SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT ZINC PHTHALOCYANINE PIGMENTS AND ITS COMBINATION PIGMENT WITH MICA TITANIA PIGMENT

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT ZINC PHTHALOCYANINE PIGMENTS AND ITS COMBINATION PIGMENT WITH MICA TITANIA PIGMENT

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In the present work, zinc phthalocyanine and tetra nitro substituted zinc phthalocyanine were sytnhesized by using phthalic anhydride and nitro phthalic acid precursor respectively under microwave irradiation. Molecular structures of these pigments were confirmed by FT-IR and UV-visible spectroscopy analyses. Furthermore, these pigments were deposited on mica-titania pigment substrate in dimethyl formamide solvent to obtain the combination pigment. FT-IR analysis was conducted to analyze the deposition of pigments onto the mica-titania surfaces. Fluorescence spectroscopy analysis was performed to observe zinc phthalocyanine, tetra nitro zinc phthalocyanine pigments, and their combination pigment with mica- titania pigments. The surface morphologies of zinc phthalocyanines on the mica titania pigments were investigated by scanning electron microscopy. Optimum deposition temperature and deposition time were determined by depositing varying amounts of zinc phthalocyanines. The paint samples of these combination pigments were prepared by alkyd based paint formulation. L*a*b* values of the paint samples were determined by color measuring spectrophotometry. The optimum deposition temperature was determined as 120 ^{o}C and the optimum deposition time was determined as half an hour and effective deposition was obtained at 120 °C. It is observed that, with the increasing amount of ZnPc, the interaction between ZnPc particles increases and they desorp the surface of mica-titania pigment. The best result was obtained with 0.08 g ZnPc at 120 ^{o}C.

Key words: mica, titania, zinc phthalocyanine, fluorescence, combination pigment.

ÖZ

FLORESANS ÇİNKO FTALOSİYANİN SENTEZLENMESİ; ÖZELLİKLERİNİN BELİRLENMESİ VE MİKA TİTAN PİGMENTLE BİRLEŞİM PİGMENTİ

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Bu çalışmada, çinko ftalosiyanin ve tetra nitro çinko ftalosiyanin pigmentlerinin sentezlenmesi mikrodalga ortamında ftalik anhidrit ve nitro ftalik asit öncülleri kullanarak gerçekleştirilmiştir. Elde edilen pigmentlerin moleküler yapıları FT-IR ve UV-Visible spektroskopi analizleri ile incelenmiştir. Mika- titan pigmentiyle çift bileşenli pigment elde etmek için, bu pigmentler dimetilformamit çözücüsü içeirsinde mika-titan üzerine çöktürülmüştür. Çöktürme deneylerinin sonuçları için FT-IR analizi gerçekleştirilmiştir. Çinko ftalosiyanin pigmentlerinin ve onların mika-titan ile oluşturdukları çift bileşenli pigmentlerin floresans özelliklerini incelemek için Floresans spektroskopi analizinden yararlanılmıştır. Mika-titan üzerindeki yüzey morfolojileri ise SEM analizi ile incelenmiştir. En uygun çöktürme sıcaklığı ve süresi, farklı miktarlarda çinko ftalosiyanin kullanılarak belirlenmiştir. Alkit esaslı boya örneğinde kullanılan bu pigmentlerin, L*a*b* değerleri ölçülmüştür.

Çift bileşenli pigment için en uygun çöktürme sıcaklığı 120 °C olarak, ve en uygun çöktürme reaksiyon süresi yarım saat olarak belirlenmiştir. Farklı miktarlarda ZnPc kullanılarak elde edilen çift bileşenli pigmentlerin floresans ölçümleri yapılmış ve ZnPc miktarının artmasıyla, ZnPc parçacıkları arasındaki etkileşimin arttığı ve bu yüzden mika- titan yüzeyini terkettikleri gözlemlenmiştir. Mika-titanın floresans etkisiyle birlikte ZnPc lerin de floresans etkilerinin arttığı, 120 °C de 0.08 g ZnPc kullanılarak elde edilen çift bileşenli pigmentte görülmüştür.

Anahtar Sözcükler: mika, titan, çinko ftalosiyanin, floresans, çift bileşenli pigment.

To Remziye - Kenan Kahya and my nephew Türker Emir Bek

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LIST OF SYMBOLS AND ABBREVIATIONS

DBU	1,8- Diazabicyclo[5.4.0]undec-7-ene
SEM	Scanning Electron Microscopy
UV-Vis	Ultraviolet - Visible
XRD	X-Ray Diffractometer
ZnPc	Zinc Phthalocyanine
TNZnPC	Tetranitro Zinc Phthalocyanine
ZnPcMT	Zinc Phthalocyanine Deposited Mica Titania Pigment
TNZnPcMT	Tetranitro Zinc Phthalocyanine Deposited Mica Titania Pigment

CHAPTER 1

INTRODUCTION

Research in the field of pigments has been continuously increasing. Such studies deal with the development of not only new types of pigments, but also different synthesis methods. Fashion, automotive, and other consumer markets especially are looking for special effect like angle- dependent color. Illusion of optical depth, eye-catching effect of angle dependent color, and ability to imitate the effect of natural pearl are the advantages of special effect pigments [1].

Phthalocyanines are macrocyclic compounds that contain 18 π electrons in their structures. They have been extensively studied because of their physical properties. Phthalocyanines, containing unsubstituted or substituted functional groups in their peripheral or non peripheral positions, are generally used as commercial dyes and pigments [2]. Molecular structure of phthalocyanine is given in Figure 1.1.

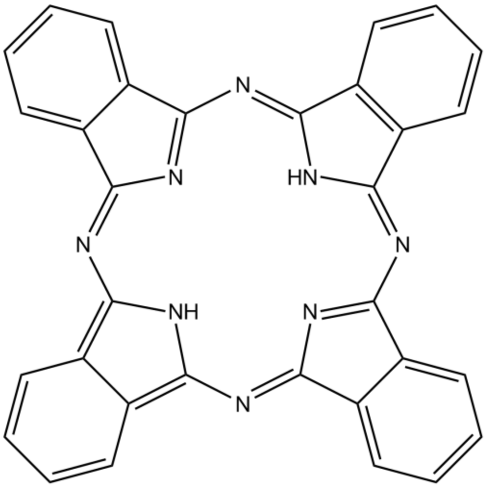


Figure 1.1 Molecular structure of phthalocyanine.

Besides introducing functional groups into the peripheral or non- peripheral positions , H ions in the middle of the structure can be replaced with different metal ions to improve physical properties. This type of phthalocyanine is called as metallophthalocynine and new properties directly depend on the metal type. Figure 1.2 shows the molecular structure of metallophthalocyanine, and M represents a metal.

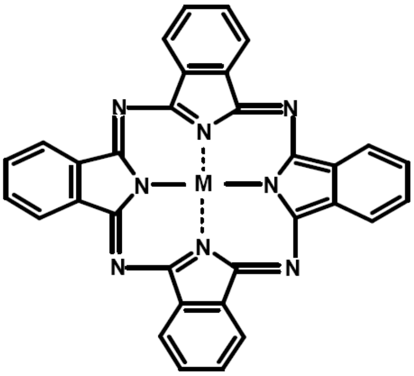


Figure 1.2 Molecular structure of a metallophthalocyanine; M represents a metal.

Metal free, unsubsituted or unsubstituted metal phthalocyanines can be synthesized by different preparation methods. Introducing functional substituents to the periphery or metal ion into the cavity bring different properties to the phthalocyanines and because of that they have drawn interest for different applications.

Phthalonitrile, phthalic anhydride, phthalic acid, and phthalimide are precursors for synthesizing metallophthalocyanines by cyclotetramerization. Moreover, metal free phthalocyanine can also be used to synthesize metallophthalocyanines with a metal source. Phthalonitrile gives higher yields than the other precursors that need additional nitrogen donor, such as urea due to lack of nitrogen in their structure. Because of these characteristics, undesired side reactions may happen. However, generally phthalic anhydride is preferred in the industry because of being an economical precursor [3]. Substituted phthalocyanines can be obtained directly from substituted precursors as starting materials or can be converted to another molecule during the reaction.

In conventional methods, synthesis reaction occurs in high boiling solvent mediums at high temperature. In the last decade, microwave irradiation has drawn special interest in organic synthesis [2, 4]. Microwave was also applied to systems under solvent free conditions [5]. Microwave irradiation provides rate enhancements and improves yields by reducing the reaction time and energy input [4].

This study aims the synthesis of zinc phthalocyanine and tetra nitro substituted zinc phthalocyaniney by microwave irradiation in solvent free conditions.

Having organic nature brings the property of being small particle size but this property creates dispersion problems for phthalocyanines pigments. They tend to agglomerate in solvent medium and this makes phthtalocyanines rather unstable. Combining these pigments with pearlescent pigments can eliminate this problem. Coating mica-titania pigments with an additional layer of organic colorant can be used to obtain such combination pigments. Phthalocyanines, quinacridones, perylenes, dioxazines, and carbon black can be used as organic pigments for this purpose.

In the literature there are few studies reported on preparation of combination pigments that not only includes complex steps and components, but also are time consuming. For example, to disperse pigments in solution milling was applied or some preparation methods were firstly applied to some compounds to obtain compatible pigment.

The objective of this study is to synthesize zinc phthalocyanines and tetra nitro substituted zinc phthalocyanines pigments that have fluorescent effect by using microwave method under solvent free conditions. Actually, zinc phthalocyanine has been used as photosensitizer, in solar cells and photodynamic therapy of cancer. However, it is used as colorant for paint applications in this study. Obtaining combination pigment between these fluorescent phthalocyanine pigments and mica-titan pigment is also the scope of this work. Dispersion of phthalocyanines pigments was achieved in DMF, and simple stirring of these pigments with mica-titania pigments gave combination pigments. Different amounts, temperatures, and reaction periods were used to optimize combination conditions. Color properties of these pigments were determined in alkyd base paint formulations.

CHAPTER 2

LITERATURE REVIEW

Properties and synthesis methods of phthalocyanine pigments, and their combination with mica-titania pigment, and relevant studies found in the literature are described in this chapter.

2.1 Effect Pigments: Types and Properties

Pigments that include lustrous, iridescent, and angle- dependent optical effects are known as effect pigments and these effect pigments can be used for functional purposes such as security printing or optical filters, for decorative or cosmetic applications or car paints.

Angle- dependent optical effects cannot be copied with copy machines or photographic techniques and this property of effect pigments brings an advantage in security field. Pearlescent and optical multilayer pigments are used on banknotes in many countries.

Illusion of optical depth, eye catching effect, and ability of easy parallel orientation of a multitude of platelet like particles are the advantages of effect pigments for decorative applications [1].

Effect pigments can be divided into two main groups; they can be substrate-free or substrate based. Former one consists of basically one optically homogeneous material, and in the latter, the substrate can be coated with a metal oxide layer. Aluminum or copper- zinc platelets pigments are well known metal effect pigments. Orientation of metal flakes, the particle shape, presence of other colorants, and binder matrix’s transparency affect the metallic appearance. Single crystalline BiOCl or polycrystalline TiO_2 in flaky shape also belongs to this substrate free group. To achieve a certain interference color, these non metallic flakes should be very thin and because of that their mechanical stability is low [1].

Substrate based effect pigments were developed as the mechanical support of an optical thin layer. Substrate based effect pigments are typically produced by the deposition of metal oxide layers on the substrate in aqueous suspension followed by a calcinations process. Flaky materials, including mica platelets, alumina flake and silica flakes can be used as substrate for pearlescent pigments. The most important optical layers consist of titania, iron(III) oxide, mixed titanium- iron oxide, silica and chromium(III) oxide [1].

Pigment particles with natural pearl essence, or crystalline organic platelets consisting of purines guanine and hypoxanthine, the crystals are found in fish scales and fish skin can be used to meet necessary requirements of pearlescent pigments. For synthetic ones, titanium dioxide coated mica, ferric oxide coated mica, bismuth oxychloride and basic lead carbonate are used [6].

2.1.2 Mica Titania Pigments

2.1.2.1 Properties

Mica based effect pigments are produced by coating mica with a metal oxide layer. Titanium dioxide is mostly used metal oxide, $TiOSO_4$ (by homogeneous hydrolysis) or $TiOCl_2$ (titration method) are used as precursor for manufacturing titanium dioxide- mica pigments. Rutile phase or anatase phase can be coated on mica surface [1]. However, rutile is preferred because it is thermodynamically more stable phase, and also, the refractive index of rutile (2.903) is greater than that of anatase (2.488). Therefore, the rutile form TiO_2 coated mica have better luster and reflectivity, color and color homogeneity [7]. Thickness of the coated TiO_2 layer is an important factor for interference color and reproducible manufacture. The layer that is 50 nm thick produces a silvery iridescence and with the increasing thickness iridescence is changed through yellow, red, blue and green. SEM micrograph of mica-titania pigment is given in Figure 2.1.

