FORMULATION OF GREEN PRINTING INK FOR CERAMIC SUBSTRATE

This report submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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2017

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **FORMULATION OF GREEN PRINTING INK FOR CERAMIC SUBSTRATE**

SESI PENGAJIAN: 2016/17 Semester 2

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.).
The members of the supervisory committee are as follow:

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(PROFESOR MADYA DR. JARIAH BINTI MOHAMAD JUOI)

ABSTRAK

Dalam kajian ini, minyak terpakai telah digunakan sebagai pengikat dakwat. Pigmen yang digunakan pula adalah serbuk karbon hitam seterusnya menghasilkan dakwat berwarna hitam. Kompaun dan ikatan bahan yang ada di dalam dakwat telah dikenalpasti dengan menggunakan kaedah FTIR dan dibandingkan dengan dakwat percetakan yang ada di pasaran. Spektrum FTIR dakwat tersebut hampir serupa dengan dakwat di pasaran kerana minyak yang digunakan mempunyai ikatan bahan yang sama dengan dakwat yang berasaskan petroleum. Percetakan skrin sutera digunakan sebagai teknik untuk mencetak dakwat ke atas substrat seramik. Untuk memastikan dakwat itu boleh dicetak menggunakan teknik tersebut, kelikatan dakwat mestilah melebihi 1000 cP. Akan tetapi, dalam kajian ini, kelikatan dakwat gagal untuk mencapai tahap yang sepatutnya kerana beberapa masalah ketika menambah kanji sebagai pemekat ke dalam formulasi dakwat tersebut. Kelikatan dakwat akhirnya kekal pada 200 cP. Tambahan pula, atas tujuan percetakan, logo UTeM telah dipilih untuk dicetak di atas substrat seramik. Dalam pemerhatian visual pada substrat yang telah dicetak, dilihat bahawa dakwat tersebut tidak dapat mengekalkan logo itu selepas dicetak. Hal ini kerana dakwat itu mempunya kelikatan yang rendah mengakibatkan kadar penyebaran yang tinggi apabila dakwat tersebut bertemu dengan substrat. Akhir sekali, untuk mengesahkan ciri-ciri dakwat yang telah dicetak, ujian lekatan telah dilakukan ke atas substrat yang telah dicetak. Selepas ujian tersebut, pengelupasan dakwat daripada substrat telah dikaji dan dilihat di bawah mikroskop optik. Ianya telah dilihat bahawa majoriti kawasan dakwat yang telah dicetak masih terlekat di atas substrat dan dakwat hanya mengelupas di kawasan ianya ditoreh.

ABSTRACT

In this research, waste cooking oil is used as the binder. The pigments for the ink was carbon black powders which resulted in black colored ink. The functional group of the ink was characterized by FTIR and was compared with the commercial ink that uses petroleum-based binders. The FTIR spectra of the ink was recognizably similar to the commercial ink due to the oil having the same functional groups as the commercial inks. Silk screen printing technique was used to print the ink onto the ceramic substrate. To ensure that the ink is suitable for the printing technique, a viscosity of more than 1000 centi Poise (cP) is needed. However, in this project, the viscosity of the ink was not achievable due to some difficulties when adding starch as the thickener to the ink. The viscosity of the ink in this research remained at 200 cP. For printing evaluation, the UTeM logo image had been chosen to be printed on the ceramic substrate. For visual observation of the printed substrate, it was observed that the ink could not retain the image on the substrate. This was due to the low viscosity of the ink resulting in high dispersion of the ink. The low surface roughness of the substrate also contributes to the dispersion of the ink on the substrate. To confirm the properties of the printed ink on the ceramic substrate, adhesion test was conducted. After the adhesion test, the peeling and flaking of the ink from the substrate was observed under an optical microscope. It was observed that most area of the printed ink sticks on the substrate and only peeling occurred at the areas where external force was applied.

DEDICATION

First of all, I dedicate this project to Allah s.w.t., who gave me strength, knowledge and patience in my everyday life.

My respectable supervisor, P. M. Dr. Jariah Binti Mohamad Juoi for her guidance throughout this project.

My beloved parents for being a pillar of strength.

My friends who have supported me through the process.

Not to forget, all the experiences I have went through that were unexpected but also valuable.

