2390	
C	631.44	1	631.44	14.41	0.0035*	

A^2	50.38	1	50.38	1.15	0.3088	
B^2	93.68	1	93.68	2.14	0.1744	
C^2	190.69	1	190.69	4.35	0.0636	
AB	200	1	200	4.56	0.0584	
AC	1458.00	1	1458.00	33.27	0.0002*	
BC	112.50	1	112.50	2.57	0.1402	
Residual	438.25	10	43.83			
Lack of Fit	364.75	5	72.95	4.96	0.0517	Not significant
Pure Error	73.50	5	14.70			
Cor Total	3352.95	19				

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

As shown in the table, the model terms C and AC being significant does not mean that the model terms A, B, AB, and BC are not important in thisstudy but it shows that, the model terms “C and AC” contributed more in the drying time study as compared to other model terms.Also, the “Lack of Fit F-value of 4.96 for prob> F value of 0.0517 implies that, it is not significant as shown in Table 4.9a, which is desirable in RSM study.

4.7.2 Coverage response

Table 4.9b showed the ANOVA analysis for coverage response of the formulated paint where binder (A), solvent (B) and pigment (C) were the three parameters varied.

Table 4.9b: Analysis of variance (ANOVA) for coverage response

Source	Sum of	DF	Mean	F-Value	Prob > F

Model	square		square			
	1.26	9	0.14	12.84	0.0002*	Significant
A	0.44	1	0.44	40.68	< 0.0001*	
B	3.816E-003	1	3.316E-003	0.35	0.5670	
C	0.37	1	0.37	33.74	0.0002*	
A^2	9.177E-003	1	9.177E-003	0.84	0.3802	
B^2	0.019	1	0.019	1.73	0.2180	
C^2	0.068	1	0.068	6.22	0.0317*	
AB	0.12	1	0.12	10.91	0.0080*	
AC	2.054E-004	1	2.054E-004	0.019	0.8935	
BC	0.22	1	0.22	20.10	0.0012*	
Residual	0.11	10	0.011			
Lack of Fit	0.084	5	0.017	3.36	0.1049	Not significant
Pure Error	0.025	5	4.996E-003			
Cor Total	1.37	19				

The model F-value of 12.84 corresponding to "prob > F" value of 0.0002 as shown in Table 4.9b signified that, the model is significant as it is less than 0.0500. In this case, the model terms: A, C, C^2, AB and BC are significant. Also, the "Lack of Fit as shown in the table is not significant which is desirble in describing a good model as its "prob > F" value is 0.1049 greater than 0.0500.

4.8 Predicted and Actual Drying Time and Coverage Relationship

Figure 4.1a and 4.1bdescribed the relationships between the predicted and actual responses respectively. This relationships is also shown in Table A_4 and A_5 of Appendix A respectively. The figurespresented the design expert parity plots of predicted drying time and coverage against their respective actual responses for the auto base paint formulated.

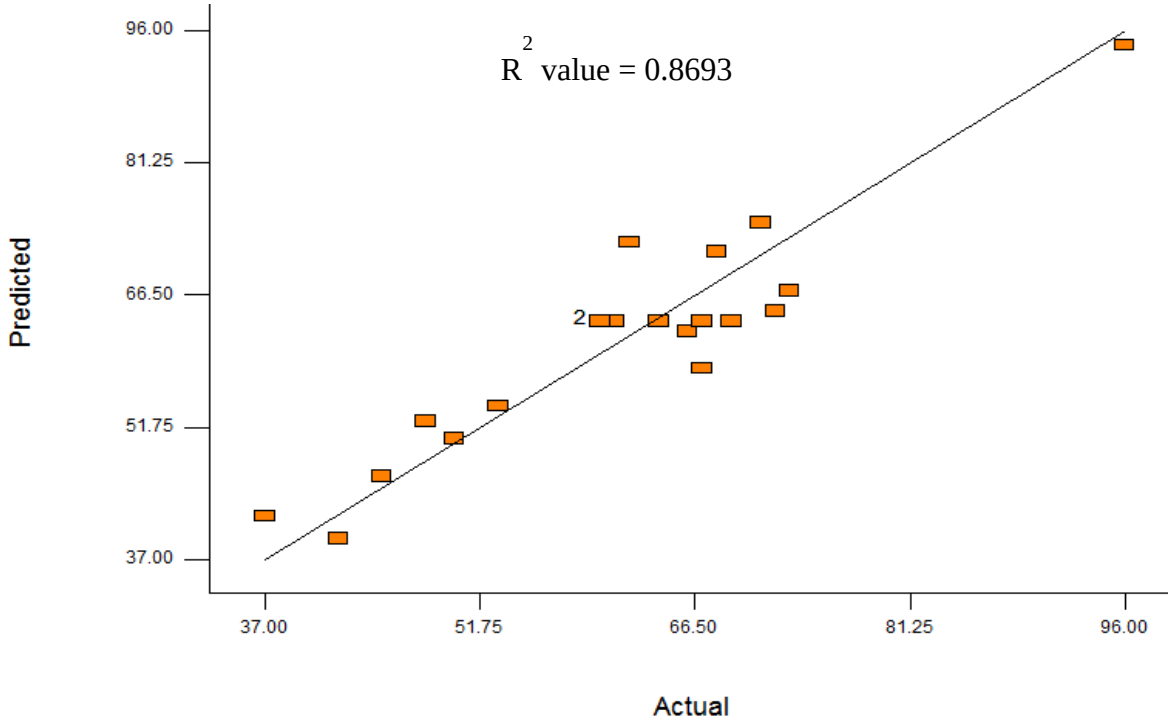


Figure 4.1a: Actual (experimental) and predicted drying time relationship of the formulated paint

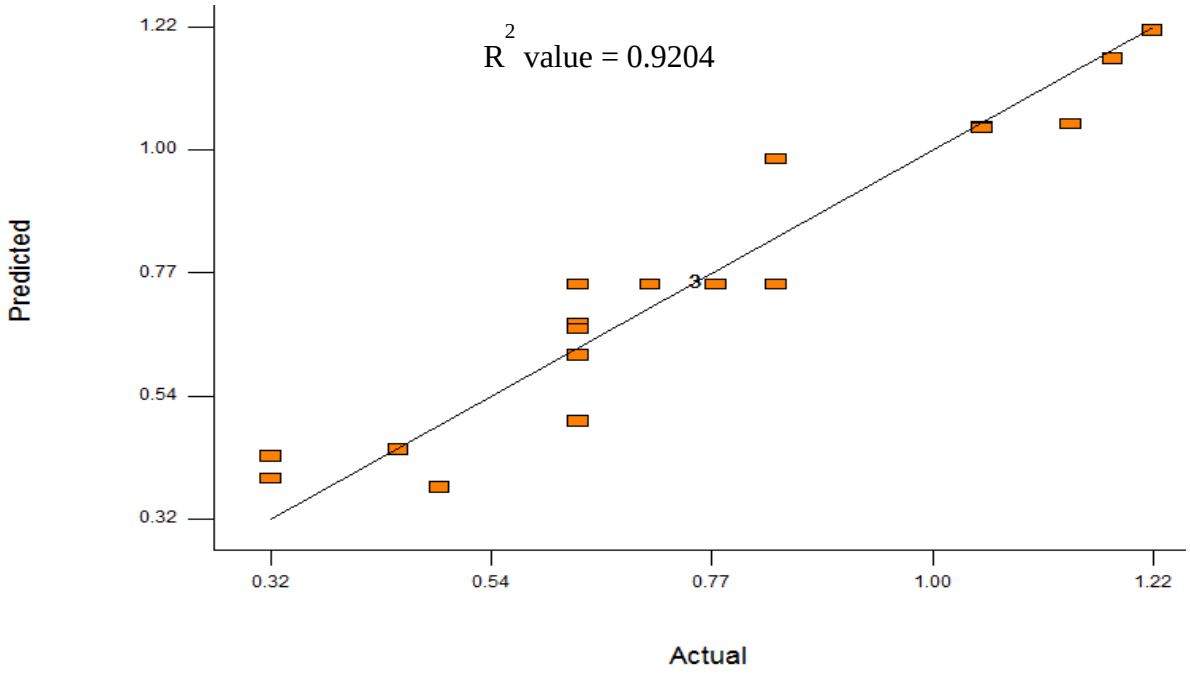


Figure 4.1b: Actual (experimental) and predicted coverage relationship of the formulated paint

As shown in Figure 4.1a, the data points were well distributed close to the regression line, which suggested an excellent relationship between the predicted and experimental (actual) values of the response. There is no outlier among the data point that could suggest inappropriate underlying assumptions of this analysis.

Also, the parity plot depicted in Figure 4.1b for the predicted and actual coverage relationship follows similar trend with that of Figure 4.1a. The data points as shown in the figure were also well distributed close to the regression which revealed that, the model developed is highly significant and adequate to represent the actual relationship between input variables and output response. The approximate distribution of data points along a straight line in both figure 4.1a and 4.1b showed a good correlation between the actual (experimental) and predicted values.