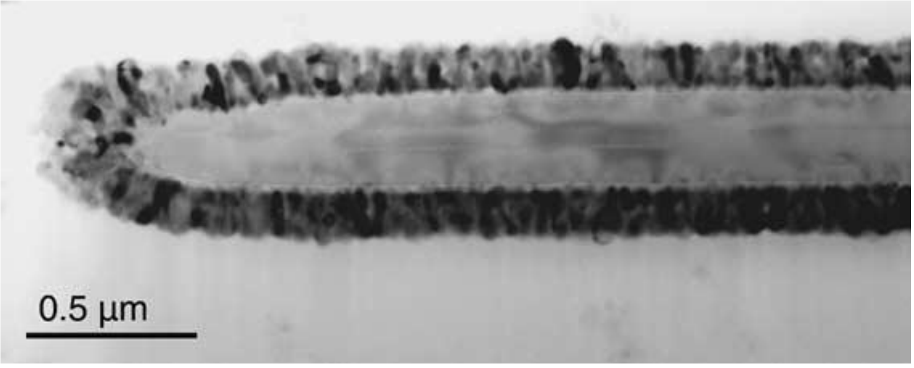


Figure 2.1 SEM micrograph of mica-titania pigment [1].

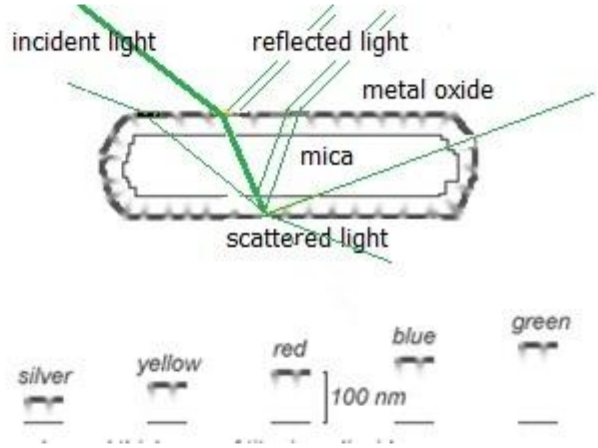


Figure 2.2 Optical representation of mica pigment coated with TiO2 [8].

Optical representation of titania coated mica pigment is shown in Figure 2.2. In metallic pigments, pigment particles reflect all incident light in one direction. However, pearl luster pigments reflect only part of the incident light some part of the light enters into the transparent particles and is partially reflected either at the interface within the pigment or at the bottom of the platelets. The internally reflected light leaves the platelets leading to interactions with adjoining pigment particles to create further reflections. The partial reflection of light and optical superimposition create interference phenomena, which together with multiple internal reflections lead to the characteristic appearance of pear luster pigments [9].

2.2 Phthalocyanines

2.2.1 Types and Properties

Phthalocyanines have macro-cyclic ring structures that contain 18 π electrons known with their electron transfer abilities. Metal free phthalocyanines contain H atoms in the center, while metal ions are inserted in their central cavity for synthesizing metallophthalocyanines. Nature of metal ions gives different properties to the phthalocyanines. Moreover, 18 π electrons in their structures are responsible from electron transfer reactions and peripheral or non-peripheral substituents [10]. Variety of these changes provide broad application areas such as electronics, opto-electronics, and photonics [11]. They are mostly used in coating industry as dye material [12]. This π conjugated system brings high absorption bands in the visible region. Their chemical and thermal stability (up to 900 ^{o}C) [13], and the presence of π- π^* transitions in the near UV/visible/near- IR region extend their usage to high-tech fields that includes semiconductor devices, photovoltaic solar cells, electrophotography, rectifying devices, molecular electronics, Langmuir-Blodgett films, electrochromism in display devices, low dimensional metals, gas sensors, liquid crystals, nonlinear optics, photodynamic reagents for cancer therapy and other medical applications and electrocatalytic reagents [14].

The main problem the researchers are faced is their aggregation tendency in solution because of molecular interactions between the macrocyclic rings. This problem limits their usage or causes diminishing of the properties in application steps. Substituted groups in peripheral or non-peripheral positions influence the properties, long alkyl, alkyloxy, alkylsulfonyl or bulky apolar groups facilitate their solvation in organic solvents, while sulfo, carboxylic acid or ammonium groups are effective for solubility in aqueous media [15].

2.2.2 Synthesis Methods

Metal phthalocyanines are the reaction product of phthalonitrile with a metal or metal salt. Different precursor like phthalic anhydride or phthalic acid, phthalimide can be used for cyclotetramerization reaction but they require additional nitrogen source like urea. In addition to these synthesis methods, they are also obtained by the reaction of o-cyanobenzamide with a metal or the reaction of metal free phthalocyanines with a metal salt. Figure 2.3 shows the different precursors for synthesis of metallophthalocyanines. Phthalonitrile provides a clean reaction and at the end of the reaction, pure phthalocyanines are obtained. However, the same is not valid for other precursors as the additional nitrogen source may cause side reactions, and some by- products may be obtained. Phthalic anhydride is the most commonly used precursor because of its low cost [16].

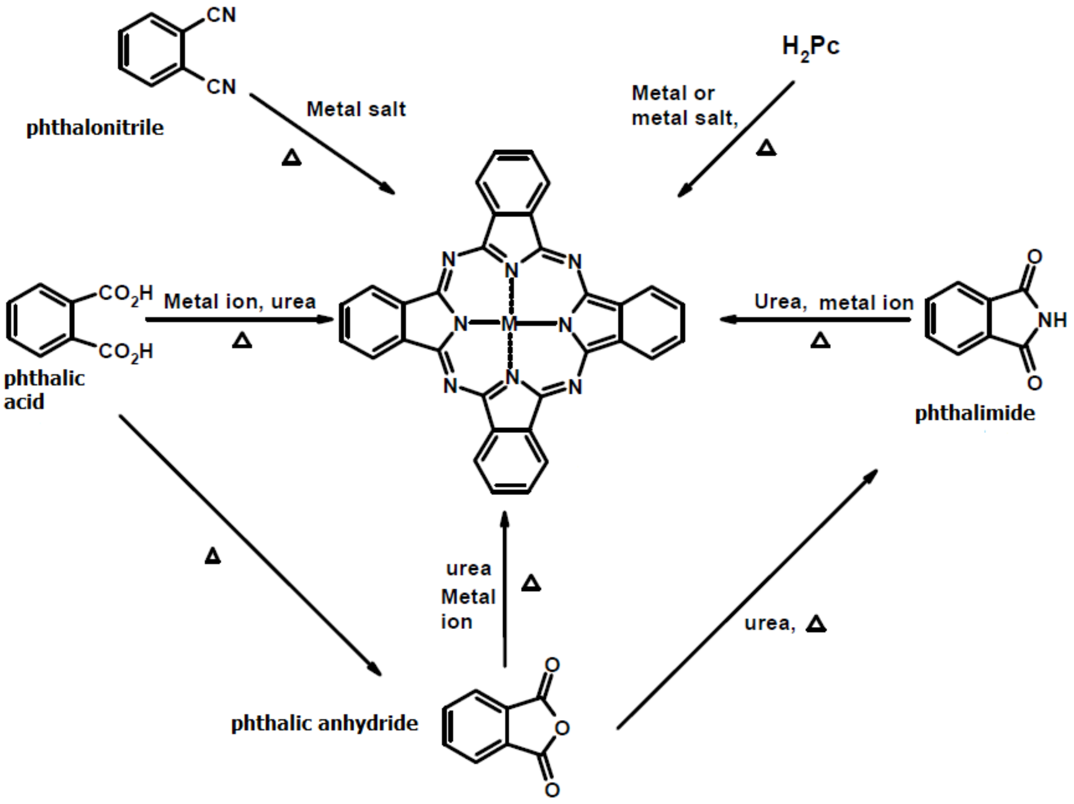


Figure 2.3 Metal phthalocyanines synthesis from different precursors [3].

In conventional method, phthalocyanines can be synthesized in high boiling solvent medium such as nitrobenzene, trichlorobenzene, dimethyl formamide (DMF), dimethyl sullfoxide (DMSO), or quinoline, and ammonium molybdate is the most effective catalyst in this synthesis [3].

In recent years, microwave irradiation is used as an alternative synthesis method for most organic synthesis processes and it has drawn attraction because of providing less reaction times, decreasing the usage amount of non volatile organic compounds, and high boiling solvents. Decreasing the high energy input and being clean are other advantages of microwave irradiation. In this method heating is delivered by microwave radiation and is distributed by conduction through a container containing the solution in traditional method. Microwave motion is distributed by polar forces and because of that water is used as the reaction medium. Usage of water also allows the metallic salt diffusion in redox process and the melted phase allows also the diffusion of the necessary salt for the course of the reaction, and thus, precursor can be used in excess.

Erdoğmuş studied substituted zinc phthalocyanines synthesis under conventional conditions. Firstly, 4-nitrophthalonitrile was substituted with phenol derivatives in DMF. For this substitution, the mixture was stirred for 30 min at room temperature; then K_2CO_3 was added to the system in portions in a time period of 4 hours. Under argon atmosphere, stirring was continued for another 24 h at room temperature. At the end of this period, the mixture was poured into a container containing 400 mL ice water. The precipitate was filtered off, washed with water and methanol, and then, dried. Methanol was used for re-crystallization and the final product was obtained after drying in oven [17].

Cui et al. synthesized zinc phthalocyanines complex in DMF under traditional conditions. They used high boiling solvents like 1-chloronaphthalene, nitrobenzene, and 1,2-dichlorobenzene. For the synthesis phthalic anhydride method was used, after stirring the mixture of phthalic anhydride, urea, zinc dichloride and ammonium molybdate for about 1 h, it was sealed in an autoclave and heated at 200 ^oC for 3 days under autogenous pressure. Purification step included washing with HCl and extraction for 24 h. Finally, the complex was re-crystallized in DMF, and $[ZnPc(H_2O)]$.2 DMF complex was obtained. In this study, they obtained zinc phthalocyanines complex after synthesizing zinc phthalocyanines, by using the traditional solvent method which requires long process time [18].

Requiring long process time, and high boiling solvents, that are harmful for the environment, are disadvantages of organic synthesis and in the last decades microwave irradiation was used as an alternative. This alternative process includes two steps, appropriate phthalocyanines precursors were prepared and followed by cyclotetramerization [4].

Csokai et al. prepared phthalonitrile derivatives as phthalocyanines precursors which was followed by cyclization under microwave conditions. In their experiments, microwave equipped with a rotating pyrex glass reactor which also includes power control mode was used. Cyclization of phthalonitrile derivatives to phthalocyanines occurred with anhydrous Zn(OAc) in 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) in 3-5 mins. After cooling the reaction product, it was precipitated in MeOH and purified by column chromatography. By this way, they obtained substituted phthalocyanines under microwave conditions; however, they started with an expensive precursor, phthalonitrile [4].

Seven et al. studied microwave synthesis of metal free phthalocyanines. They started with 4-nitrophthalonitrile, after reacting with dimethyl phenol derivatives, cyclotetramerization occurred using Li as catalyst and n-pentanol as solvent. Reaction mixture was subjected to microwave irradiation at 440 W power for 10 mins. For purification acetic acid was added, after solvent removing, column chromatography was used. For comparison, they; also used conventional method, phthalonitrile precursor was dissolved in n-pentanol, and heated under argon atmosphere after addition of Li the reaction was continued for 24 h and similar purification steps were followed. They concluded that, microwave irradiation is more effective, faster and energy efficient system [19].

Shaabani et al. synthesized metal free and metallophthalocyanines complexes of Cu, Co, Ni, Zn, Pd, Pt, and Ru. For metal free phthalocyanine phthalonitrile, as a phthalocyanines precursor, as catalysts hexamethyldisilazane (HMDS), and $(NH_4)_2SO_4$, as solvent DMF, were irradiated. After filtering, the recovered solid product was washed with methanol and dissolved in sulfuric acid. It was then poured into water and precipitated, then filtered and washed with distilled water and dried in oven. For further purification, it was extracted with methanol. To obtain metallophthalocyanines different phthalocyanines precursors were used namely phthalonitrile (PN), phthalimide (PI), and phthalic anhydride (PA). HMDS and paratoluen sulfonic acid (p- TsOH) were used as catalyst. This time, the obtained crude product, was washed with cold water and acetone. After drying, sulfuric acid was used to dissolve it and precipitate from distilled water. UV-Vis and FTIR spectrometry results confirmed that metal free phthalocyanine and different kinds of metallophthalocyanines were obtained by this microwave method [20].

Shaabani studied microwave method under solvent free conditions by using phthalic anhydride as starting material. In this study, Cu, Co, Ni and Fe phthalocyanine complexes were prepared in dry media conditions in which no solvent used. 900 W power was used for microwave irradiation. Phthalic anhydride, urea, copper chloride, and ammonium molybdate mixture was irradiated for 6 min. To purify, reaction product was washed with 5% caustic soda, water, 2% HCl and water respectively. Re-crystallization was applied from H_2SO_4, and finally methanol and methylene chloride were used for extraction. In this study, no solvent was used, but it is known that to provide the energy transfer to the raw materials requires a polar medium and this can be achieved by using water as the reaction medium [21].

Jung et al. synthesized Cu, Mn, Al, Co and Zn phthalocyanines under solvent free conditions in microwave. Phthalic anhydride, urea and metal chloride were the raw materials and ammonium molybdate was the catalyst. Reaction flask was equipped with a thermocouple, a reflux condenser and a motor- driven stirrer. After heating to 120 ^{o}C with a heating rate of 5 ^{o}C /min, it was heated to 170 ^{o}C and 230 ^{o}C with a heating rate of 2^{o}C/min. The system was maintained at those temperature ranges for 0.5 to 4 hours while stirring continuously. Product was washed with methanol, filtered, acid treated with sulfuric acid, alkali treated with NaOH, and then, washed with water until the solution became neutral. After filtration, it was dried at 105 ^{0}C. SEM pictures revealed that different kinds of metal phthalocyanines showed different morphologies due to different reactivity of metal chlorides [5].