ACKNOWLEDGEMENTS

Bismillahirrahmanirrahim. *Alhamdulillah*. Thanks to Allah whom with His will gave me the opportunity to complete my Final Year Project (FYP).

First of all, I would like to express my gratitude to all those who had gave me this possibility to complete this FYP report. I am deeply in debt to my main project supervisor Prof. Madya Dr. Jariah Binti Mohamad Juoi, who taught and exposed me to things that I do not know. Even though she had her schedules packed, she would always slip me in for short meetings whenever I had trouble or had questions regarding my project.

My friends from the Engineering Materials department also supported me throughout this project. I want to thank them for their help, support and valuable suggestions. Last but not least, I would like to give my thousand thanks to everyone especially my families for providing me with unfailing support and continuous encouragement throughout my years of studies and through the process of completing my FYP. This accomplishment would not have been possible without them. Thank you.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

VOC	-	Volatile organic compound
WCO	-	Waste cooking oil
ASTM	-	American Society for Testing and Materials
ANPA	-	American Newspaper Publishers Association
FTIR	-	Fourier transform infrared
GIG	-	Good innovative glass
BHT	-	Butylated hydroxytoluene
cP	-	centi Poise

CHAPTER 1

INTRODUCTION

1.1 Background Study

In this sophisticated era, green issues give the biggest impact to the countries that are currently at the stages of modernization, such as Malaysia that will achieve a state of modern country on the upcoming year of 2020. Through modernization, there will be an increase of constructions, vehicles and even deforesting. All of this will cause air pollution and contribute to the thinning of ozone layer which will then contribute to global warming. Having to reduce these problems and finding an alternative to resolve this problem can be a major impact in any country. It is not only for the sake of safety for the environment, it will also give a high impact to the country's economic issues.

Printing is one of the major steps in any manufacturing industries in Malaysia. It is the basic needs for any manufacturing industry to have, from the initial product preparation to the final packaging of the product, there must be at least one printing process in the production line. Given the large size of the printing practice, it is not surprising that it also generates a significant amount of pollution. The chemicals from the inks are all petroleum-derived. The majority of the chemicals are used as components for printing ink formulations. Toluene is without a doubt the most used chemical, regarding for 75% of all toxic chemicals used in printing. From these petroleum-derived chemicals, silently they will evaporate and cause the emission of volatile organic compounds (VOCs) in the atmosphere ("Volatile organic compounds (VOCs)," 1990).

VOCs are a concern because it can evaporate and room temperature under normal atmospheric conditions. It is a concern due to their reaction with nitrogen oxide in the presence of sunlight. This reaction forms ground-level ozone (O_3). If the concentration of VOCs is high, this ground-level ozone can be harmful to human health. Because of this problem, VOCs are regulated by the 1990 Clean Air Act ("Volatile organic compounds (VOCs)," 1990). Sources of VOCs are typically petroleum-based such as fuel, solvents, paints, cleaning solutions, and as well as inks. Furthermore, exposure to VOCs can harm human health. With short-term exposure, the consequences can be headaches, eye irritations, and nausea. Hence, due to the increasing awareness of volatile organic compound emissions, there have been studies on finding alternatives to substitute petrochemicals to renewable resources.

Through the development of inks, vegetable oil-based inks were created to replace petroleum-based inks. These oil-based ink was proven to reduce the emission of VOC released during printing process. Besides that, materials from renewable resources are frequently used to replace petrochemical ink ingredients. The most successfully used oil-based ink is the soybean oil-based ink. It has been effectively used to print on paper by multiple printing applications such as inkjet printers and lithographic printing. The use of this ink also gives better improvement compared to the original ink.

On the other hand, printing is not only done on paper but other type of surfaces as well, and ceramic surfaces is not an exception. Decoration on ceramic surfaces has become a working field especially in the graphic design and artistry field. The drawback is that this is also a factor to the VOC emission. When vegetable oil-based ink was achieved for printing on paper, little or no study has been done for printing on ceramic surfaces. Therefore, the novelty of this research is to formulate oil-based ink for ceramic substrates.