4.9 3D-Surface Plots of Variable Parameters and Responses Studied (Drying Time and Coverage)

The 3D response surface plots generally illustrate the effects of the independent variables and their interactive effects on the responses (Li *et al*., 2012). Also, the shape of the corresponding contour plots usually indicates whether the mutual interactions between the independent variables with their responses are significant or not. Thus an elliptical nature of the contour plots usually indicates that the models are significant (Li *et al*., 2012). The 3D plots shown in Figure 4.2a and 4.2b illustrate the effect of binder and solvent on the drying time and coverage responses respectively.

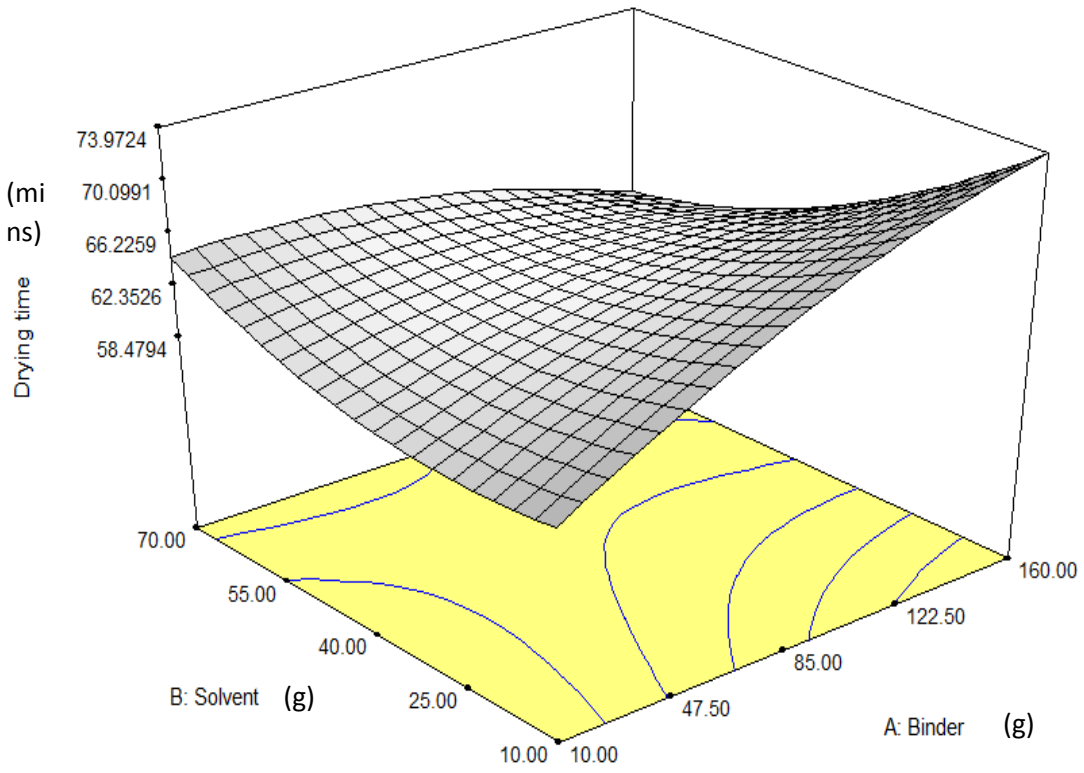


Figure 4.2a: 3D plot of drying time against solvent versus binder

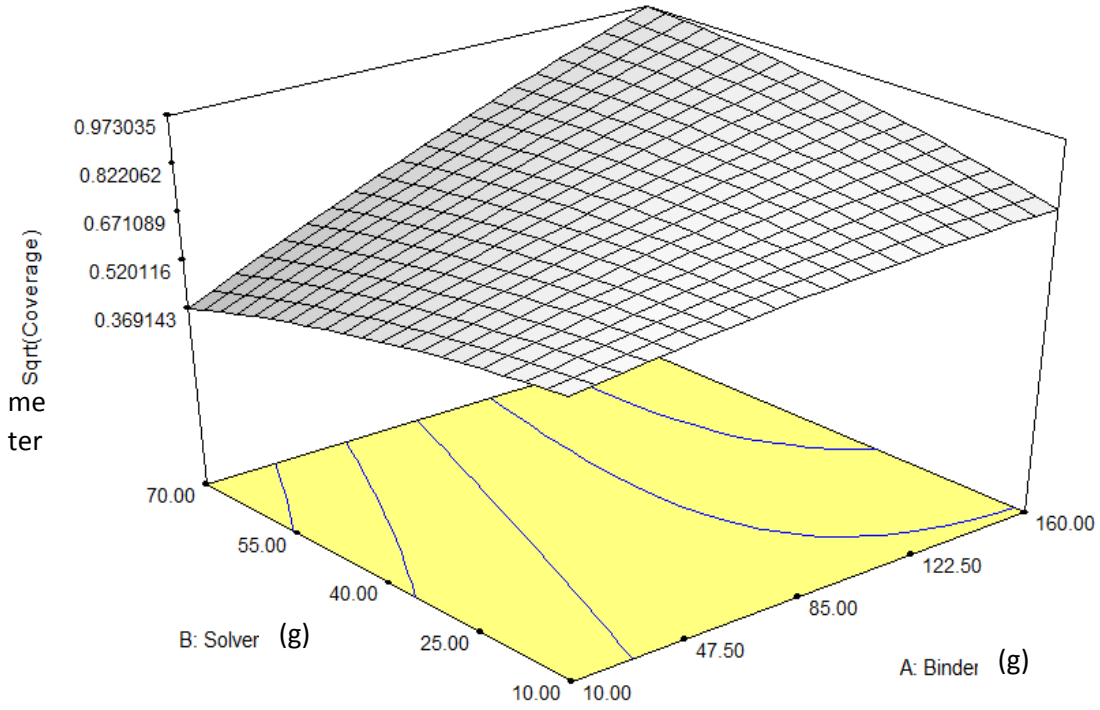


Figure 4.2b: 3D plot of coverage against solvent versus binder

The effects of binder and solvent contents on drying time for auto base paint are depicted in Figure 4.2a. As the binder and solvent contents vary (either increasing or decreasing), the drying time changes. As shown in the same figure for instance, at binder content of 160g (x-axis) and solvent content of 70g (z-axis), the corresponding drying time on y-axis is 62 minutes. Thus, several plots for other runs of varying parameters against drying time in the same graph resulted to the 3D surface plots as shown in Figure 4.2a. Also, the variation in drying time showed that the interactions between the variable parameters are significant, as evidenced from the elliptical nature of the contours plots.

Also, Figure 4.2b shows the interactions between binder and solvent contents with their corresponding coverage response. As shown in the figure,as the solvent contents

decrease with increase in binder contents, the coverage response increase. Thus, several of these interactions between binder and solvent contents against coverage response resulted to the three dimensional surface plot as shown in Figure 4.2b. Also, the three dimensional surface plots of solvent-pigment against drying time response, binder-pigment against drying time response, solvent-pigment against coverage response and binder-pigment against coverage response are displayed in Figure A_1, A_2, A_3 and A_4 in Appendix A respectively, which followed similar trend with Figure 4.2a and 4.2b. Therefore, the trend shows that, the interactions between binder, solvent and pigment with their respective responses (drying time and coverage) are highly significant as evidence from the elliptical nature on the surface contour as depicted in Figure 4.2a, 4.2b, A_1, A_2, A_3 and A4.

4.10 Optimized Solutions from the Simulated Responses

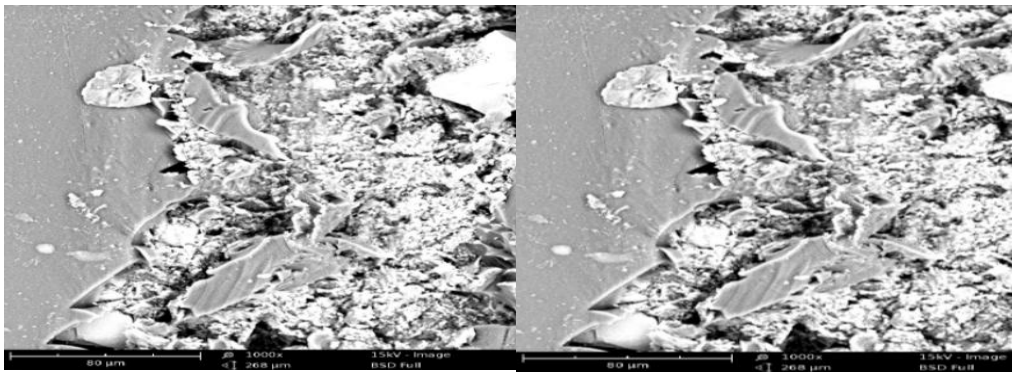
Section 4.9 discussed the variable parameters interactions with both drying time and coverage responses individually, where the models developed as depicted in Equation 4.1 and 4.2 for drying time and coverage respectively were proved to be highly significant and adequate to represent the actual relationship between the input variables (parameters varied) and output responses (drying time and coverage). However, the incorporation of these responses desirable parameters (input and output data) required for simulation using the numerical optimization feature of design expert through "Response Surface Methodology" (RSM) technique as shown in Figure A_5 of Appendix A. Thus, ten optimized solutions from hundreds of possible simulated combinations were obtained with their respective desirability.Table 4.10 shows the optimized solutions, where solution number one of the optimized solution was selected by the tool for self-healing auto base paint formulation.