Villemin et al. synthesized different metallophthalocyanines (Mg, Zn, Cd, Cu, Ni, Pd, Pt, Co, Fe, Ru, Rh, Ti, Cr, Mn, V, Mo, UO_2, Eu) by using microwave method. Moreover, modified microwave oven for dry reactions was also used for synthesizing. The results obtained were compared with the conventional microwave method results. As starting materials phthalodinitrile and tetrachlorophthalic anhydride were used. Firstly, metallophthalocyanines were synthesized directly from phthalodinitrile and hydrated metallic salt which does not only provide activation of the raw materials but also help diffusion of the metallic salt without using organic solvent by using commercial microwave for 5 to 15 minutes. Product was washed with water, acetone and dichloromethane and dried under pressure. Extraction step was applied with acetonitrile and dried at 110 ^{o}C. Similar experiments were also conducted for the phthalic anhydride case. However, this time only Fe, Co, Cu phthalocyanines chlorides were obtained. In these experiments, urea was also added to the system as a nitrogen source and the final product was washed with 1M HCl, and then, neutralized with 1M NaOH and finally washed with water. Similar extraction step was applied and then the product was dried. UV-Vis and FTIR spectroscopy results showed that metallophthalocyanines were obtained in all cases but modified microwave which was equipped with a mixing unit and rotary evaporator gave the best yields [22].

Shaya studied microwave irradiation method for synthesis of hexadeca substituted zinc phthalocyanines and related unsymmetrical derivatives. Phthalonitrile derivatives were firstly prepared by substitution with phenolic compounds, and then, they were mixed with zinc acetate dehydrate and a catalytic amount of DBU in n-hexanol. This mixture was heated to 140 ^{o}C with reflux for 12 h under argon atmosphere with stirring. After cooling to room temperature, solvent was removed. Column chromatography was finally applied to purify the final product [23].

Idowu and Nyokong studied tetra substituted zinc phthalocyanine derivatives for photophysical and photochemical applications. They started from phthalonitrile derivatives and for phthalocyanines, they used cyclotetramerization method. Zn(OAc) was used as the metal source and phthalonitrile derivatives were mixed with it. Reaction was carried under N_2 atmosphere for 18 h that was followed by cooling to room temperature. To precipitate the product MeOH:H_2O mixture was used, and the product was filtered off and washed with water [24].

Cong et al. investigated the UV-Vis spectra of peripherally substituted tetranitrometallophthalocyanines (TNMPcs) and non-peripherally substituted TNMPcs. These different substitutions cause two kinds of Q bands. By different substitution, phthalocyanine properties could be controlled. TNMPcs were synthesized from 4-nitro-o-phenyleneimine and 3-nitrophthalic anhydride. Their UV-Vis spectra were recorded. Results showed that Q band splitting into two and this splitting occurred because of isomers or dimers. Variety of substitution of nitro group gave different electronic effects on Pc rings and this was observed from UV-Vis analysis results [25].

Shaabani et al. synthesized Ni,Cu, Co, Mn, Fe, Pd tetranitro phthalocyanines complexes under solvent free and reflux conditions. 3-nitrophthalic anhydride, urea, metal chloride and ammonium heptamolybdate were irradiated in microwave for 1 min at high power and then for 1 min at medium power. After grinding the product, it was boiled with 1 M HCl, filtered and washed with water until the solution was neutral. Similar steps were applied with 1 M NaOH, and this time solid material was stirred in methanol, filtered and dried. In reflux synthesis, same raw materials were suspended in nitrobenzene in a round bottom flask with a condenser. After irradiation in microwave at high power for 5 min, obtained product was filtered and washed with methanol and purified as described previously. Elemental analysis, UV-Vis and IR results confirmed formation of phthalocyanines [26].

Alzeer et al. studied tetranitro zinc phthalocyanine under conventional conditions. For the synthesis, 4- nitrophthalic anhydride, urea, zinc chloride and ammonium molybdate were used in nitrobenzene under nitrogen atmosphere at high temperature, 185 ^{o}C. Reaction was continued for 4 h, and then the solution was cooled and diluted with toluene. Centrifugation was applied to collect the precipitate; the final solid product was washed with toluene, water, MeOH/ether, EtOAc/hexane and dried [27].

Lokesh et al. studied microwave method for synthesis of platinum tetranitro phthalocyanine. As phthalocyanines precursors, nitrophthalonitrile was chosen and it was mixed with platinic(IV) chloride. 540 W irradiation was applied for the first 2 minutes, and then, power was increased to 720 W for 3 mins to complete the reaction. Water and ethanol were used to wash the crude product, and extraction was applied with acetone. Finally, it was dried in oven at 45 ^{o}C [28].

Liu et al. studied microwave irradiation to obtain zinc phthalocyanines complexes with porphyrin. As starting material phthalonitrile and its derivatives were used and the reaction was performed in DBU [29].

2.3 Fluorescence

Luminescence is the term to describe the process in which electronically excited molecules emit a light. Depending on the nature of the excited state, it is divided into two categories, fluorescence and phosphorescence. If the excited electron is paired to the second electron which is in the ground state orbital by opposite spin, molecules emit a photon when returning to the ground state. This process is called as fluorescence and typical fluorescence lifetime is near 10 ns (10^{-9} s). In phosphorescence mechanism, light emission occurs from excited triplet state. In this excited state, electron is paired to the second electron by same spin. Unlike the fluorescence mechanism, transitions to the ground state are forbidden and because of that emission related to that, lifetimes are longer than the former one, they are typically milliseconds to seconds [30]. Schematic representations of ground state, excited singlet state and excited triplet state are given in Figure 2.4.

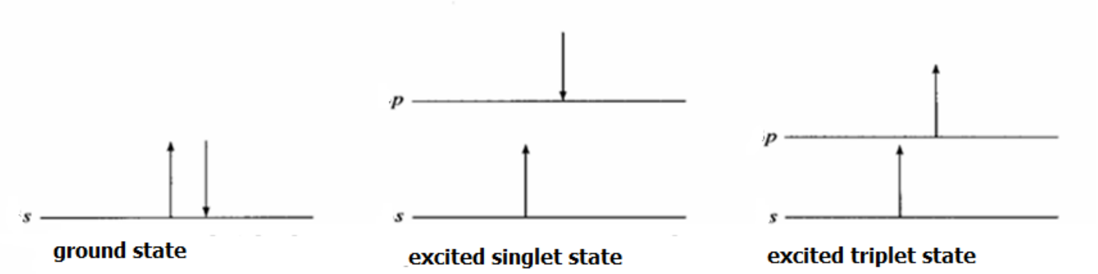


Figure 2.4 Schematic represantations of ground state, excited singlet state and excited triplet state.

Fluorescence occurs generally in aromatic molecules which have conjugated π electrons in their structures. To investigate the spectroscopy of a molecule, emission spectrum of it is plotted by fluorescence intensity versus wavelength (nm) or wavenumber (cm^{-1}). Emission spectra change with the chemical structure of the molecules and the solvent used for solvation. Typical absorption and emission spectra of two molecules are given in Figure 2.5 [30] .

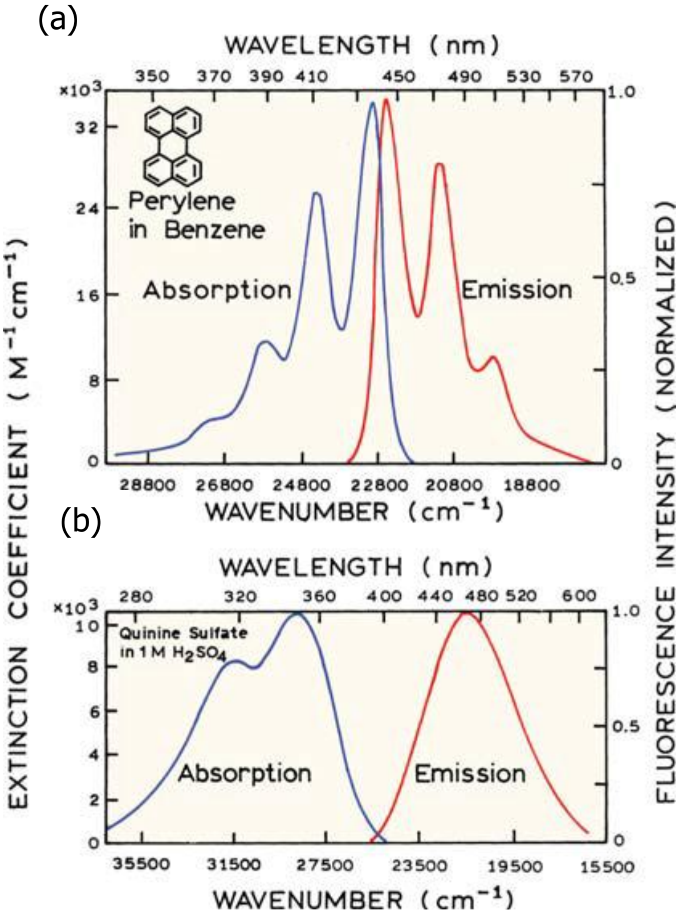


Figure 2.5 Absorption and fluorescence emission spectra of (a) perylene and (b) quinine sulfate. Emission spectra cannot be correctly presented on both the wavelength and wavenumber scales. The wavenumber presentation is correct in this instance (See reference [30] for details.).

To illustrate absorption and emission processes, Jablonski diagram which is given in Figure 2.6 is used. It represents the processes that can occur in the excited state. S_0, S_1, and S_2 represent the ground, first and second electronic states, respectively and these are shown in the figure with bold black thick lines. Furthermore, every electronic state has own vibrational levels and these are shown in the figure with thin gray lines.

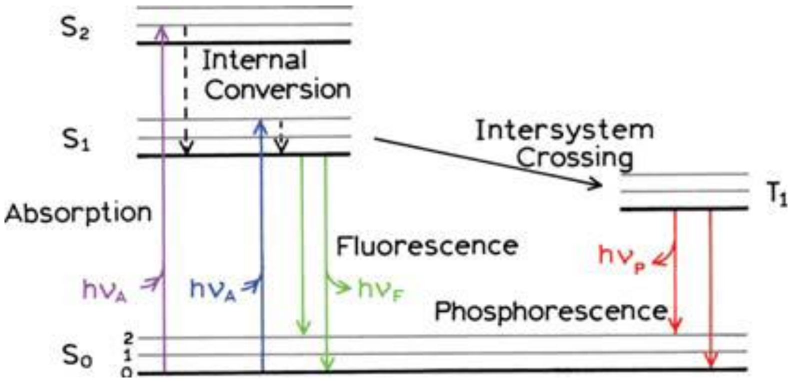


Figure 2.6 Jablonski Diagram.

There are two alternatives for the molecules, it can be excited to level of S_1 or it can go to higher electronic state S_2. Sometimes molecules turn to the lowest vibrational level of S_1 due to the rapid relaxation within 10^{-12} s or less. This process is called as internal conversion. Fluorescence emission occurs from a thermally equilibrated excited state, the lowest energy vibrational level of S_1.

Some molecules undergo a spin conversion from S_1 state to the first triplet state T_1. Emission from this state is termed as phosphoresence and relative to the fluorescence mechanism is generally shifted to lower energy that means longer wavelengths. Intersystem crossing is the name of the conversion that occurs from S_1 to the T_1 state. Molecules are forbidden to undergo ground state directly from T_1 state and this brings smaller rate constants relative to the fluorescence. Heavy atoms facilitate intersystem crossing and enhance phosphoresence mechanism. Therefore, molecules that contain heavy atoms like bromine and iodine are frequently phosphorescent [30].

2.3.1 Fluorescence Zinc Phthalocyanines

Ogunsipe et al. studied solvent effects on the fluorescence properties of zinc phthalocyanines derivatives. Zinc phthalocyanines were supplied as commercial but its derivatives, pyrdino zinc phthalocyanines, zinc octaphenoxyphthalocyanine and zinc octaestronephthalocyanine were synthesized. Their fluorescence spectrum was taken in DMSO, THF, DMF, pyridine, n-butylamine, benzonitrile, benzene and toluene. They showed that, zinc phthalocyanine and its derivatives have fluorescence effect and its quantum yield and other photochemical properties change with solvent types [31].

In the literature, fluorescence zinc phthalocyanines, effects of solvents [15], [31] and effects of substitutents [17], [32] on its properties were also investigated.

Kimura et al. studied dendritic zinc phthalocyanines [33]. In their study, zinc phthalocyanines were used as the core of the dendrimers. Polyether-amides were the functional groups that diminishes aggregation tendency of zinc phthalocyanines. Besides investigating the generation effects on aggregation, they also studied changes in fluorescence properties of dendrimeric phthalocyanine. They claimed that molecules do not show fluorescence in aggregate state whereas their fluorescent properties become apparent with decreasing aggregation.