1.2 Problem Statement

The thinning of the ozone layer gets an attention of all expertize around the world because when the ozone layer becomes thin and decompose from O_2 to O_3, it will give a big impact to the environment such as greenhouse effect. Global warming can cause tones of iceberg melt and increase the level of the sea water and increasing the world temperature. In Malaysia, beside the increasing of transportations and smoke from the industries, the silently evaporation of paints, coatings and inks also contribute to the greenhouse effect especially the ones which has petroleum-based materials as their contents. So that in order to reduce the factors of the greenhouse effect, the paints, coatings and inks industries started to use an alternative component in their formulation. Using vegetable oil-based binders is one of the solution.

Over the recent years, printing ink manufacturers moved toward more sustainable inks. Water-based and UV-curing systems have already started to replace petroleum solvent-based inks which results in a reduction of volatile organic compounds (VOCs) released during printing process. In addition, materials derived from renewable resources are now more frequently used to replace petrochemical ink ingredients such as polymeric binders. The development of vegetable oil-based inks is already a success and are now applied in many printing industries especially in the news letterpress. However, this type of ink is only done on paper as the substrate but not on ceramic substrate.

Ceramic decoration is now becoming a trend through the years. Porcelains, clays, windows, glasses and tiles are being decorated as part of household decorations, tourist attractions, art exhibitions and many more. These ceramic surfaces are being printed on and painted on with the petroleum-based inks. Therefore, because if this, this research is carried out in order to introduce a new idea in the printing of ceramic surfaces. The idea is by using vegetable oils as the binders for the ink replacing the petroleum-based binders. This will reduce the fact that printing ink on ceramic substrate contributes VOCs emissions.

The idea to this project is that, printing ink is one of the factors contributing to the volatile organic compounds (VOCs) emissions and waste cooking oil has an issue about its disposal. In order to improve this situation, the waste cooking oil will be reused as a binder component of the ink to replace the petroleum-based inks. Transesterification of the waste cooking oil is the crucial part of this thesis as well as the ratio between oil, solvent, pigments and additives since it might be different if using vegetable oils. The rheological properties of the ink are also important for the ink to be printable onto the substrate and binds and become inseparable from the substrate, which is a ceramic surface. With the correct process, the production of the green printing ink for ceramic substrate can be achieved.

1.3 Objectives

The objectives of this project are:

i. To study the effect of waste cooking oil in the formulation of printing ink.

ii. To determine the properties of green printing ink for ceramic substrate.

1.4 Scope of study

The main focus of this research is to formulate a green printing ink for ceramic substrates. The 'green' content from this project is waste cooking oil (WCO).

Firstly, the sample WCO was prepared by visual inspection to remove any contaminants such as scraps of foods from the cooking process. Then, it was used as a binder for the ink. The formulation for the ink is important because the different amount of binders, solvents, pigments and additives would give different effect to the final product of the ink and will affect the physical properties and binding behavior between the ink and the substrate.

This project discusses and introduces the processing of the ink based upon the formulation of the soybean oil-based printing inks.

1.5 Significance of study

The study of formulation of green printing ink for ceramic substrate can be a revolution in decoration of ceramic surfaces in the industry as well as crafts and graphic design field. This study will also contribute to reduce negative environmental impact thru reducing the VOCs emission. Hence, inks for ceramic surfaces will not give rise to the harmful emission anymore. Furthermore, the properties of oil-based inks give similar and as well as improved quality compared to the original petroleum-based inks. If the ink is applied onto a ceramic surface, the image and color production might also give a better resolution despite it has to be fired in very high temperatures. With the creation of green printing ink, it can be added to another list of green technology creation in the country.

1.6 Summary

The objectives of this research is to formulate printing ink from waste cooking oil and to determine the properties of the ink for the application on ceramic substrate. The objectives were obtained from the problem statement and findings from previous studies. The objectives will be achieved by the characterization of the ink and the properties of the ink once it binds to the substrate. Therefore, if the results are positive, the formulation of green printing ink for ceramic substrate can be achieved.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews on the basics of printing inks, vegetable oil-based inks and printing on ceramic surfaces. In describing inks components, composition and properties of inks was included and the derivation of inks from vegetable oils from previous researches was included. Inks and printing techniques for ceramic surfaces is also studied as to narrow down the scope of study.

2.2 Printing Inks

Printing ink means printable materials with definite color rendering power (Griebel *et al.*, 1996). Ink basically contains colorants which are either pigments or dyes, binders, solvents and additives. Pigments to add color, binders which is also called resins or polymers to disperse the pigments and carry the ink to the substrate and bind it there. The binders usually have to be dissolved in the solvent, and the solvent can be water-based or solvent-based. However, solvents may not be present in the ink formulation, which depends on the nature of the binder used (Pekarovicova & Husovska, 2016). The topic in the following explains the basic components in a printing ink formulation.