Table 4.10: Optimized auto base paint formulation solutions

Solutions Number	Binder (g)	Solvent (g)	Pigment (g)	Drying time (mins)	Coverage (m^2)	Desirability	
1	160.00	38.35	10.00	40.4426	1.31073	0.927	Selected
2	160.00	37.68	10.00	40.5278	1.31356	0.927	
3	157.74	39.87	10.00	40.6992	1.29474	0.921	
4	160.00	26.32	10.00	42.3647	1.36124	0.898	
5	160.00	14.08	10.00	45.1645	1.36124	0.898	
6	160.00	12.86	10.00	45.4888	1.36089	0.895	
7	160.00	67.43	10.00	39.1795	1.11601	0.886	
8	159.60	69.76	10.00	39.3909	1.09201	0.877	
9	118.08	40.97	10.00	47.8887	1.1116	0.814	
10	134.19	67.68	10.00	45.634	0.935756	0.782	

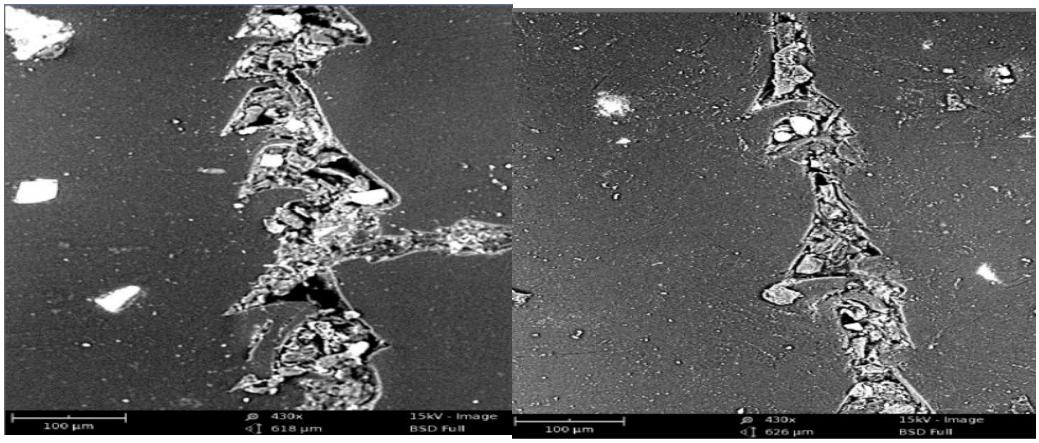
4.11 Self-Healing Property of Chitosan Investigation on the Formulated Paint

The self-healing property of chitosan on the scratched substrates coated with self-healing car paint formulated was studied using scanning electron microscope (SEM) based on investigation condition of 0 minute and 60 minutes before and after exposing to sunlight respectively. The test was conducted on five samples labelled as 0.0% (control sample), 0.5%, 1.0%, 1.5% and 2.0% chitosan concentrations. Figure 4.3 depicted SEM analysis of the five samples.



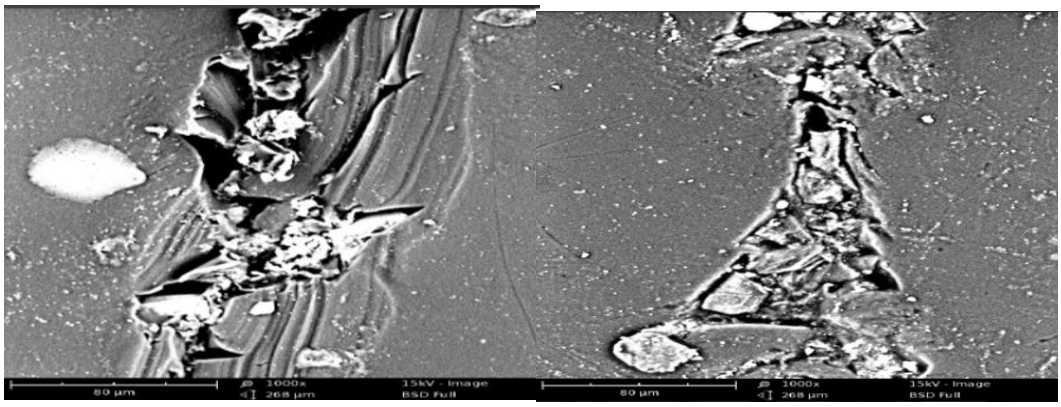
(a) (b)

Figure 4.3a and b: 0% chitosan concentration (control sample) at 0 minute and 60 minutes respectively



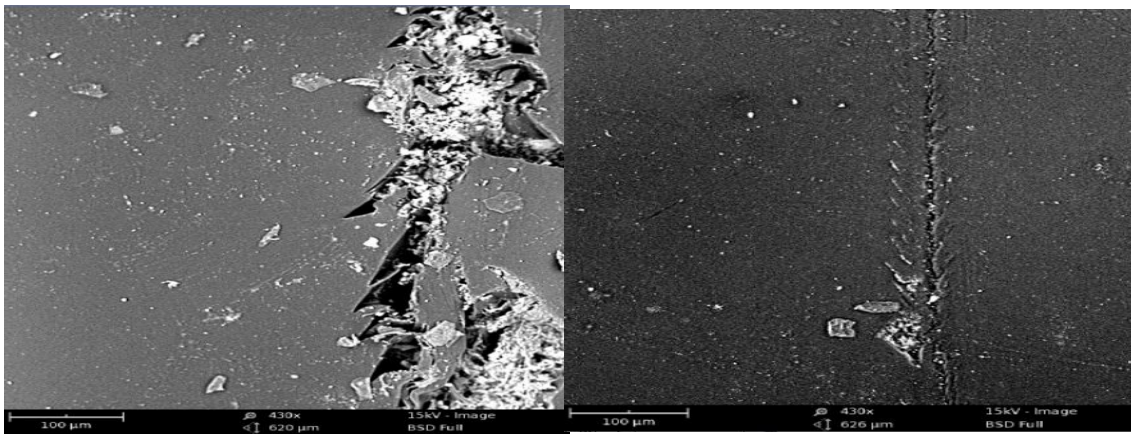
(c) (d)

Figure 4.3 c and d: 0.5% chitosan concentration at 0 minute and 60 minutes respectively



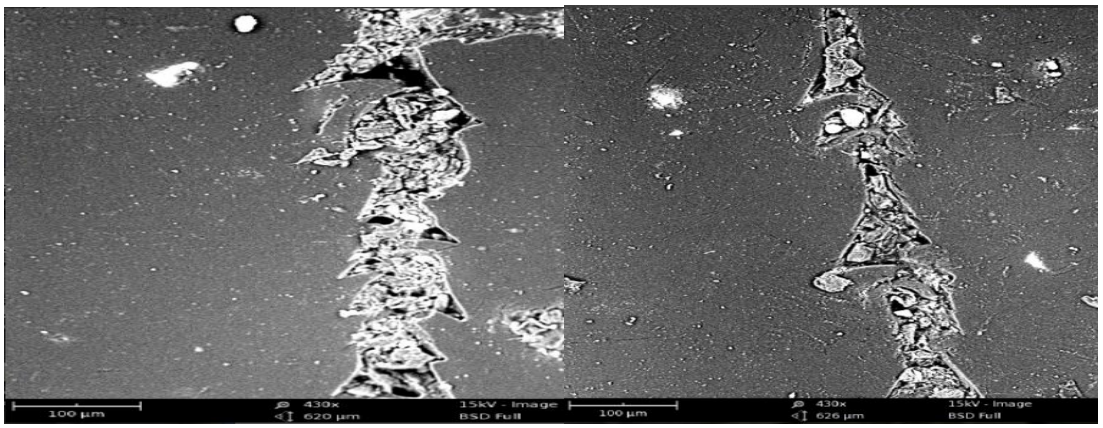
(e) (f)

Figure 4.3 e and f: 1.0% chitosan concentration at 0 minute and 60 minutes respectively



(g) (h)

Figure 4.3 g and h: 1.5% chitosan concentration at 0 minute and 60 minutes respectively



(i) (j)

Figure 4.3i and j: 2.0% chitosan concentration 0 minute and 60 minutes respectively

Figure 4.3 (a toi) showed the SEM micrographs of short oil alkyd paint reinforced with chitosan at different concentration as indicated appropriately. The reinforcement formed composite coatings which exhibit self-healing property as indicated in the micrograph nature from the SEM analysis done.This study is an evidence from the SEM micrograph of sample that contains 0% chitosan concentration (control sample) as depicted in Figure 4.3 a and b. As shown in the Figure, there is no clear differences between the micrograph in Figure 4.5a and 4b respectively (i.e. at 0 minute and after been exposed to sunlight for 60 minutes). As also shown in Figure 4.5 c and d, though the dimensions

in both cases were not quantified but, it is clear that the dimension of scratched damaged in the Figure 4.5c is wider than that of Figure 4.5d. This can be attributed to the presence of chitosan (which has the tendency to initiate self-healing) on thesurface coating sample. Similar trend was observed from Figure 4.5 e and f that contain 1% chitosan concentration. Thus, based on the observations from the SEM micrographs shown in the Figures, it can be said that the presence of chitosan in the composite coating exhibits self-healing characteristic as evidence from the micrograph image difference between Figure 4.5e and 4f as compared to the control sample shown in Figure 4.5a and b. Figure 4.5g and 4h showed composite surface coating containing 1.5% chitosan concentration at 0 minute and after 60 minutes observations respectively. The scratch damages done to the sample labelled Figure 4.3g was nearly completely self-repaired after been exposed to sunlight for 60 minutes as depicted by SEM micrograph in Figure 4.3h. Finally, the self-healing property of chitosan was also displayed by SEM micrograph as evidence from the extent of damage differences between Figure 4.3i and 4.3j. Thus, the effect of 2.0% chitosan present on the scratched damage composite coating after been exposed to sunlight for 60 minutes proves that chitosan has a self-healing property.