2.4 Mica Based Combination Pigments

In combination pigments, oxide coated mica pigment is further coated with an absorption pigment or dye. The absorption colorant should be coated uniformly and adhere to the oxide coated mica particles. The interaction between absorbing colorant and interference pigments results in special effect. Besides this effect, dispersion problems that are linked to the absorption pigments due to their small particle size and large specific surface area can be avoided by this method [9]. The structure of a combination pigments is schematically shown in Figure 2.7.

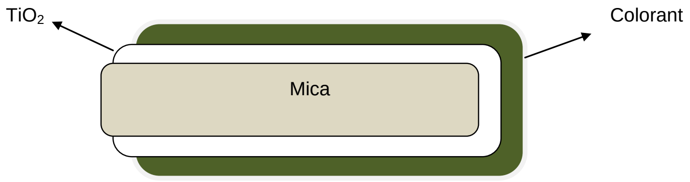


Figure 2.7 Schematic structure of a combination pigment.

Armanini et. al. studied and patented a combination pigment by dispersing insoluble colored pigments such as phthalocyanine blue, carbon black, 00quinacridone in water and then combining of it with suspension of mica or oxide coated mica. For deposition, precipitate of a polyvalent cation (Al, Cr) and an anionic polymeric substance (albumin, xanthan gum) were used [34]. The anionic polymeric substance is required to achieve deposition and to prevent agglomeration of absorption pigment particles. The polyvalent cation solution is added to maintain the pH of the medium in the desired range.

After the precipitation, wet cake was filtrated, washed with water and dried at 120 °C.

Noguchi patented the synthesis of colored flaky pigments by adhering a finely divided color pigment (Ultramarine blue, iron blue, phthalocyanine blue, etc.) onto a flaky substrate (mica, talk, mica titania) [35]. High molecular weight polymeric substances such as polyethylene glycols, polypropylene glycols, polyvinyl pyyrolidones, polyacrylates were used to adhere the color pigment to the flaky substrate. Sand mill, ball mill or roll mill was used to grind the color pigment and then it was dispersed in a high molecular weight compound that was in hot water and/or alcohol. After that, the flaky substrate was suspended in a solution of high molecular weight compound. Finally, suspension of pigment and suspension of flaky substrate were mixed, the color pigment was precipitated. Precipitated solid was filtered and dried.

Topuz studied the combination pigment of mica-titania with copper phthalocyanine. Copper phthalocyanine and tetracarboxamide copper phthalocyanine have been synthesized by microwave method. For copper phthalocyanine synthesis urea, phthalic anhydride, copper chloride and ammonium heptamolybdate were used and trimellitic anhydride was used instead of phthalic anhydride in tetracarboxamide copper phthalocyanine synthesis. After the reaction, the product was purified by washing with HCl, NaOH, hot water and ethanol. After drying the product at the oven, it was dispersed in DMF and it was combined with the mica-titania at different temperatures. SEM results of combination pigment of CuPc with mica-titania pigment showed that CuPc has deposited on mica-titania surfaces in rod like crystal and tetracarboxamide copper phthalocyanine displayed amorphous structure on the mica surfaces at all temperatures [8].

CHAPTER 3

EXPERIMENTAL

In this chapter, the materials used in this work are explained. Also detailed information on the synthesis of zinc phthalocyanine, tetranitro substituted zinc phthalocyanine and combination of these pigments with mica-titania pigments methods are also given. Characterization methods used in each step are also described.

3.1 Materials

To synthesize zinc phthalocyanine, urea was used as the nitrogen donor, phthalic anhydride (PA) was used as phthalocyanine precursor, zinc chloride ($ZnCl_2$) was used as the metal source and ammonium heptamolybdate tetrahydrate (AHM) was the catalyst of the system. To obtain tetranitro substituted zinc phthalocyanine, 3- nitrophthalic acid (NPA) was used instead of phthalic anhydride but metal source and catalyst were the same. Dimethyl formamide (DMF), ethyl acetate (EtOAc), ethanol, hydrochloric acid (HCl), and sodium hydroxide (NaOH) were used in washing step to remove impurities. Mica- titania pigment synthesis procedure has been explained in our group’s previous work [8]. The structural formulas of the materials used in this study were tabulated in Appendix A.

3.1.1 Urea

Urea is an organic compound with a formula of $(NH_2)_2CO$. It was supplied by Merck. Its properties are given in Table 3.1 and also its structural formula is given in Appendix A.

Table 3.1 Properties of urea used in this study.

Molecular weight (g/mol)	60.06
Density (g/ml)	1.32
Appearance	White solid

3.1.2 Phthalic Anhydride (PA)

It is an organic compound with a chemical formula of $C_6H_4(CO)_2O$. It was supplied by Merck. As it is mentioned before, it was used as precursor for phthalocyanine. Phthalonitrile directly gives phthalocyanine without any nitrogen source. However, it is more expensive than other precursor. Therefore phthalic anhydride is chosen in this study. Only one disadvantage is that it gives lower yield compared to the phthalonitrile. Its properties are given in Table 3.2 and structural formula of it is given in Appendix A.

Table 3.2 Properties of phthalic anhydride used in this study.

Molecular weight (g/mol)	148.1
Density (g/ml)	1.53
Appearance	White solid

3.1.3 Zinc Chloride

It is an inorganic compund with the chemical formula of $ZnCl_2$. It is supplied by Merck, Germany. It was used to metallate the phthalocyanine. Its properties are given in Table 3.3.

Table 3.3 Properties of zinc chloride used in this study.

Molecular weight (g/mol)	136.3
Density (g/ml)	2.91
Appearance	White crystalline solid

3.1.4 Ammonium Heptamolybdate

It is also an inorganic compound with the chemical formula of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. It was supplied by Merck, Germany. It was used as a catalyst for synthesizing metal phthalocyanine. Its properties are given in Table 3.4 and chemical structure is shown in Appendix A.

Table 3.4 Properties of ammonium heptamolybdate used in this study.

Molecular weight (g/mol)	1235.9
Density (g/ml)	2.5
Appearance	White crystalline solid

3.1.5 3-Nitro Phthalic Acid

3- Nitro phthalic acid is slightly yellow crystalline powder with the chemical formula of $O_2NC_6H_3$-1,2-$(CO_2H)_2$. It was supplied by Sigma-Aldrich, Germany. It was used in the synthesis of tetranitro substituted zinc phthalocyanine as phthalocyanine precursor. Its properties are given in Table 3.5 and structural formula is also shown in Appendix A.

Table 3.5 Properties of 3- nitro phthalic acid used in this study.

Molecular weight (g/mol)	1235.9
Density (g/ml)	2.5
Appearance	Pale- yellow crystalline solid

3.1.6 Dimethyl formamide (DMF)

Dimethyl formamide with a chemical formula of $(CH_3)_2NCHO$ is a polar organic solvent. It was supplied by Merck, Germany. It was used in the purification step of zinc phthalocyanine synthesis and also in the combination of zinc phthalocyanine pigment with mica-titania pigment. Table 3.6 lists its properties and its structural formula is given in Appendix A.

Table 3.6 Properties of dimethyl formamide used in this study.

Molecular weight (g/mol)	73.1
Density (g/ml)	0.94
Appearance	Clear liquid

3.1.7 Ethyl Acetate

Ethyl acetate is an organic compound and its chemical formula is $CH_3COOCH_2CH_3$. It was used in the purification step of zinc phthalocyanine pigment. It was supplied by Merck, Germany. Its properties are listed in Table 3.7 and its structural formula is given in Appendix A.

Table 3.7 Properties of ethyl acetate used in this study.

Molecular weight (g/mol)	88.1
Density (g/ml)	0.89
Appearance	Clear liquid

3.2 Synthesis of Materials

3.2.1 Synthesis of Zinc Phthalocyanine Pigments

3.2.1.1 The Synthesis of Unsubstituted Zinc Phthalocyanine (ZnPc)

Urea (184 mmol) and phthalic anhydride (36 mmol) were ground in an agate mortar for 10 minutes. Then, zinc chloride (15 mmol) and ammonium molybdate (0.13 mmol) were also added and another grinding step was applied for 10 minutes. Then, the mixture was wetted with 5 ml distilled water in a flask and heated in a microwave oven (600 W). To remove unreacted raw materials, purification step was applied. This step started with hot water (70 ^{o}C), and continued with 6 M HCl(40 ^{o}C), 1 M NaOH, hot water and ethanol followed by filtration. After these steps, some impurities were still present, hence, purification was continued with the DMF and EtOAc. After dissolving wet cake in DMF, it was precipitated to EtOAc by dropwise and it was cooled to room temperature. The resulting pigment was dried in an oven at 120 ^{o}C. This procedure is summarized in Figure 3.1 and the chemical reaction of the synthesis is given in Figure 3.2.

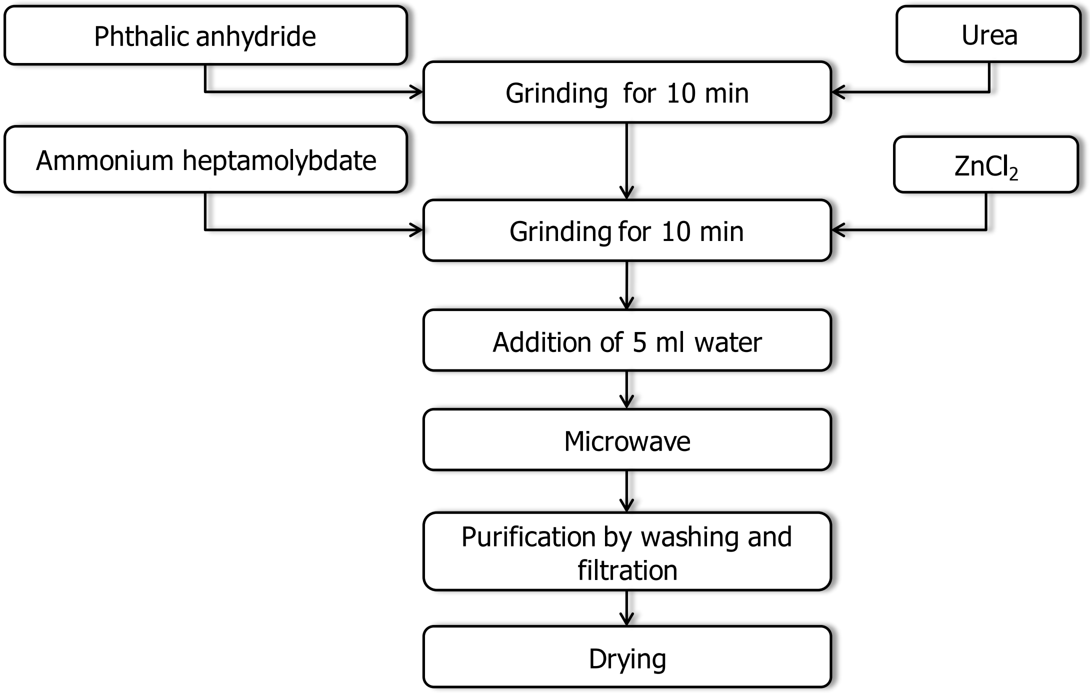


Figure 3.1 Flow diagram for synthesis of ZnPc.

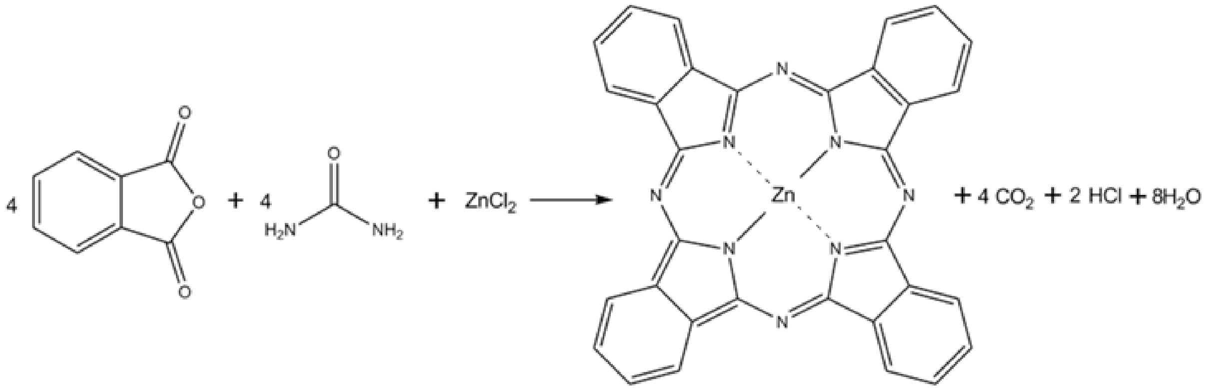


Figure 3.2 Synthesis reaction of unsubstituted zinc phthalocyanine.

3.2.1.2 The Synthesis of Tetra Nitro Zinc Phthalocyanine (TNZnPc)

Urea (184 mmol) and 3- nitro phthalic acid (36 mmol) were ground in an agate mortar for 10 minutes. Then zinc chloride (15 mmol) and ammonium molybdate (0.13 mmol) were also added and another grinding was applied for 10 minutes. Then, the mixture was wetted with 5 ml distilled water in a flask and heated in a microwave oven (600 W). To remove unreacted raw materials, purification step was applied. This step started with hot water (70 ^{o}C), and continued with 6 M HCl (40 ^{o}C), 1 M NaOH, hot water and ethanol followed by filtration respectively. The resulting pigment was dried in oven at 120 ^{o}C. Chemical reaction of this synthesis is given in Figure 3.3.