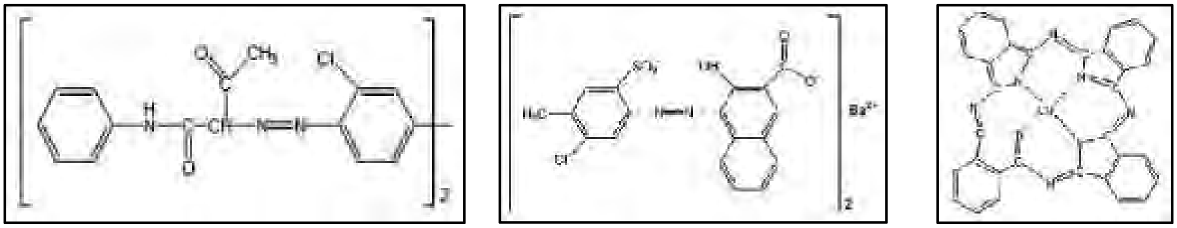
2.2.1 Colorants

Colorants is the substance that color the ink and make it opaque (Ahmed, 2007). In the printing ink formulation, this substance can be either pigment or dye. According to (Pekarovicova & Husovska, 2016), pigment is a material that is not soluble in its binder but creates dispersion of small particles less than one micron in size. On the other hand, dye is soluble in its vehicle.

Pigments can be categorized into two groups, inorganic and organic pigments. Inorganic pigments are generally cheaper and they do not provide as saturated color as organic pigments, and they may be more abrasive than organic pigments. In contrast, organic pigments are synthesized from petroleum, natural gas, or carbon-containing raw materials (Pekarovicova & Husovska, 2016). For every printing technique, the same pigment chemistries are used. Table 2.1 shows some common inorganic pigments used in printing inks and Figure 2.1 shows the example of inorganic pigments.

Table 2.1: Common inorganic pigments (Clark, 2008).

Inorganic pigments	Production	Advantages	Disadvantages	Color(s)
Carbon black	Decomposition of carbonaceous matter	High strength, good color, light and weather resistant	Thickens paint	Black
Titanium dioxide	Synthesized	High strength, high opacity, cheap, good UV resistace	Forms radicals that degrade the binder	White
Iron oxides	Mined although can be synthesized	Light and weather resistant, unreactive	Cannot produce clean shades	Yellow, red, brown, black
Azurite ($Na_7Al_6Si_4O_{24}S_2$)	Kaolin (Na_2CO_3), Sulphur and carbon heated together above 800˚C	Rich colors	Fades on contact with acid	Blue



(a) (b) (c)

Figure 2.1: (a) Diarylide yellow ($C_{32}H_{26}C_{12}N_6O_4$)/Pigment yellow (PY 12), (b) Barium and calcium salts of rubine red/Pigment red (PR 48:1), (c) Copper phthalocyanine ($C_{32}H_{16}N_8Cu$)/Pigment blue (PY 15) (Pekarovicova & Husovska, 2016).

The particle size of the pigment is very important. As the particle reduces, the color intensity (strength) of the pigment increases and gives better range in color and viscosity of the ink. Essentially, the opacity peaks around a particle size off 0.3µm (Ahmed, 2007). Besides that, for the pigment to be effective, it has to be evenly dispersed in the solvent and in contact with the binder. For the pigment to be in contact with the binder, this layer has to be displaced and this displacement is known as wetting. If a pigment is not properly wetted, it may result in color streakiness, therefore solvents and pigments must be chosen properly to result in a well wetted pigment. To improve the wetting properties between the pigment and binder, wetting agents are used (Clark, 2008).

2.2.2 Binders

From (Griebel, Kocherscheid, & Stammen, 1996), it was stated that printing inks are made up from polymers as binding agents for the pigments within the ink. It was said that from the German disclosure DE 2534845/A1 revealed that unblended thermoplastics are to act as binders in ink with softening temperature from 90˚C to 140˚C. However, thermoplastics are characterized by their high ranging softening temperatures. Therefore, the published type of ink came down to a printable viscosity at very elevated temperatures only, which were not accessible in printing business.