In summary, it can therefore be said from the results obtained in this work that; chitosan has self-healing effect as it was reported in literatures but the optimum self-healing result is highly dependent on its right proportion to the total paint raw materials used during formulation as proved from the result obtained on 1.5% chitosan concentration as compared to that of 0.5%, 1.0% and 2.0% chitosan concentrations.

4.12 Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Formulated Paint

Fourier Transform Infrared Spectroscopy (FTIR) analysis is an analytical technique that identify functional groups and in some cases inorganic materials. It was done in this work to determine the functional groups present in the raw materials that constitute the formulated paint. The significant of this analysis is to ascertain that, the functional groups shown in alkyd paint and chitosan structures as depicted in Equation 2.2 are actually present in the final products.

Figure 4.4a, 4.4b and 4.4c depicted the FTIR graph of the raw synthetic chitosan used in this work, the formulated car paint and formulated self-healing car paint respectively.

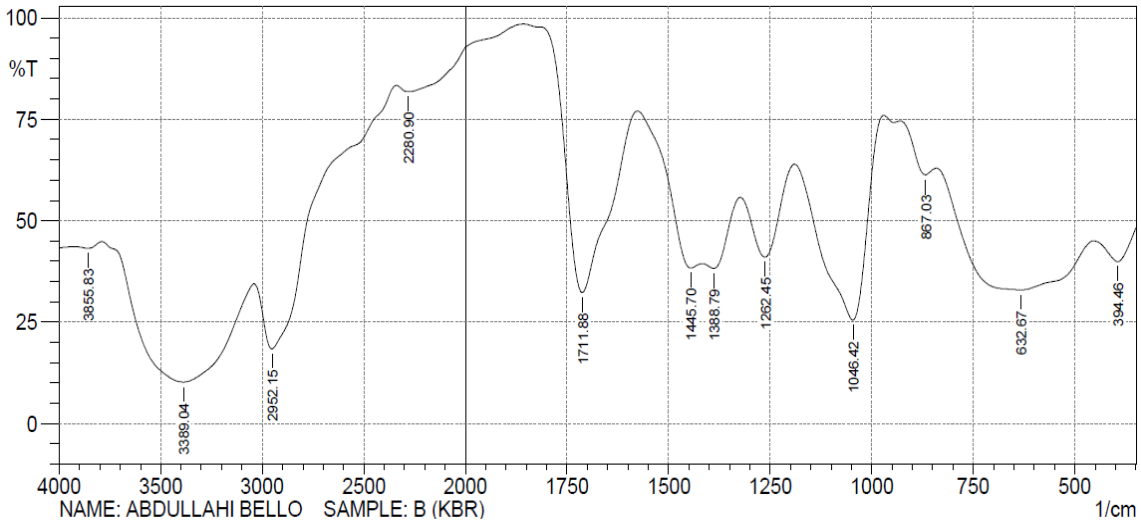


Figure 4.4a: FTIR spectrum of raw chitosan used in the paint formulation

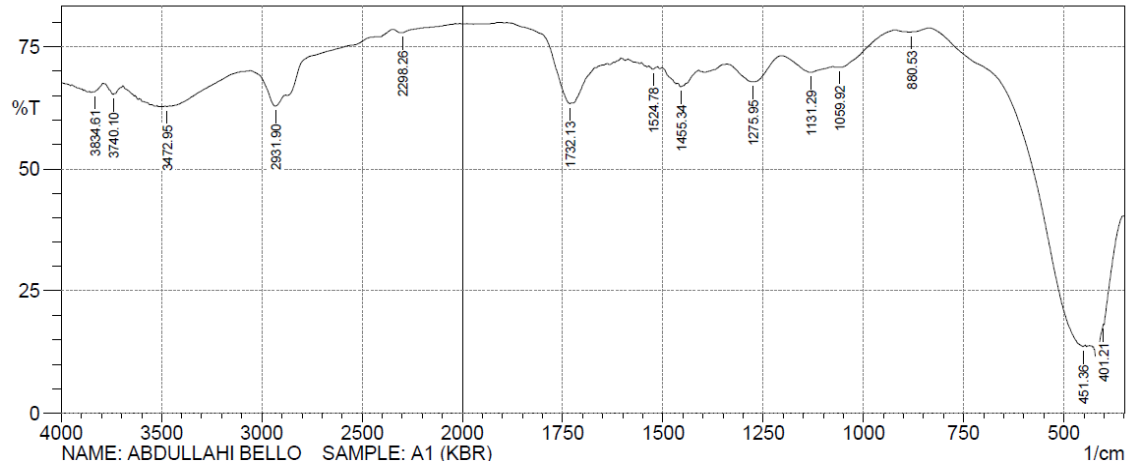


Figure 4.4b: FTIR spectrum of the formulated car paint without chitosan

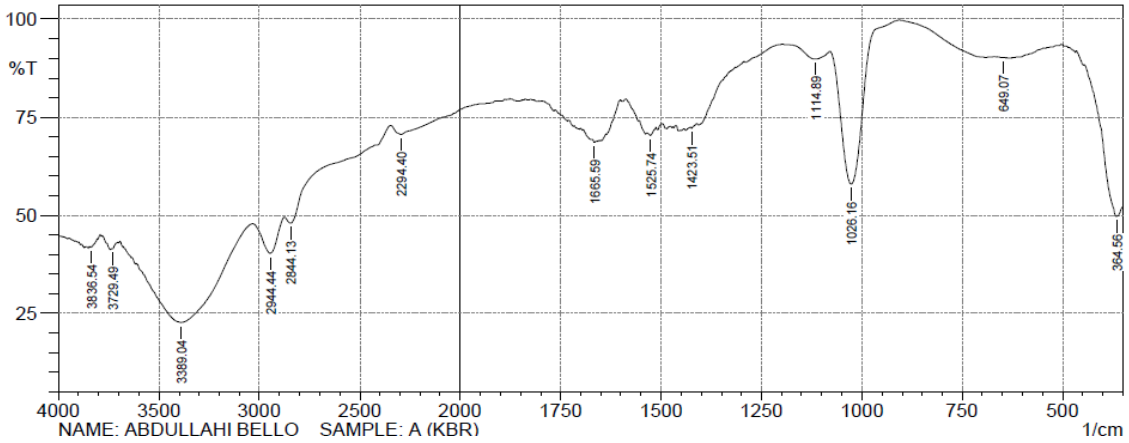


Figure 4.4c: FTIR spectrum of the formulated self-healing car chitosan

Figure 4.4a, 4.4b and 4.4c respectively represent raw chitosan, formulated car paint without chitosan and formulated self-healing car paint with chitosan. The FTIR characterised raw chitosan used in this work was depicted in Figure 4.4a, as it can be seen from the Figure, the NH_2(amine functional group) having band IR range (3500-3300)cm^{-1}as reported by Geoge, (2011) occurs at a peak position of 3389.04, with OH (hydroxyl group) stretch occur at an absorption peak position of 2952.15 which falls within the IR band range of (3400-2400)cm^{-1}(Geoge, 2011; Subhashree*et al.*, 2011). These confirmed the present of OH and NH_2 functional groups in the chitosan structure as it was earlier stated in Equation 2.4. Also, the CH_2functional group attachment with

OH functional group that forms pendant hydroxyl group (CH_2OH) has a peak position of 1046.42cm^{-1}which falls in the IR range of (1085-1050)cm^{-1}as reported by Geoge, (2011) and Subhashree*et al*., (2011). Also, as shown in Figure 4.4b, the C=O functional stretch appears in the range of 1720-1708 cm^{-1} at a peak position of 1732.13, as present in benzene-1, 2-dicarboxylic anhydride (phthallic anhydride) within the alkyd resin paint structure depicted in Equation 2.4.Also, the CH_2(methylene group) and CH (methyne group) of monoglyceride structure that forms part of alkyd resin paint as depicted in Equation 2.4 are in infrared red (IR) range of (2940-2915)$cm^{-1}$with peak position of 2931.26and (1310-1290)cm^{-1}having peak position close to 1275.95 respectivelyas shown in Figure 4.4b.Figure 4.4c showed similar trend with Figure 4.4b. As it was shown in the Figure, NH_2 also occurs in a band peak position of 3389.04cm^{-1} while CH_2 occur close to pick position of 2944.44cm^{-1}. Also, the OH group was found in a peak position of 2844.13cm^{-1}. The OH group depicted in Figure 4.4a and 4.4c have IR absorbance value of 2952.15$cm^{-1}$and 2844.13cm^{-1} respectively. This shows that, the OH group present in the chitosan used and the self-healing formulated paint that contains chitosan as (self-healing agent) occur in different IR peak position, which may be due to other additives present in the formulated paint. However, the NH_2 functional group present in both cases were found in the same IR peak position which is an evidence that, chitosan (the self-healing agent) is present in the self-healing formulated paint which is not present in the formulated paint without chitosan as depicted in Figure 4.4a, 4.4b and 4.4c respectively.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMENDATIONS

This section gives the conclusions and recommendations made at the completion of investigations carried out from this work.