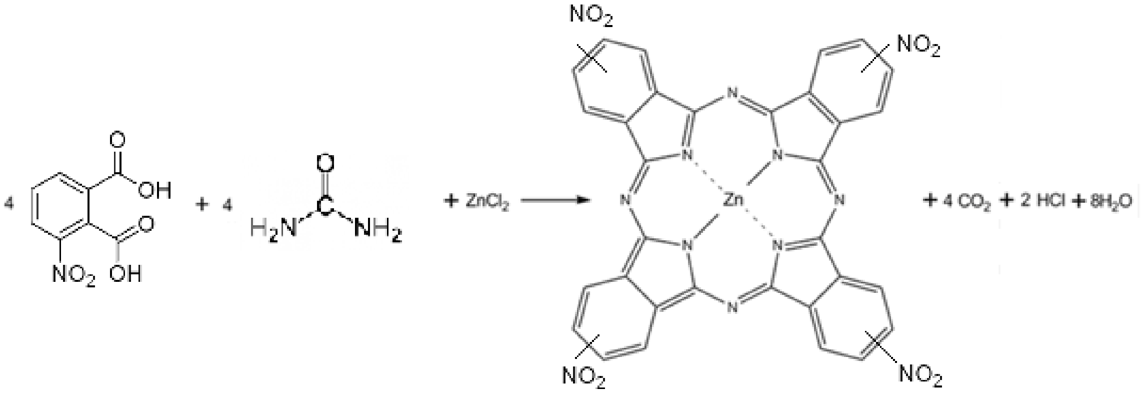


Figure 3.3 Synthesis reaction of tetra nitro substituted zinc phthalocyanine.

3.2.2 Synthesis of Combination Pigments

In this step, initially zinc phthalocyanine pigment was dispersed in DMF and then, titania coated mica pigment (0,6 g) was added into the solution. The suspension was filtered and washed again with DMF. Washing process was continued until the supernatant liquid became colorless. Finally, wet cake was dried in an oven at 120 ^{o}C. Different time intervals were carried out to optimize the effective deposition time. Also, different amounts of zinc phthalocyanine pigment was dispersed in DMF to obtain best results. To find optimum deposition temperature four different temperature were chosen. Table 3.8 lists different parameters for combination of zinc phthalocyanine pigment with mica-titania pigment. The procedure is given in Figure 3.4.

Table 3.8 Parameters for combination pigments ZnPcMT.

	Time (hour)	**Temperature (^{o}C)**	**Amount of ZnPc (g)**	**Weight ratio of ZnPc to MT (w/w)**
P1	0.5	25	0.04	0.067
P2	0.5	50	0.04	0.067
P3	0.5	90	0.04	0.067
P4	0.5	120	0.04	0.067
P5	1	120	0.04	0.067
P6	2	120	0.04	0.067
P7	0.5	50	0.08	0.133
P8	0.5	90	0.08	0.133
P9	0.5	120	0.08	0.133
P10	0.5	50	0.16	0.267
P11	0.5	90	0.16	0.267
P12	0.5	120	0.16	0.267

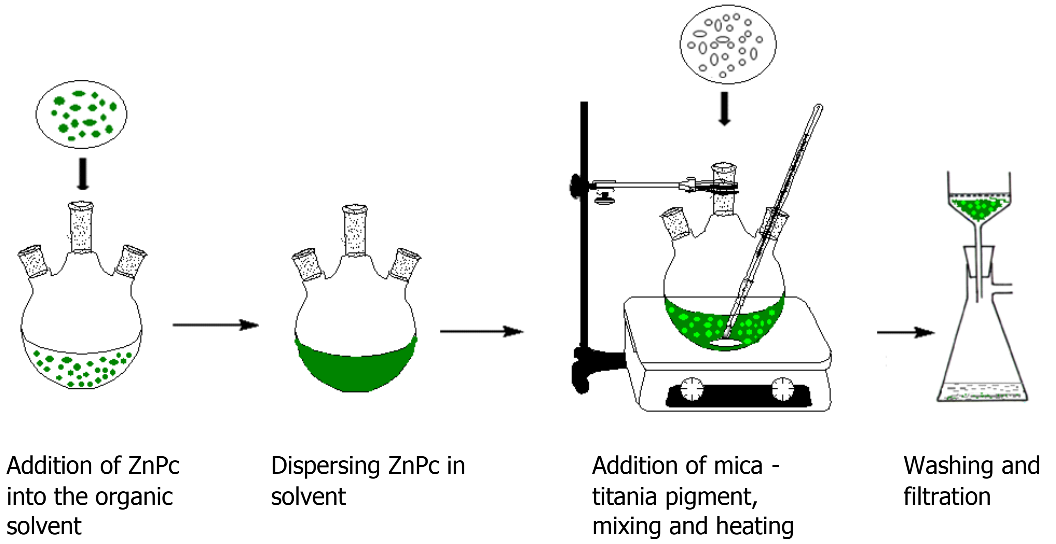


Figure 3.4 Experimental procedure for combination of ZnPc and MT.

3.2.2.1. Synthesis of Tetranitro Zinc Phthalocyanine Deposited Mica Titania Pigment (TNZnPcMT)

This synthesis was similar to the synthesis of zinc phthalocyanine deposited mica titania pigment. However, here tetra nitro substituted zinc phthalocyanine was used instead of zinc phthalocyanine pigment. Same parameters were also tried for these combination pigments.

Table 3.9 Parameters for combination pigments TNZnPcMT.

	Time (hour)	**Temperature (^oC)**	**Amount of TNZnPc (g)**	**Weight ratio of TNZnPc to MT (w/w)**
P13	0.5	25	0.026	0.043
P14	0.5	50	0.026	0.043
P15	0.5	90	0.026	0.043
P16	0.5	120	0.026	0.043
P17	0.5	120	0.052	0.087
P18	0.5	120	0.104	0.173

3.2.3 Preparation of an Alkyd Based Paint Formulations

Different mica phthalocyanine pigments that were obtained at 50 ^oC, 90 ^oC and 120 ^oC were used to obtain different paint samples. Weight ratio of paint components is given in Table 3.10. In this formulation, white spirit was used as solvent for alkyd resin; cobalt naphthenate was used as surface dryer. Generally, lead naphthenate is also used as dryer however, recent regulations limits its usage because of causing mutation in living organisms. Alkyd resins are prepared by reacting polyols with polyacid or anhydrides and modifying with oils.

Table 3.10 Alkyd paint formulation.

Formulation	% (w/w)
Long oil alkyd resin (60%)	89.52
White Spirit	7.96
Cobalt naphtanate	0.55
Mica phthalocyanine pigment	2.00

For preparation alkyd resin based paint, long oil alkyd resin (8.95 ml), white spirit (0.80 ml), cobalt naphthenate (0.06 ml), and mica phthalocyanine pigment (0.2 g) were mixed and then the mixture was stirred in a magnetic stirrer for 15 minutes. After obtaining homogeneous dispersion, it was spreaded on glass plates by paint applicator and left to dry at room temperature.

3.3 Characterization

The morphology of the zinc phthalocyanine, tetra nitro zinc phthalocyanine, zinc phthalocyanine deposited mica titania pigment and tetra nitro zinc phthalocyanine deposited mica titania pigments were characterized by Scanning Electron Microscopy (SEM) in Bilkent University National Nanotechnology Research Center (Ulusal Nanoteknoloji Araştırma Merkezi – UNAM) (Model No: FEI SEM Quanta 200 FEG).

Zinc phthalocyanine and tetra nitro substituted zinc phthalocyanine pigments were characterized by Fourier Transform Infrared (FTIR) Spectroscopy to observe functional group in the structure (Model No: Thermo Scientific Nicolet6700). Similarly, combination pigments were also analyzed by this method.

UV-Visible Spectroscopy (Model No: Cary 5000) analysis was performed to observe the main absorbance values of zinc phthalocyanine and tetra nitro zinc phthalocyanine pigments in UNAM.

Fluorescence Spectroscopy (Model No: Cary Eclipse- Varian) analysis was conducted to determine the fluorescence properties of the zinc phthalocyanine and tetra nitro zinc phthalocyanine pigments. This equipment was also located in UNAM.

To confirm the deposition of zinc phthalocyanine on mica titania surface XRD (X-Ray Diffractometer) analysis (Model No: RIGAKU – D/Max-2200/PC) that is located in Metallurgical and Materials Engineering, METU was used.

Elementel Analysis was conducted the nitrogen amount of combination pigments. This equipment was located in Central Laboratory at METU (Model No: LECO, CHNS – 932)

Furthermore, paint properties upon the use of zinc phthalocyanine and tetra nitro zinc phthalocyanine deposited mica titan pigments were also investigated. The colors were measured by color spectrophotometer with D65 light source. (Model: X-rite 65).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary studies

To synthesize zinc phthalocyanine, series of experiments were performed. As indicated in the introduction part, when phthalic anhydride is used as precursor for phthalocyanine synthesis some additional nitrogen source is needed in the reaction. Different mol ratios of urea to phthalic anhydride (U:PA) were conducted and their characterizations were done by FTIR analysis. The results are given in Figure 4.1.

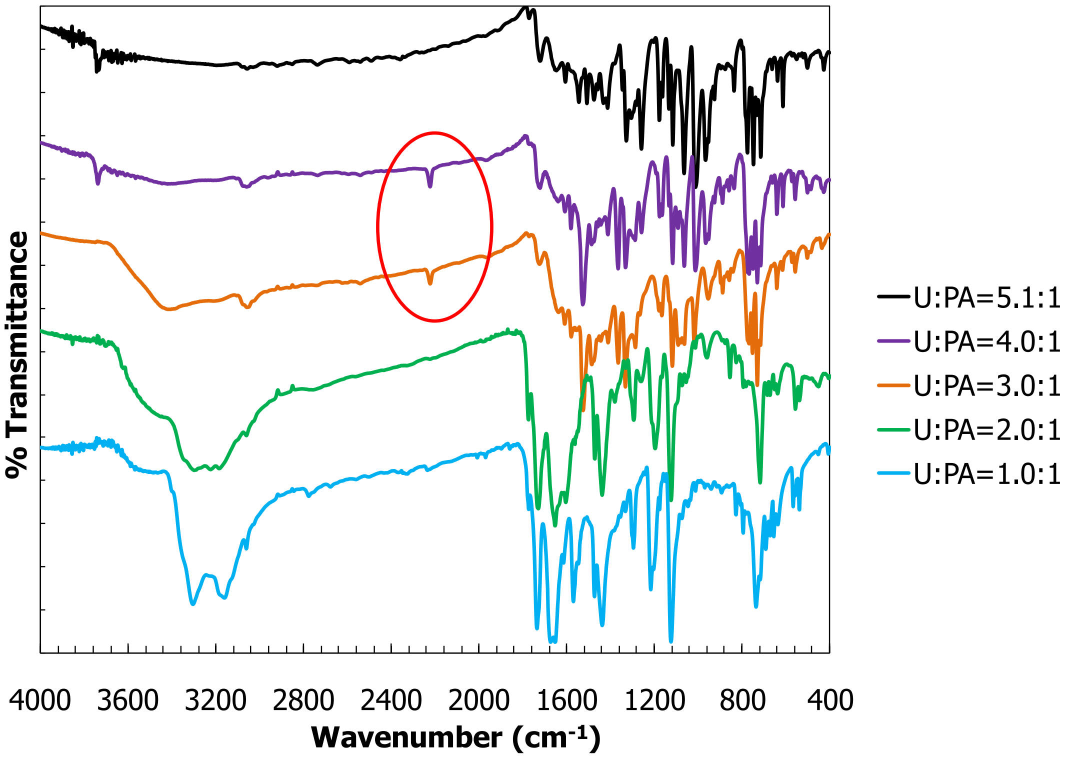


Figure 4.1 FTIR spectra of different ZnPc samples.

The main characteristic peak of phthalocyanine molecule is at 1006 cm^{-1} for N-H streching, and 1062 cm^{-1} for N-H streching in zinc phthalocyanine. Also metal phthalocyanines show three strong peaks in 1000-1200 cm^{-1} region. These peaks are not observed as in the case when the ratio of U:PA was 1:1 and 2:1 (U:PA). In addition, in region 3000-3200 cm^{-1}, only one peak, 3041 cm^{-1} for the aromatic C-H streching belongs to the zinc phthalocyanine. In these two cases, zinc phthalocyanine did not form. To show it clearly, same graph was redrawn in 1200 cm^{-1}- 400 cm^{-1} range and it is seen in Figure 4.2. When the ratio was increased to 3:1 and 4:1, peaks became observable. However, 2200 cm^{-1}, asymmetric streching vibrations of –NCO groups that refer to the cyanate formation became apparent. This indicates that, urea decomposes to cyanate rather than reacting with phthalic anhydride. All peaks showed up for 5.1:1 case in the range 1700-900 cm^{-1}.

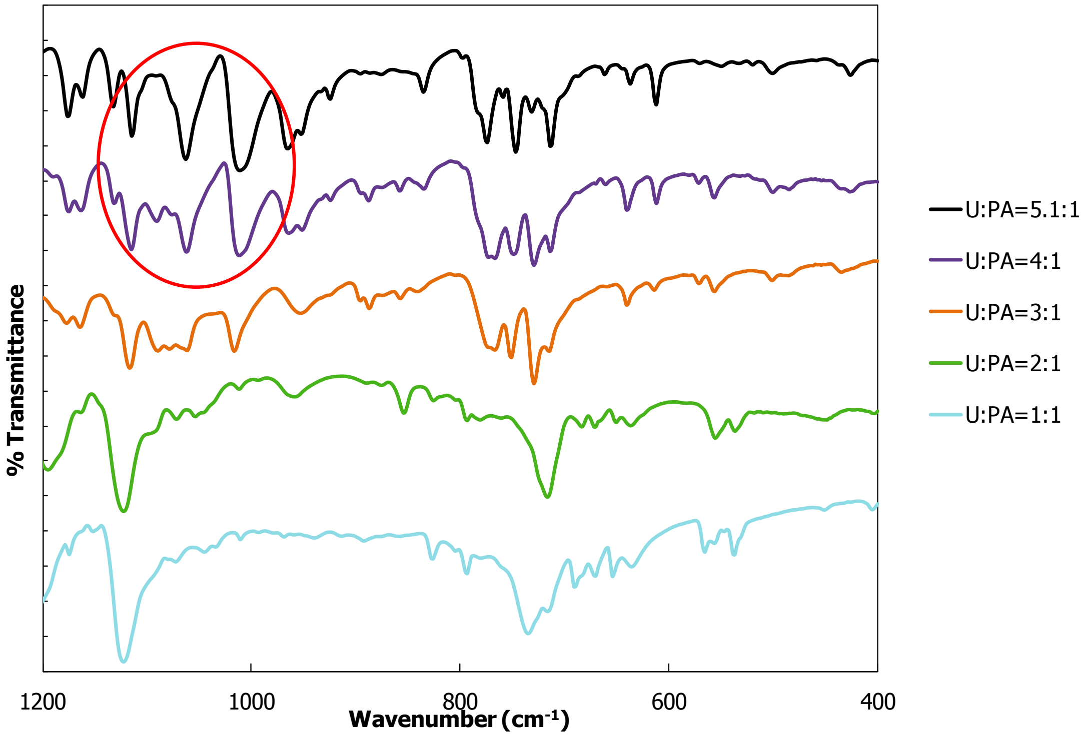


Figure 4.2 FTIR spectra of different ZnPc samples in between 1200 cm^{-1} – 400 cm^{-1}

In the literature there are many different washing methods for purifying the product. Therefore, different solvents were used to purify the sample, and their FTIR spectra were also taken. Figure 4.3 shows the sample, that was washed with chloroform, DMF and finally with ethanol after microwave irradiation. The peak that is seen at 2200 cm^{-1} indicates cyanate formation in the sample.

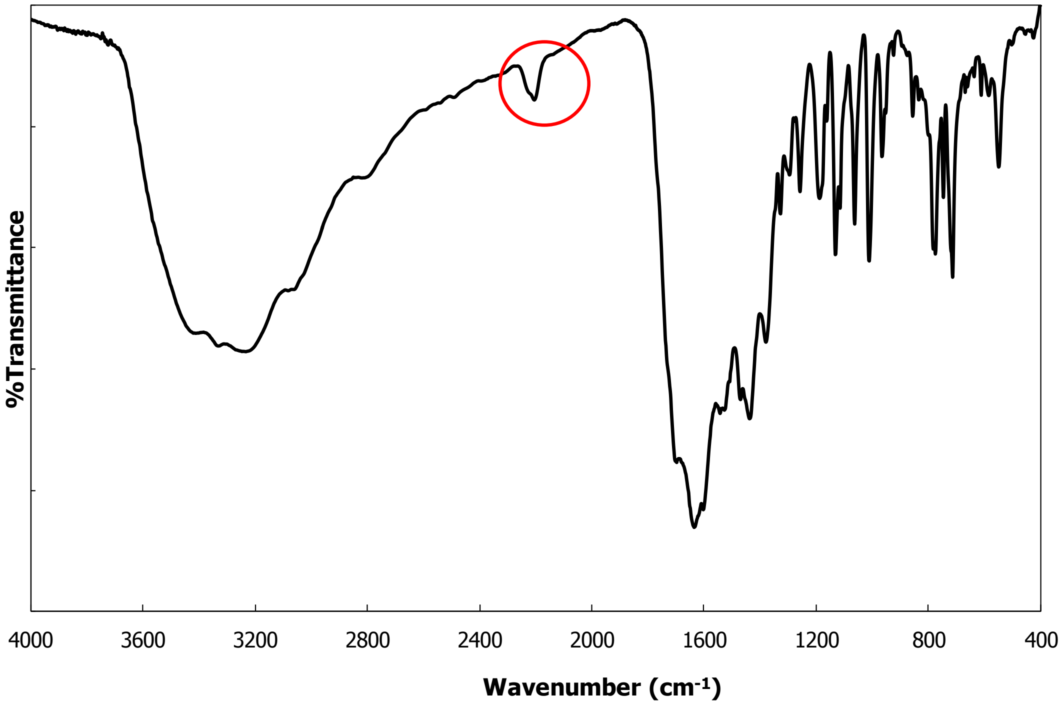


Figure 4.3 FTIR spectrum of ZnPc sample

4.2 Zinc Phthalocyanine and Tetranitro Zinc Phthalocyanine

Figure 4.4 shows the FTIR spectrum of ZnPc. Two peaks appearing at 3049 and 2910 c8m^{-1} are attributed to the symmetric C-H stretching in the ring and in the alkyl respectively. The peak at 1609 cm^{-1} is due to the C=C macrocycle ring deformation in pyrole and at 1506 cm^{-1} is due to the C=N stretching. C-C stretching in isoindole appeared at 1428 and 1332 cm^{-1}. The -NH bending vibration peak is at 1006 cm^{-1} and this band disappeared when the H atoms in the middle of the structure were replaced with metal ion. This is shown by the peak at 1062 cm^{-1} that corresponds to the C-H bending in plane deformation. C-H bending out of plane deformation is observed at 909, 882 and 728 cm^{-1}. The peaks at 1284, 1162 and 1070 cm^{-1} are attributed to

C-N stretching in isoindole, C-N in plane bending, and -C-H in plane bending, respectively. FTIR spectrum of TNZnPc is given in Figure 4.5. The peaks that belong to the N-O symmetric stretching and asymmetric stretching are seen at 1340 cm^{-1} and 1540 cm^{-1}. Experiments were repeated several times and reproducible results were obtained.

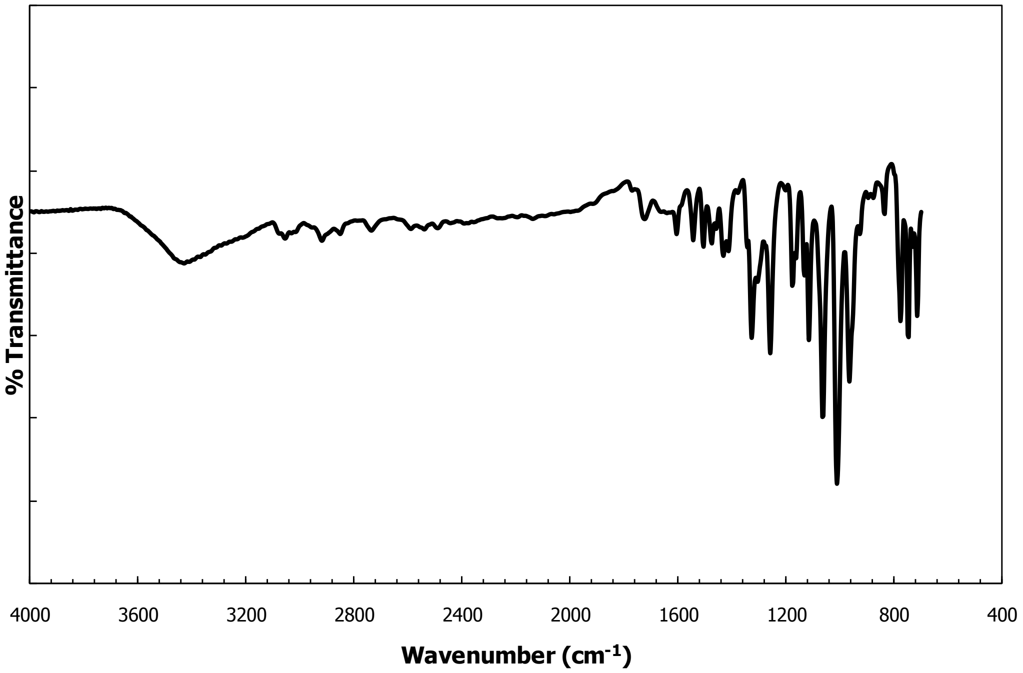


Figure 4.4 FTIR spectrum of ZnPc.

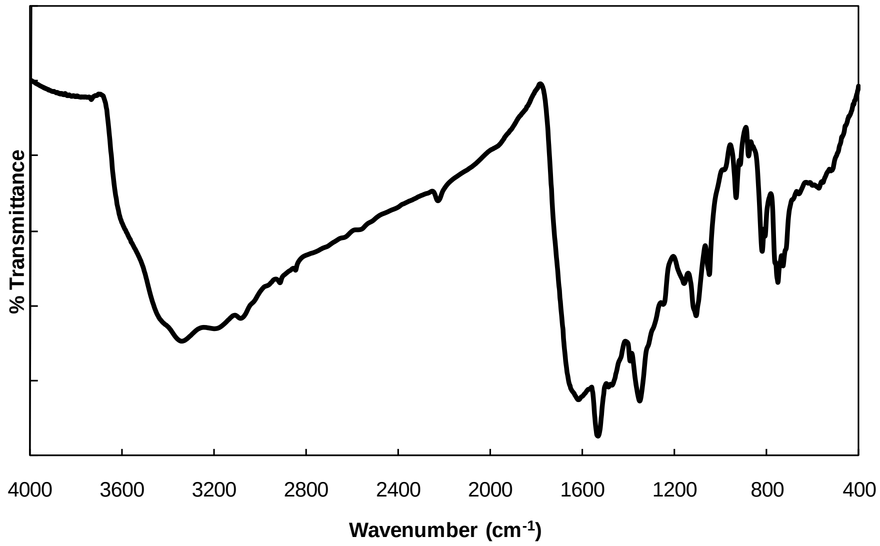


Figure 4.5 FTIR spectrum of TNZnPc.

The UV-visible spectrum of the ZnPc and TNZnPc pigments are given in Figure 4.6 and Figure 4.7, respectively. Characteristic absorption of phthalocyanine complexes in the B band region at 300-400 nm and Q band region at 650-700 nm are clearly seen. The B band the Q bands both arise from π–π* transitions and can be explained by considering the four frontier orbitals (HOMO and LUMO orbitals). ZnPc shows absorption at 367 nm and TNZnPc shows at 340 nm and because of this absorption in B band they have green color. At the Q band, ZnPc shows absorption at 670 nm with a shoulder at 605 nm and TNZnPc shows absorption at 674 nm with a shoulder at 608 nm. This is due to the aggregation of the phthalocyanine molecules in DMF. Dye-dye interaction is stronger than the interaction between the solvent molecules and phthalocyanine molecules. Because of that, solvation of monomer is prevented. Splitting of Q band (peak that seen at 605 nm and 608 in ZnPc and TNZnPc, respectively) is the evidence of this aggregation.

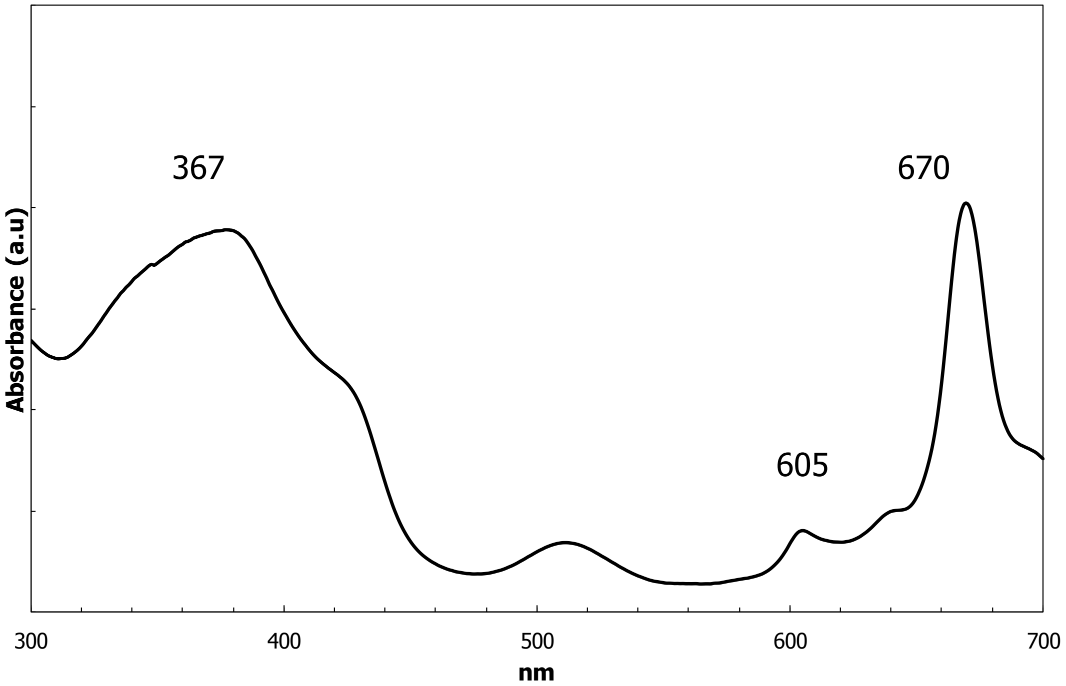


Figure 4.6 UV-Visible spectrum of ZnPc.