5.1 CONCLUSIONS

At the completion of this investigation, it can be concluded that, model was developed using RSM for paint formulation where optimum values were obtained.

The model showed that the second-order polynomial model was sufficient to describe and predict the responses of drying time and coverage of auto base paint formulated.

The analysis of variance (ANOVA) showed that, the interactions between the independent parameters (binder, solvent and pigment) varied, had significant effects on the drying time and coverage responses studied.

It was observed that, run 8 of the formulated paint had the best physico-mechanical properties as compared with other runs as evidence from its close agreement with ASTM and PAN standard car paint specifications.

Addition of chitosan in the formulation showed self-healing property as evidence from the SEM analysis. However, it was observed that, the optimum self-healing investigation is dependent on the incorporation of chitosan right proportion; 1.5% chitosan concentration had the best self-healing performance on the optimum paint formulation adopted in this work.

The FTIR analysis of the raw chitosan, the formulated paint without self-healing property and self-healing formulated paint revealed that, the predicted functional groups in the raw materials and the formulated products were actually present.

5.2 RECOMMENDATIONS

From the investigation, the following recommendation may be drawn.

The self-healing property of chitosan on surface coating should be investigated in future researches with time variation to demonstrate or study gradual healing process, unlike in this work where the studied was limited to (0-60) minutes.

Indigenous chitosan synthesis should be encourage by setting up a process plant for its mass production since the raw materials are largely available in Nigeria, especially in the southern part of the country.

More microscopic device such as transmission electron microscope (TEM) should be provided and accessible for better view of extent of damage and repair of scratched substrates.

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APPENDIX A

Table A_1: Density of the formulated auto base paint

Run	Weight of empty bottle (W_1) (g)	Weight of sample (W_2) (g)	$W_1 + W_2$ (g)
1	2.45	9.56	12.01
2	2.45	11.11	13.56
3	2.45	9.77	12.22
4	2.45	11.47	13.92
5	2.45	10.56	13.01
6	2.45	10.07	12.54
7	2.45	8.75	11.20
8	2.45	8.96	11.41
9	2.45	11.80	14.25
10	2.45	10.85	13.30
11	2.45	10.86	13.31
12	2.45	10.18	12.63
13	2.45	9.44	11.89
14	2.45	12.22	14.67
15	2.45	10.85	13.30
16	2.45	10.23	12.68
17	2.45	10.56	13.01
18	2.45	10.46	12.91
19	2.45	10.44	12.89
20	2.45	10.42	12.87

Table A_2: Drying time and coverage

RUN	DRYING TIME	COVERAGE	AMOUNT SPRAYED (2ml)
1	62	1.1	2
2	67	1.1	2
3	64	0.7	2
4	48	0.1	2
5	50	0.2	2
6	53	0.2	2
7	42	1.3	2
8	37	1.5	2
9	96	0.4	2
10	67	0.6	2
11	69	0.6	2
12	72	0.4	2
13	45	1.4	2
14	68	0.1	2
15	60	0.5	2
16	60	0.6	2
17	71	0.4	2
18	61	0.4	2
19	73	0.4	2
20	66	0.7	2

Table A_3: Design of experimental status

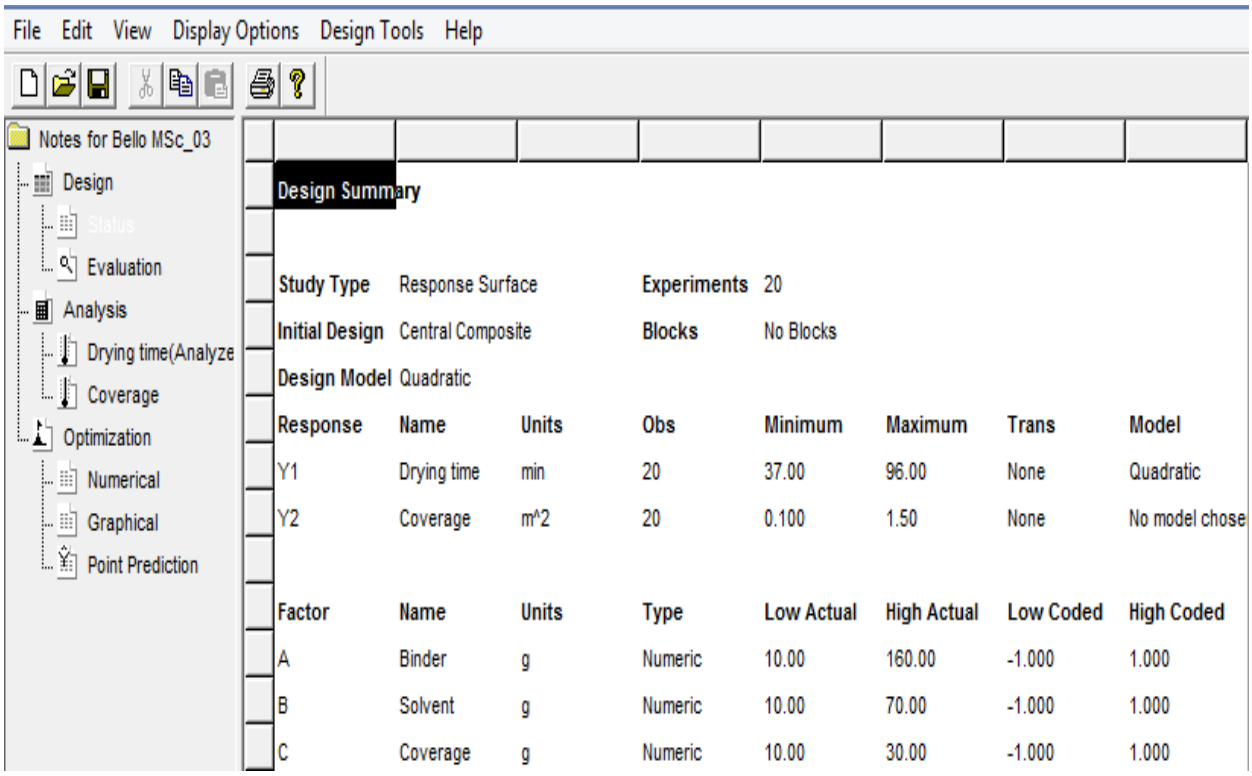


Table A_4: Statistical diagnostic of predicted actual time in minutes for each run

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	67.00	58.33	8.67	0.670	2.280	1.054	3.122	2
2	45.00	46.29	-1.29	0.670	-0.338	0.023	-0.322	13
3	68.00	71.34	-3.34	0.670	-0.878	0.156	-0.867	14
4	42.00	39.30	2.70	0.670	0.710	0.102	0.691	7
5	48.00	52.43	-4.43	0.670	-1.163	0.274	-1.187	4
6	96.00	94.38	1.62	0.670	0.425	0.037	0.407	9
7	50.00	50.44	-0.44	0.670	-0.115	0.003	-0.109	5
8	62.00	72.40	-10.40	0.670	-2.733	1.515	-5.156 *	1
9	53.00	54.11	-1.11	0.607	-0.268	0.011	-0.255	6
10	66.00	62.45	3.55	0.607	0.855	0.113	0.843	20
11	71.00	74.55	-3.55	0.607	-0.857	0.113	-0.844	17
12	73.00	67.01	5.99	0.607	1.444	0.323	1.540	19
13	37.00	41.85	-4.85	0.607	-1.168	0.211	-1.192	8
14	72.00	64.72	7.28	0.607	1.756	0.477	2.002	12
15	69.00	63.57	5.43	0.166	0.898	0.016	0.889	11
16	60.00	63.57	-3.57	0.166	-0.591	0.007	-0.570	16
17	61.00	63.57	-2.57	0.166	-0.425	0.004	-0.407	18
18	60.00	63.57	-3.57	0.166	-0.591	0.007	-0.570	15
19	67.00	63.57	3.43	0.166	0.568	0.006	0.547	10
20	64.00	63.57	0.43	0.166	0.071	0.000	0.068	3

Table A_5: Statistical diagnostic of predicted actual coverage in square meter for each run

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	1.05	1.04	9.625E-003	0.670	0.161	0.005	0.152	2
2	1.18	1.17	0.017	0.670	0.291	0.017	0.277	13
3	0.32	0.43	-0.12	0.670	-1.919	0.747	-2.290	14
4	1.14	1.05	0.095	0.670	1.582	0.508	1.734	7
5	0.32	0.39	-0.074	0.670	-1.240	0.312	-1.278	4
6	0.63	0.50	0.14	0.670	2.261	1.037	3.069	9
7	0.45	0.44	3.071E-003	0.670	0.051	0.001	0.049	5
8	1.05	1.04	0.011	0.670	0.182	0.007	0.173	1
9	0.49	0.37	0.11	0.607	1.758	0.478	2.007	6
10	0.84	0.98	-0.14	0.607	-2.202	0.750	-2.912	20
11	0.63	0.68	-0.043	0.607	-0.652	0.066	-0.632	17
12	0.63	0.62	0.014	0.607	0.208	0.007	0.198	19
13	1.22	1.22	5.799E-003	0.607	0.089	0.001	0.084	8
14	0.63	0.67	-0.035	0.607	-0.533	0.044	-0.513	12
15	0.77	0.75	0.025	0.166	0.267	0.001	0.254	11
16	0.77	0.75	0.025	0.166	0.267	0.001	0.254	16
17	0.63	0.75	-0.12	0.166	-1.225	0.030	-1.261	18
18	0.71	0.75	-0.042	0.166	-0.442	0.004	-0.423	15
19	0.77	0.75	0.025	0.166	0.267	0.001	0.254	10
20	0.84	0.75	0.087	0.166	0.918	0.017	0.910	3