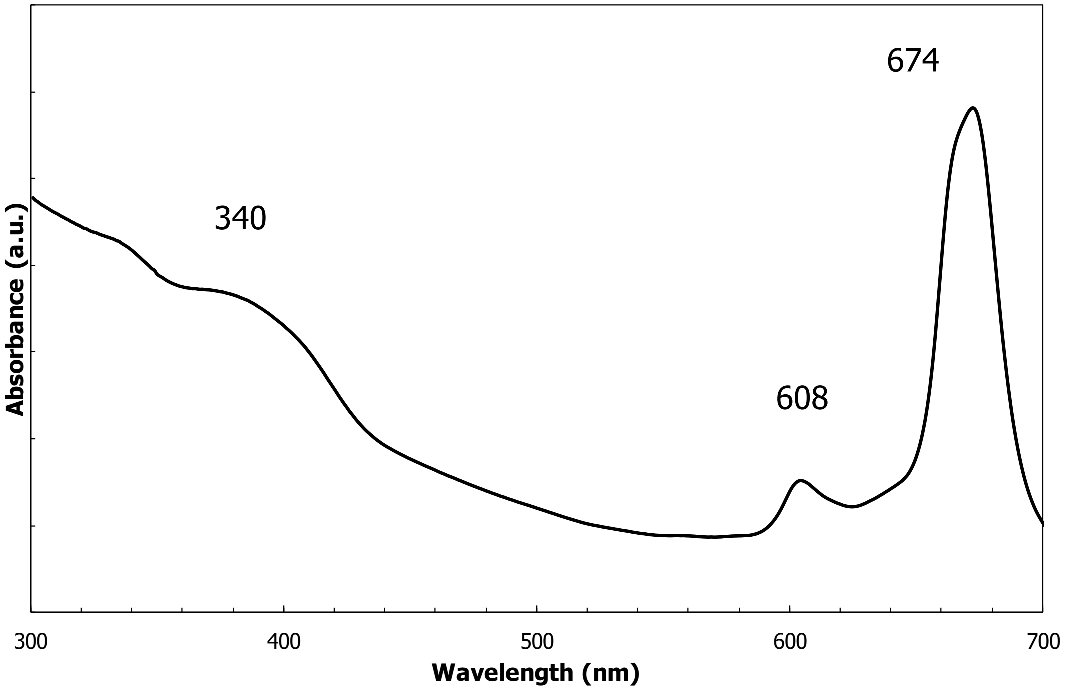


Figure 4.7 UV-Vis absorption spectra of TNZnPc.

Figure 4.9 shows the fluorescence spectrum of ZnPc pigment dispersed in DMF. It is seen that DMF has no fluorescence property, and the emission spectrum with a peak at 680 nm is totally due to ZnPc pigments. Fluorescence spectrum of TNZnPc is also given in Figure 4.8 and similar to the ZnPc case, the emission at 680 nm is totally due to the TNZnPc.

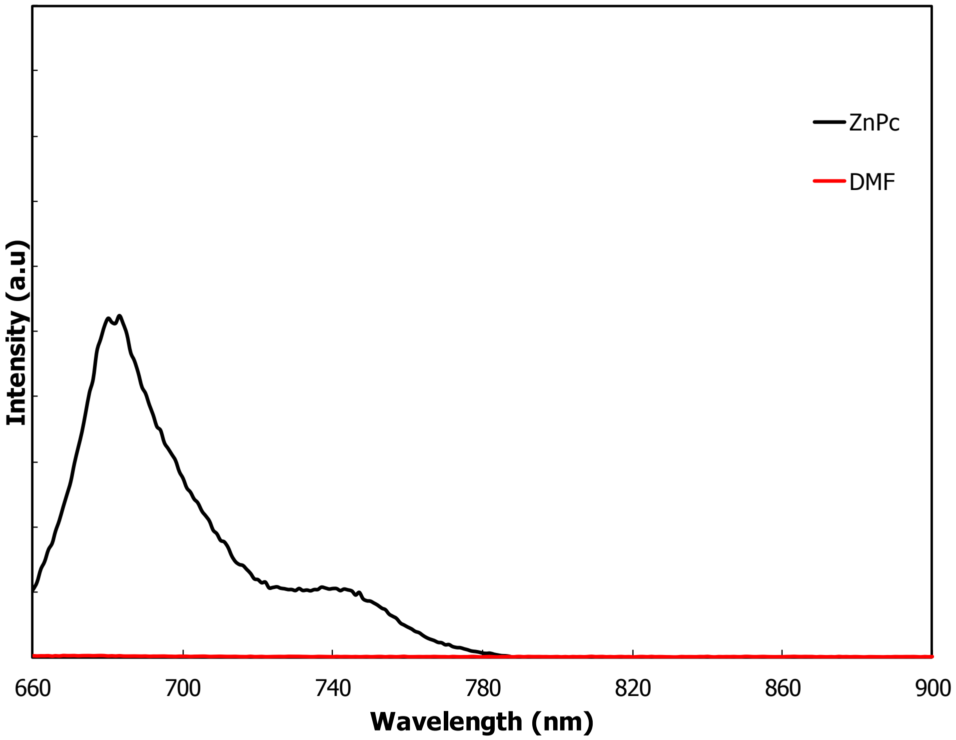


Figure 4.8 Fluorescence spectrum of ZnPc.

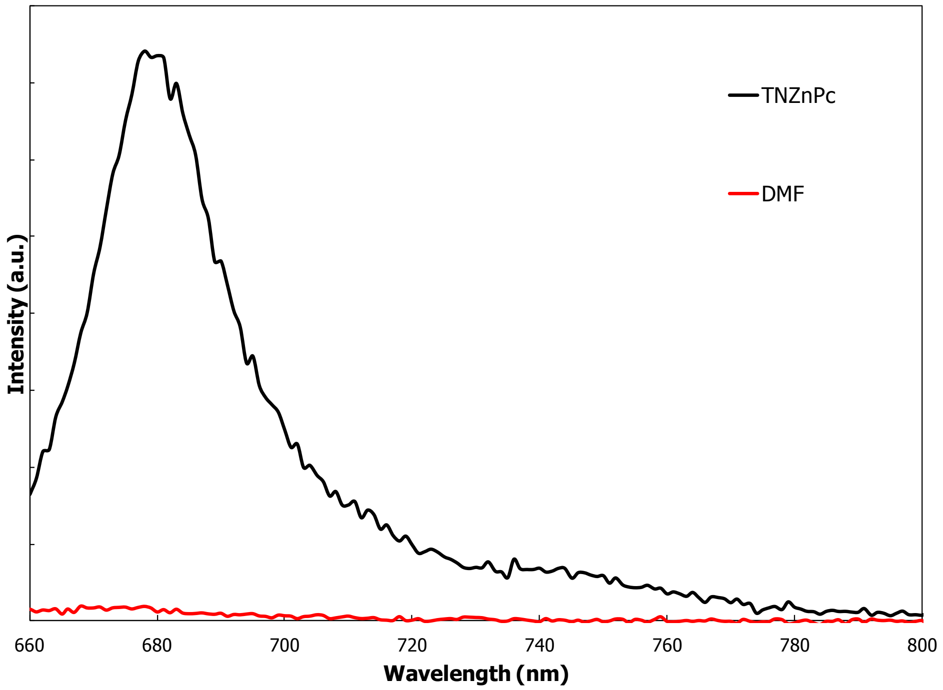


Figure 4.9 Fluorescence Spectrum of TNZnPc.

4.3 Combination Pigments

4.3.1 FT-IR Analysis Results of ZnPcMT Pigment

Figure 4.10 displays the FT-IR spectra of ZnPcMT pigment at different temperatures, MT pigment, and ZnPc pigment.

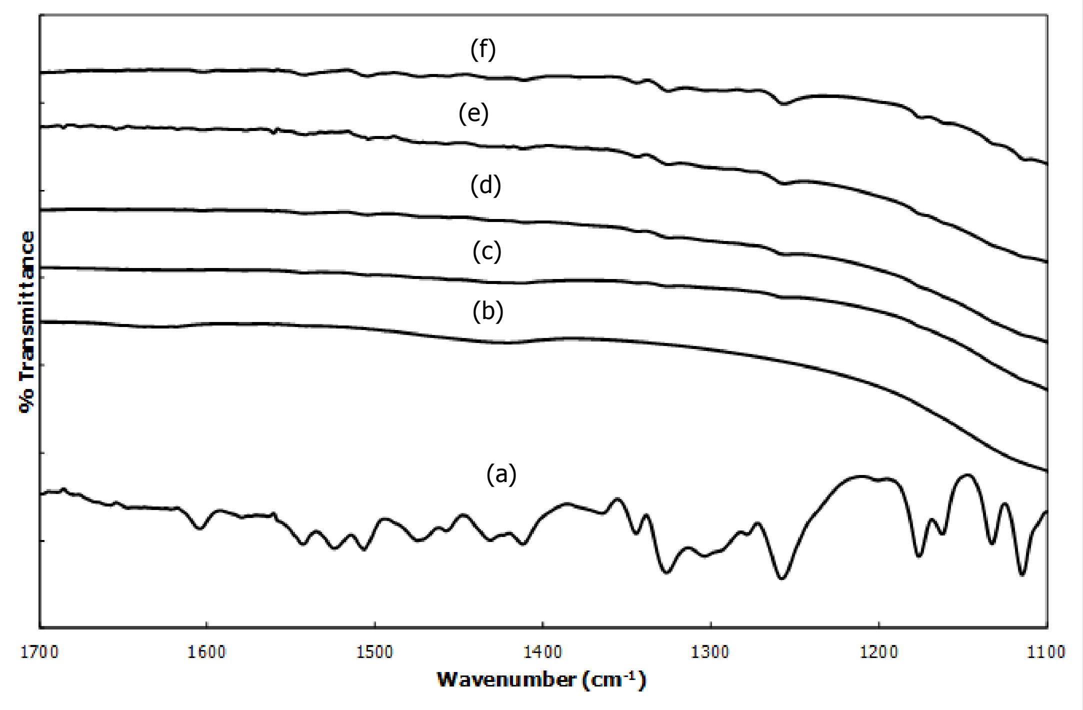


Figure 4.10 FT-IR spectra of ZnPcMT pigment at (a) ZnPc, (b) mica titania, (c) 25°C , (d) 50°C, (e) 90°C, (f) 120°C.

The characteristic peaks of ZnPc cannot be seen at low temperatures, namely at 25 ^{o}C and 50 ^{o}C in Figure 4.10, but peaks became somewhat clear with the increase in temperature. The deposition of zinc phthalocyanine on mica-titania pigment was not achieved at low temperatures. High temperature is needed for the deposition. To see it clearly, the spectrum was redrawn in 800-700 cm^{-1} range, and presented in Figure 4.11.

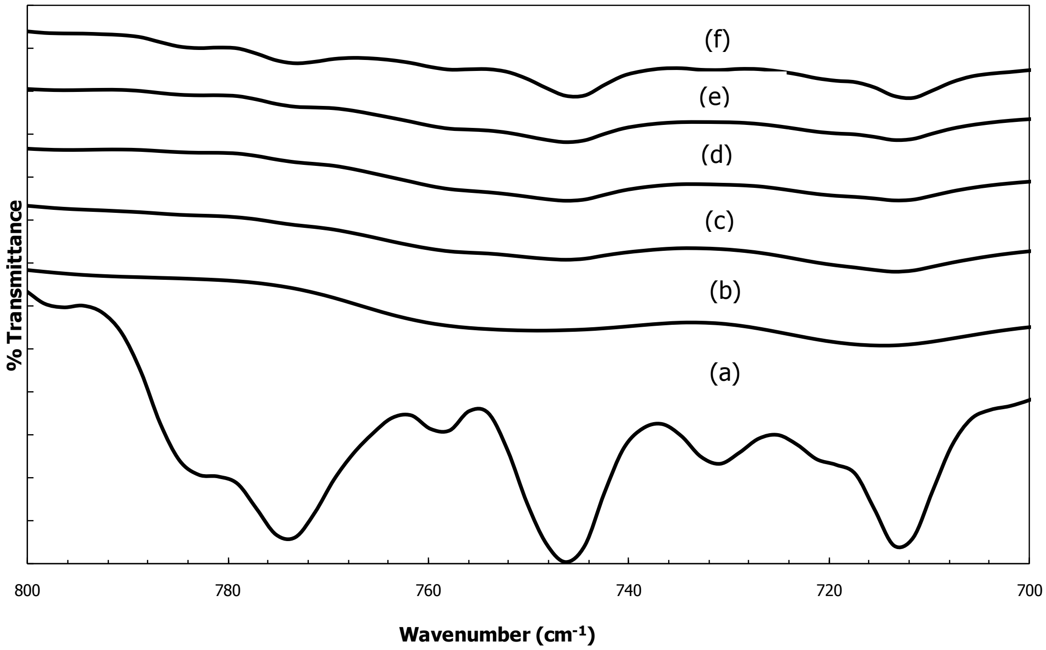


Figure 4.11 FT-IR spectra of ZnPcMT pigment between 700- 800 cm^{-1} at (a) ZnPc, (b) mica titania, (c) 25°C, (d) 50°C, (e) 90°C, (f) 120°C.