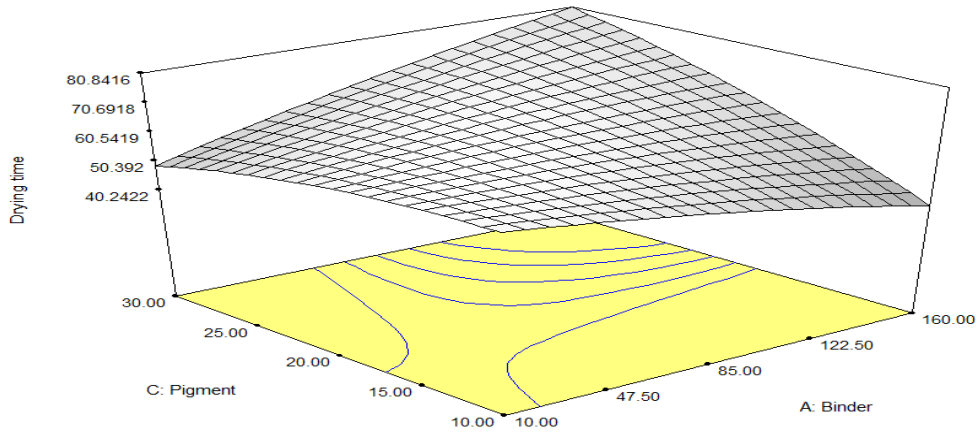


Figure A_1: Three dimensional relationship between binder-pigment interactions against drying time response of the formulated paint

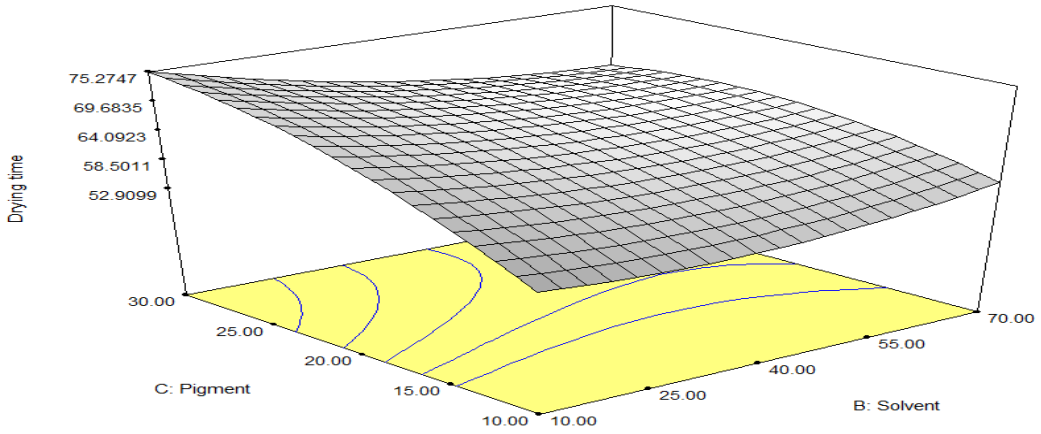


Figure A_2: Three dimensional relationship between solvent-pigment interactions against drying time.

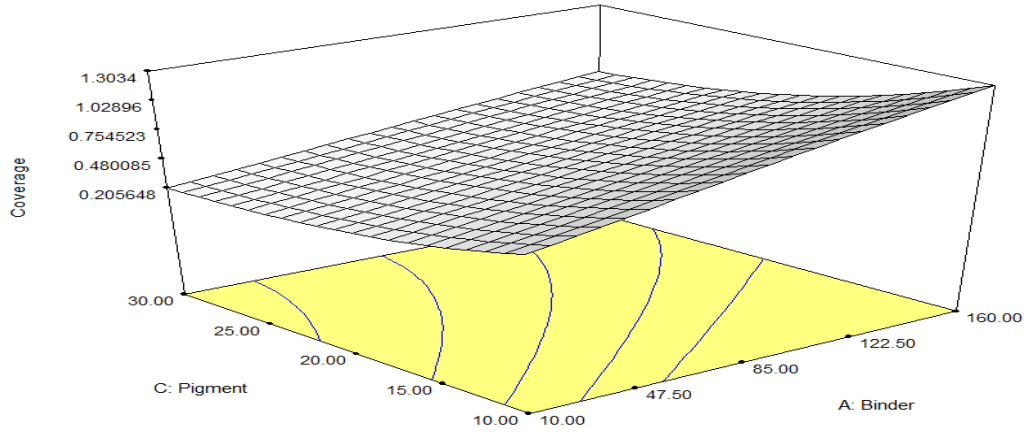


Figure A_3: Three dimensional relationships between binder-pigment (coverage agent) interactions against coverage response

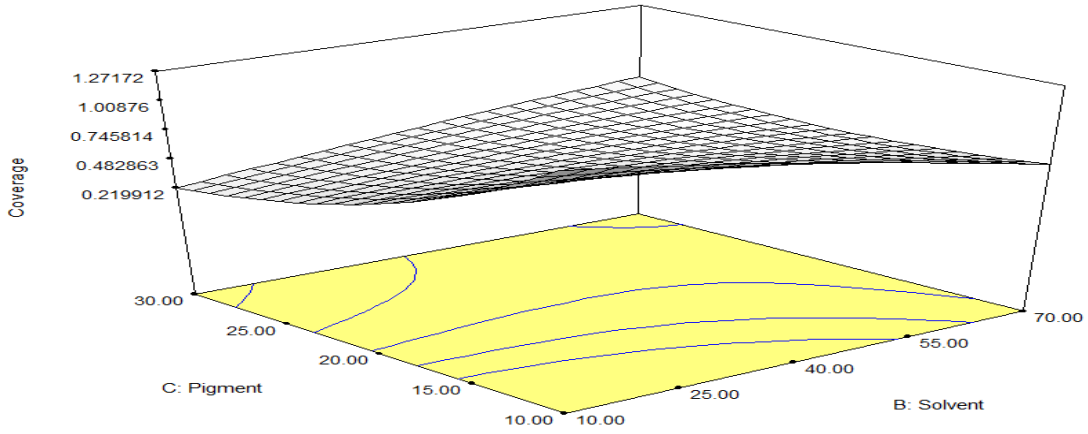


Figure A_4: Three dimensional relationships between solvent-pigment (coverage agent) interactions against coverage response

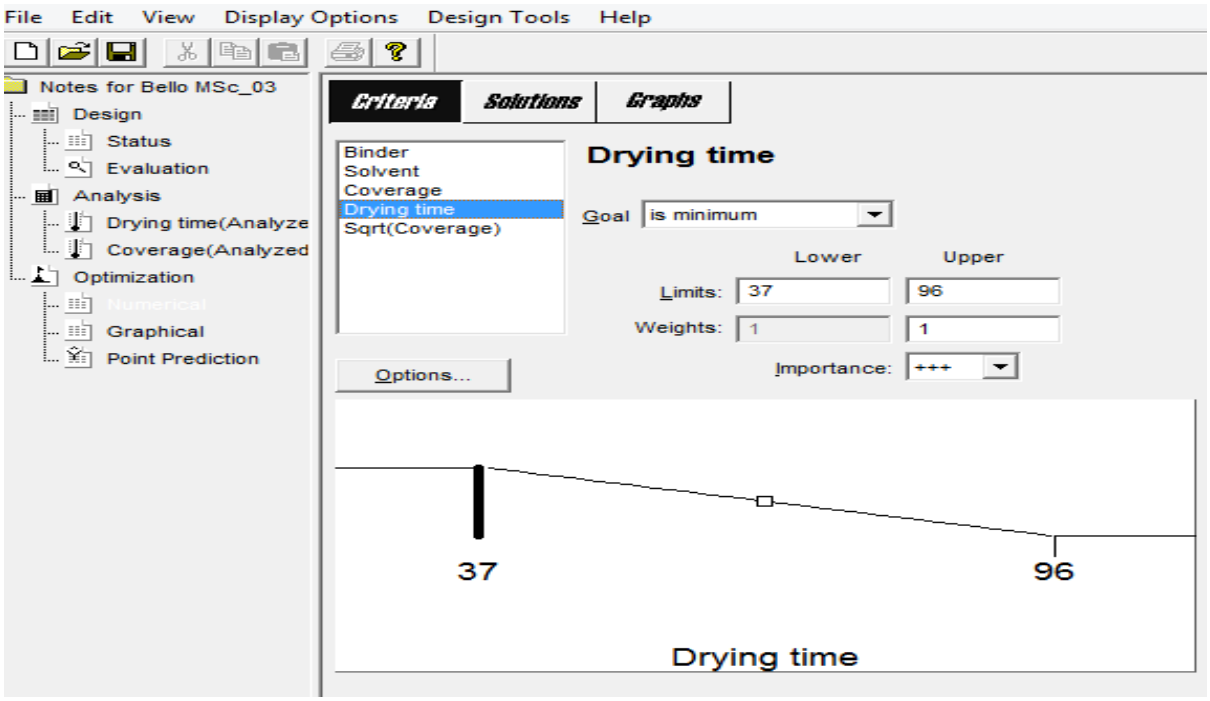
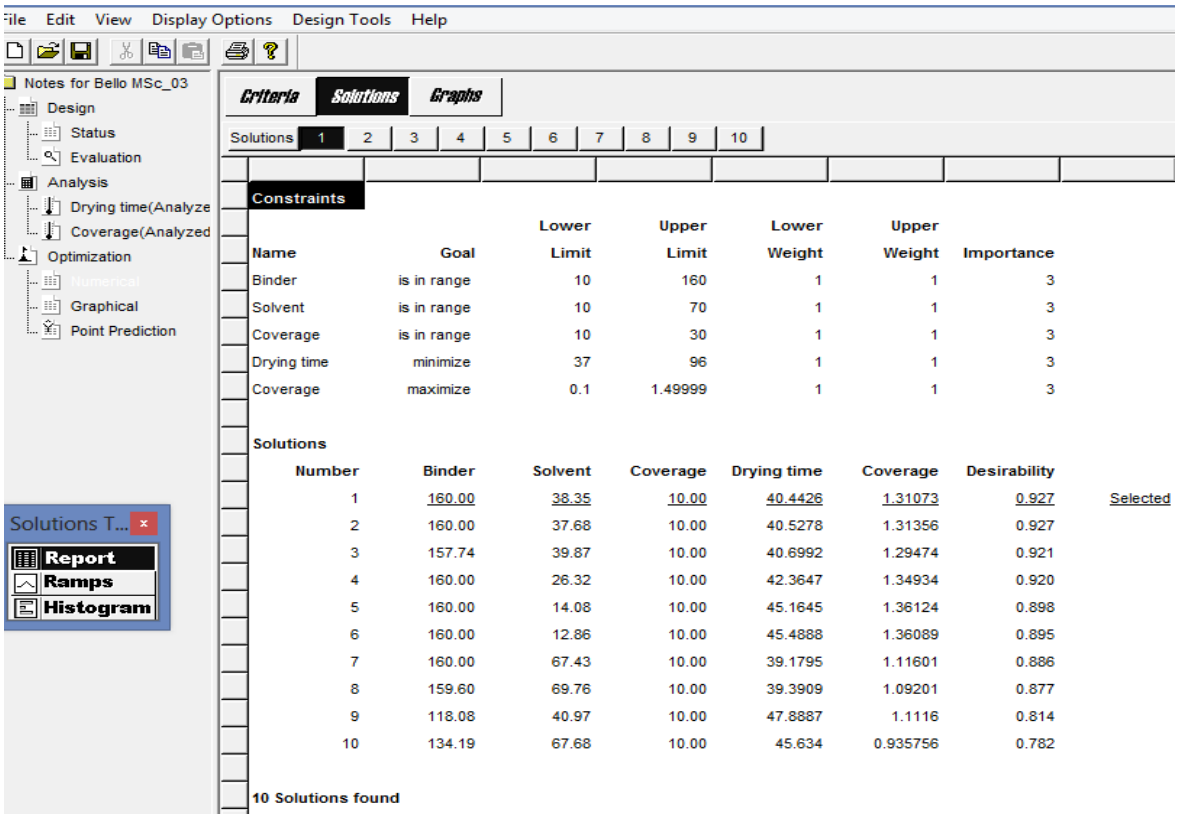


Figure A_5: Optimization of drying time and coverage responses simulation interface

Table A_6: Optimization solutions of the auto base paint



Constraints

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Binder	is in range	10	160	1	1	3
Solvent	is in range	10	70	1	1	3
Coverage	is in range	10	30	1	1	3
Drying time	minimize	37	96	1	1	3
Coverage	maximize	0.1	1.49999	1	1	3

Solutions

Number	Binder	Solvent	Coverage	Drying time	Coverage	Desirability	
1	160.00	38.35	10.00	40.4426	1.31073	0.927	Selected
2	160.00	37.68	10.00	40.5278	1.31356	0.927	
3	157.74	39.87	10.00	40.6992	1.29474	0.921	
4	160.00	26.32	10.00	42.3647	1.34934	0.920	
5	160.00	14.08	10.00	45.1645	1.36124	0.898	
6	160.00	12.86	10.00	45.4888	1.36089	0.895	
7	160.00	67.43	10.00	39.1795	1.11601	0.886	
8	159.60	69.76	10.00	39.3909	1.09201	0.877	
9	118.08	40.97	10.00	47.8887	1.1116	0.814	
10	134.19	67.68	10.00	45.634	0.935756	0.782	

10 Solutions found

APPENDIX B

Table B_1: ASTM auto base standard specifications (ASTM, 2009)

Paint properties	ASTM testing code	Grade/response	Remarks
Film thickness	D709	7.2±0.8µm (1.8±0.2 mile)	Accepted
Gloss value	E284	≥85	High gloss
Coverage	D4214	-	-
Chemical resistance	D1308	0	No trace of stain
Colour stability	E1499	A	Consistence
Heat resistance	D2485	A and B	Accepted
		C and D	Failed/Rejected
Punch test	D2794	1 and 2	Accepted
		3 and 4	Failed/Rejected
Cross-scratch test	D5178	1 and 2	Accepted
		3 and 4	Failed/Rejected
Drying time	D1640		

Table B_2: PAN auto base paint standard specifications (PAN, 2013)

Paint properties	Grade/response	Remarks
Film thickness	7.5-15 µm	Accepted
Gloss value	≥85	High gloss
Cross-scratch test	A or B	Accepted
	C or D	Failed
Punch test	A or B	Accepted
	C or D	Failed
Colour stability	A	Stable
Heat resistance	A and B	Accepted
	C and D	Failed/Rejected
Chemical resistance	A and B	Accepted
	C and D	Failed
Coverage	-	-
Drying time	50-60 minutes	

Table B_3: Gloss value of the formulated auto base paint on coated substrates (Raw results from PAN industrial laboratory)

Run	Gloss value 1	Gloss value 2	Gloss value 3	Gloss value 4	Average
1	85.0	82.6	78.1	76.3	80.35
3	80.7	82.5	82.5	85.2	82.7
7	71.5	86.3	59.5	88.2	76.4
8	84.4	91.1	89.3	88.9	88.4

13	83.6	73.0	62.5	78.2	74.3

Table B_4: Film thickness analysis on the coated substrates (Raw results from PAN industrial laboratory)

S/N				Run 1	Run 3	Run 7	Run 8	Run 13
	Body white	Cata	Primer	Top coat	Top coat	Top coat	Top coat	Top coat
1	17.9	24.4	58.1	124	115	97	78.1	130
2	17.6	25.1	61.3	115	127	114	81.1	113
3	20.5	23.8	59.2	130	120	113	86.9	149
4	17.7	24.4	58.8	141	118	114	104	140
5	17.2	25.3	57.8	81	126	115	93.8	158
6	16.9	24.4	59.8	137	132	102	92.7	144
7	16.2	24.2	61.1	142	127	118	88.8	104
8	18.4	23.7	56.9	62	110	116	86.3	65.3
Average	17.8	24.4	81.5	116.5	121.9	111.1	89.0	125.4

Where:

Cata = Cata surface thickness – Body white thickness

Primer thickness = Primer coated thickness – Cata surface thickness

Top coat thickness = Top coat paint thickness – Primer coated surface thickness

Table B_5: Infrared absorption band characteristics of some functional groups

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Alkanes and	2850-3000	s	C-H stretch
Alkyls	1450-1470	s	C-H bend
	1370-1390	m	CH_3 C-H bend
	1365 + 1395 (two bands)	m	$-CH(CH_3)_2$ or $-(CH_3)_3$ bend
	715-725	w	$-(CH_2)_n$ bend
Alkenes	3020-3140	w-m	=C-H stretch
	1640-1670	vw-m	C=C stretch
$RCH=CH_2$	910 + 990 (two bands)	m + s	=C-H bend
$RR'C=CH_2$	885-895	s	=C-H bend
cis-RCH=CHR'	665-730	m-s, broad	=C-H bend
trans-RCH=CHR'	960-980	s	=C-H bend
RCH=CR'R"	790-840	s	=C-H bend
Alkynes			
R-C≡C-H	3265-3335	s, sharp	≡C-H stretch
	2100-2140	m	C≡C stretch
	610-700	s, broad	≡C-H bend
R-C≡C-R'	2190-2260	vw-w	C≡C stretch
Alkyl halides			
R-F	1000-1350	vs	C-F stretch
R-Cl	750-850	s	C-Cl stretch
R-Br	500-680	s	C-Br stretch
R-I	200-500	s	C-I stretch
Alcohols	3300-3400	s, broad	O-H stretch
C=C-CH_2-OH	1035-1050	m-s	C-O stretch
R-CH_2-OH (1°) or C=C-CH(R)-OH	1050-1085	m-s	C-O stretch
RR'CH-OH (2°) or C=C-CRR'-OH	1085-1125	m-s	C-O stretch
RR'R"C-OH (3°)	1125-1205	m-s	C-O stretch
Ar-O-H	1180-1260	m-s	C-O stretch
Ethers			
R-O-R'	1085-1150	s	C-O-C stretch
Ar-O-R	1020-1075 and 1200-1275 (two band)	m-s	=C-O-C sym. & asym. stretch
Aldehydes	2700-2725	m	H-C=O stretch
R-CH=O	1720-1740	s	C=O stretch
C=C-CH=O or Ar-CH=O	1685-1710	s	C=O stretch
Ketones			
RR'C=O	1710-1720	s	C=O stretch
C=C-C(O)-R	1665-1685	s	C=O stretch
Ar-C(O)-R	1675-1695	s	C=O stretch
four member cyclic	1770-1780	s	C=O stretch
five member cyclic	1740-1755	s	C=O stretch
six member cyclic	1710-1720	s	C=O stretch

Class of Compounds	Absorption, cm^{-1}	Intensity	Assignment
Carboxylic Acids	2500-3500	s, broad	O-H stretch
R-C(O)-OH	1710-1715	s, broad	C=O stretch
C=C-C(O)-OH or Ar-C(O)-OH	1680-1710	s	C=O stretch
Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310	s-vs	O=C-O-C stretch
R-C(O)-O-R	1735-1750	s	C=O stretch
C=C-C(O)-O-R or Ar-C(O)-O-R	1715-1730	s	C=O stretch
R-C(O)-O-Ar	1760-1790	s	C=O stretch
Acyl Chlorides			
R-C(O)-Cl	1785-1815	s	C=O stretch
Ar-C(O)-Cl	1770-1800	s	C=O stretch
Anhydrides			
R-C(O)-O-C(O)-R	~1750 + ~1815	s,s	C=O symmetric
Ar-C(O)-O-C(O)-Ar	~1720 + ~1775 (both two bands)	s,s	& asym. stretch
Nitriles			
R-C≡N	2240-2260	m-s	C≡N stretch
C=C-C≡N or Ar-C≡N	2220-2240	s	C≡N stretch
Amines			
$R-NH_2$	~3400 + ~3500 (two bands)	w	N-H symmetric & asym. stretch
	1580-1650	w-m	N-H bend
RR'N-H	3310-33350	w	N-H stretch
Amides			
$R-C(O)-NH_2$	3200-3400 and 3400-3500 (two bands)	w-m	N-H symmetric & asym. stretch
	1650-1690	s, broad	C=O stretch
	1590-1655	m-s	N-H bend
R-C(O)-NH-R	3400-3500	w-m	N-H stretch
	1640-1690	s, broad	C=O stretch
	1510-1560	m-s	N-H bend
R-C(O)-NR'R"	1630-1680	m-s	C=O stretch
Nitro Compounds			
$R-NO_2$	~1550 and ~1370	s s	N-O symmetric & asym. stretch
C=C-NO_2 or Ar-NO_2	~1525 and ~1335 (both two bands)	s s	N-O symmetric & asym. stretch
Aromatic Compounds	3010-3100	m	Ar C-H stretch
	1450-1600 (two to four bands)	m-s sharp	ring C=C stretch
monosubstituted	730-770 and 690-710 (two bands)	s s	C-H bend C-H bend
o-disubstituted	735-770	s	C-H bend
m-disubstituted	750-810 and 690-710	s s	C-H bend C-H bend
p-disubstituted	810-840	s	C-H bend

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Source: (Subhashree*et al*., 2011)

Table B_6: Infrared correlation chart

A Simplified Infrared Correlation Chart				
	Type of Vibration		Frequency (cm^{-1})	Intensity
C-H	Alkanes	(stretch)	3000-2850	s
	$-CH_3$	(bend)	1450 and 1375	m
	$-CH_2-$	(bend)	1465	m
	Alkenes	(stretch)	3100-3000	m
		(out-of-plane bend)	1000-650	s
	Aromatics	(stretch)	3150-3050	s
		(out-of-plane bend)	900-690	s
	Alkyne	(stretch)	~3300	s
	Aldehyde		2900-2800	w
			2800-2700	w
C-C	Alkane	not interpretatively useful		
C=C	Alkene		1680-1600	m-w
	Aromatic		1600 and 1475	m-w
C≡C	Alkyne		2250-2100	m-w
C=O	Aldehyde		1740-1720	s
	Ketone		1725-1705	s
	Carboxylic Acid		1725-1700	s
	Ester		1750-1730	s
	Amide		1670-1640	s
	Anhydride		1810 and 1760	s
	Acid Chloride		1800	s
C-O	Alcohols, Ethers, Esters, Carboxylic Acids, Anhydrides		1300-1000	s
O-H	Alcohols, Phenols			
	Free		3650-3600	m
	H-bonded		3500-3200	m
	Carboxylic Acids		3400-2400	m
N-H	Primary and Secondary Amines and Amides			
	(stretch)		3500-3100	m
	(bend)		1640-1550	m-s
C-N	Amines		1350-1000	m-s
C=N	Imines and Oximes		1690-1640	w-s
C≡N	Nitriles		2260-2240	m
X=C=Y	Allenes, Ketenes, Isocyanates, Isothiocyanates		2270-1950	m-s
N=O	Nitro ($R-NO_2$)		1550 and 1350	s
S-H	Mercaptans		2550	w
S=O	Sulfoxides		1050	s
	Sulfones, Sulfonyl Chlorides, Sulfates, Sulfonamides		1375-1300 and 1200-1140	s s
C-X	Fluoride		1400-1000	s
	Chloride		800-600	s
	Bromide, Iodide		<667	s

Source: (Geoge, 2011)

Table B_7: Comparative FTIR analysis of fluoroquinlones

(a) Prominent FTIR Peaks of Norfloxacin		
Peaks(cm-1)	**Groups**	**Peak assignment**
3550-3500	Hydroxyl group	Intermolecular H -bonding by single bridge
3500-3300	Imino-moity of Piperazinyl groups	NH stretching vibration
3000-2950	Aromatic,cyclic enes	υ=CH & Ar-H
2750-2700	Ethyl group	υCH_3 of C_2H_5
2500	Acid group	υOH group
1700	Carbonyl of acids	υC=O stretching vibration
1650-1600	Quinolones	υN-H bending vibration
1500-1450	O-C-O group of acid	υ_s stretching vibration of O-C-O group
1300-1250	Hydroxyl group	δO-H bending vibration
1050-1000	C-F groups	υC-F
950-900	Amines	δNH bending vibration
800	Aromatic m – distribution	δAr-H
(b) Prominent FTIR peaks of Ofloxacin		
Peaks(cm-1)	**Groups**	**Peak assignment**
3050-3000	Hydroxyl group	O-H stretching vibration, intremolecular H-bonded
3000-2950	Aromatic,cyclic enes	υ=CH & Ar-H
2750	Alkyl groups	υCH_3
1750-1700	C=O group of acids	υC=O stretching vibration
1650-1600	Quinolines	δN-H bending vibration
1550-1500	Alkyl groups	υCH_3 and υCH_2
1450-1400	Methylene group in Benzoxazine	stretching vibration of CH_2
1400-1350	Hydroxyl group	δO-H bending vibration
1250-1200	Oxo group	C-O-C stretching vibration
1050-1000	Fluorine group	C-F stretching
950-800	Aromatics & enes	=C-H out of plane bending vibration

(Subhashree, *et al*., 2011)

Table B_8: Saturated aliphatic and olefinic frequencies

Group frequency (cm^{-1})	Functional group/assignment
	Methyl ($-CH_3$)
2970–2950/2880–2860	Methyl C–H asym./sym. stretch
1470–1430/1380–1370	Methyl C–H asym./sym. bend
1385–1380/1370–1365	*gem*-Dimethyl or "iso"- (doublet)
1395–1385/1365	Trimethyl or "*tert*-butyl" (multiplet)
	Methylene ($>CH_2$)
2935–2915/2865–2845	Methylene C–H asym./sym. stretch
1485–1445	Methylene C–H bend
750–720	Methylene $-(CH_2)_n-$ rocking ($n \geq 3$)
1055–1000/1005–925	Cyclohexane ring vibrations
	Methyne ($>CH-$)
2900–2880	Methyne C–H stretch
1350–1330	Methyne C–H bend
1300–700	Skeletal C–C vibrations
	Special methyl ($-CH_3$) frequencies
2850–2815	Methoxy, methyl ether O–CH_3, C–H stretch
2820–2780	Methylamino, N–CH_3, C–H stretch

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
C=C	1680–1620	Alkenyl C=C stretch
	1625	Aryl-substituted C=C
	1600	Conjugated C=C
C–H	3095–3075 +3040–3010	Terminal (vinyl) C–H stretch
	3095–3075	Pendant (vinylidene) C–H stretch
	3040–3010	Medial, *cis*- or *trans*-C–H stretch
C–H	1420–1410	Vinyl C–H in-plane bend
	1310–1290	Vinylidene C–H in-plane bend
C–H	995–985 + 915–890	Vinyl C–H out-of-plane bend
	895–885	Vinylidene C–H out-of-plane bend
C–H	970–960	*trans*-C–H out-of-plane bend
	700 (broad)	*cis*-C–H out-of-plane bend

(John, 2000)