To see the change in deposition with temperature, peak analysis was conducted. CorelDRAW program was used and changes in the heights of the peaks were measured. C-C stretching in isoindole appeared at 1332 cm^{-1} was chosen as standard and changes in its heights at different temperatures were measured. Figure 4.12 shows the FTIR spectrum of ZnPcMT at 120 °C and the Figure 4.13 represents the results of the program. Same analysis was performed for all temperature cases and their figures represented in Appendix D. Table 4.1 shows the change in the ratio of the peaks in all cases. Also, with obtained ratios of the heights that are calculated according to results of the program, heights of (c) peaks were recalculated by keeping the height of (a) peak constant at 38.69. Percentage of increments was calculated with Eqn. 1, first value was taken as 2.14 and their results were also shown in Table 4.1. Results indicate that, the height of the peak increases with increasing temperature that means deposition becomes more observable with increasing temperature.

$$\% \text{ Increment} = \frac{(\text{Last value- First Value}) * 100}{\text{First Value}} \qquad \text{(Eqn1.)}$$

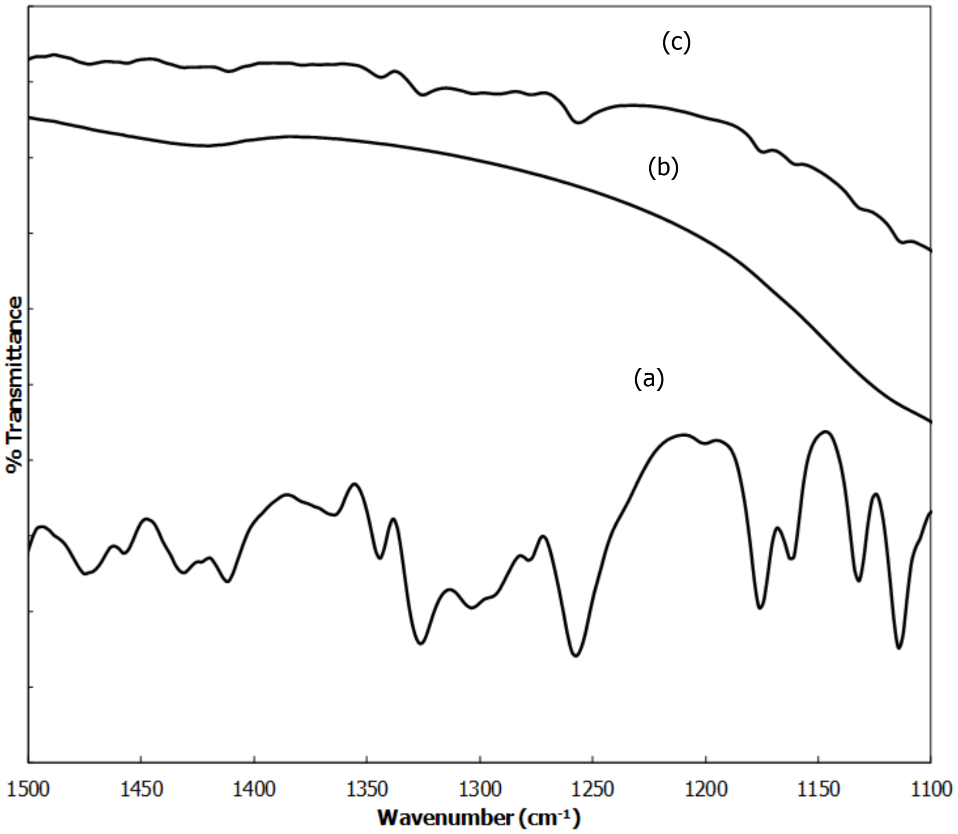


Figure 4.12 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c) ZnPcMT at 120°C

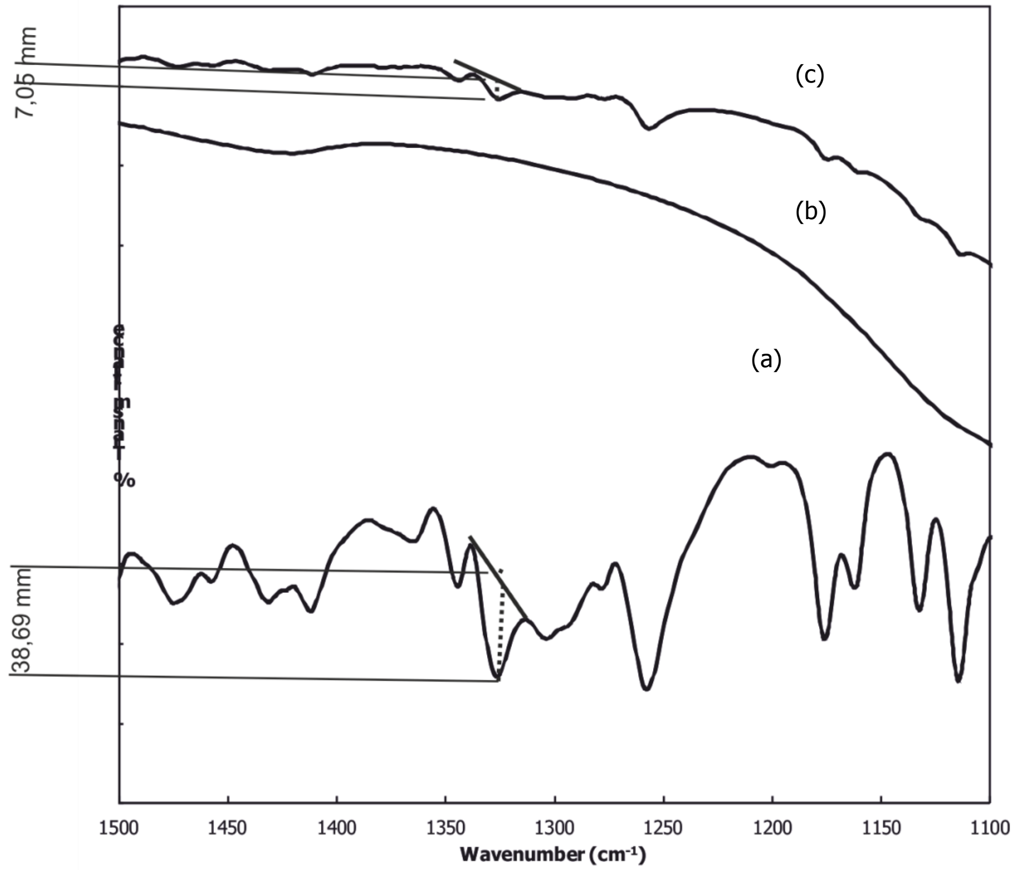


Figure 4.13 CorelDRAW results of peak analysis of ZnPcMT pigment at 120 °C (a) ZnPc, (b) mica titania, (c) 120°C.

Table 4.1 Changes in the ratio of the peaks at different temperatures.

	Ratio of the heights of the peaks (a/c)	**Height of c peaks**	**% increment**
25 °C	39.03/2.16=18.07	38.69/18.07=2.14	0.00
50 °C	32.25/3.00=10.75	38.69/10.75=3.60	68.22
90 °C	25.13/3.30=7.62	38.69/7.62=5.07	136.92
120 °C	38.69/7.05=5.49	38.69 /5.49 = 7.05	229.44

The crystallinity was examined by analyzing the XRD spectrum of the pigment and it is concluded crystalline ZnPc is shown on MT. (Figure 4.14-c).

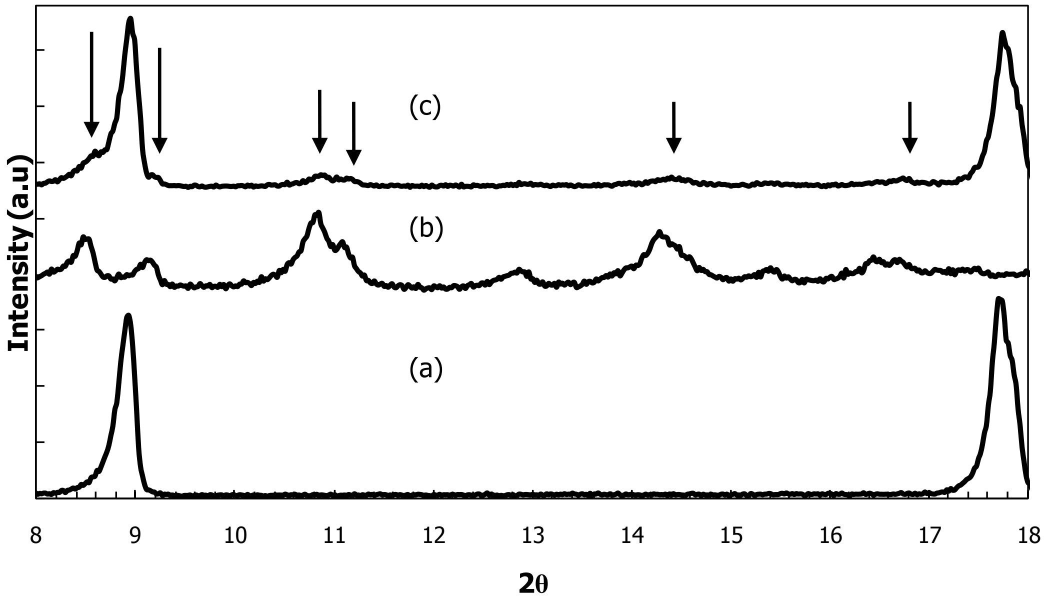


Figure 4.14 XRD patterns of (a) MT, (b) ZnPc, (c) ZnPcMT at 120°C.

After determining the optimum deposition temperature, the deposition time was investigated. ZnPc pigment was deposited on mica-titania pigment surface at different time intervals, ½ hour, 1 hour, and 2 hours. Figure 4.15 represents the FT-IR spectra of ZnPcMT pigments.

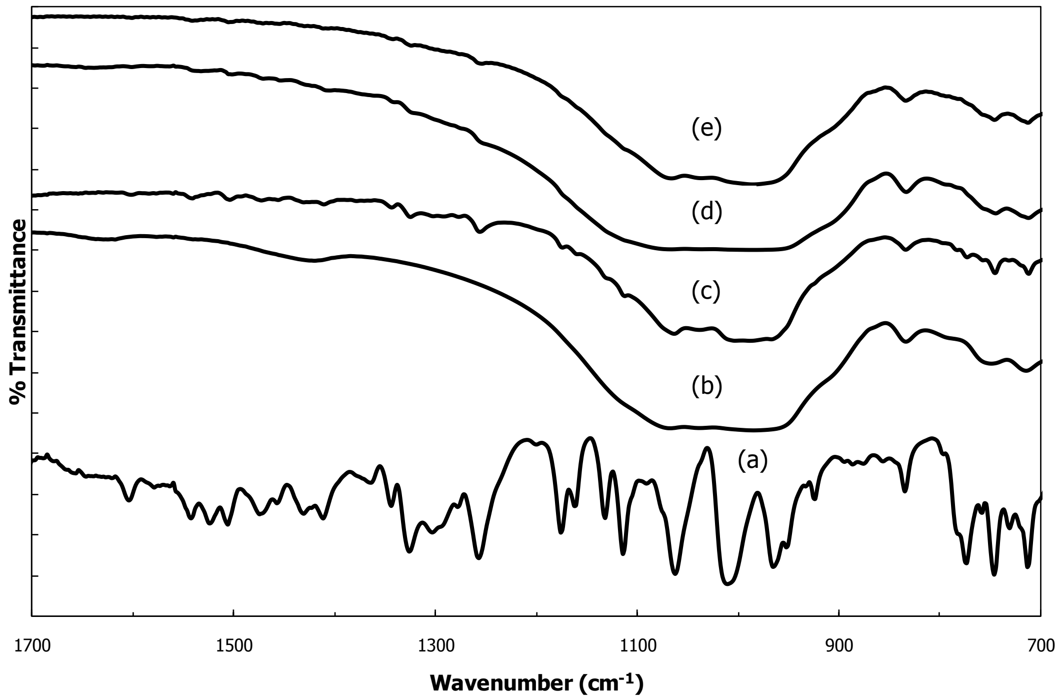


Figure 4.15 FTIR spectra of ZnPcMT deposited mica-titania pigments. Deposition after different time intervals at 120 °C (a) ZnPc , (b) MT, (c) ½ hour, (d) 1hour, (e) 2 hours.

The characteristic peaks of zinc phthalocyanine produced at different time intervals can be clearly seen from Figure 4.15. The most intense peaks were observed in the case when zinc phthalocyanine pigment was deposited on mica-titania pigment in half an hour. After this time interval, the zinc phthalocyanine layer on mica-titania becomes thicker and as a result of this, zinc phthalocyanine molecules interact with each other and leave the surface rather than being deposited on it. That is, thickness enhances desorption. To see it clearly, the spectra of different samples were redrawn in 900-700 cm^{-1} range in Figure 4.16.

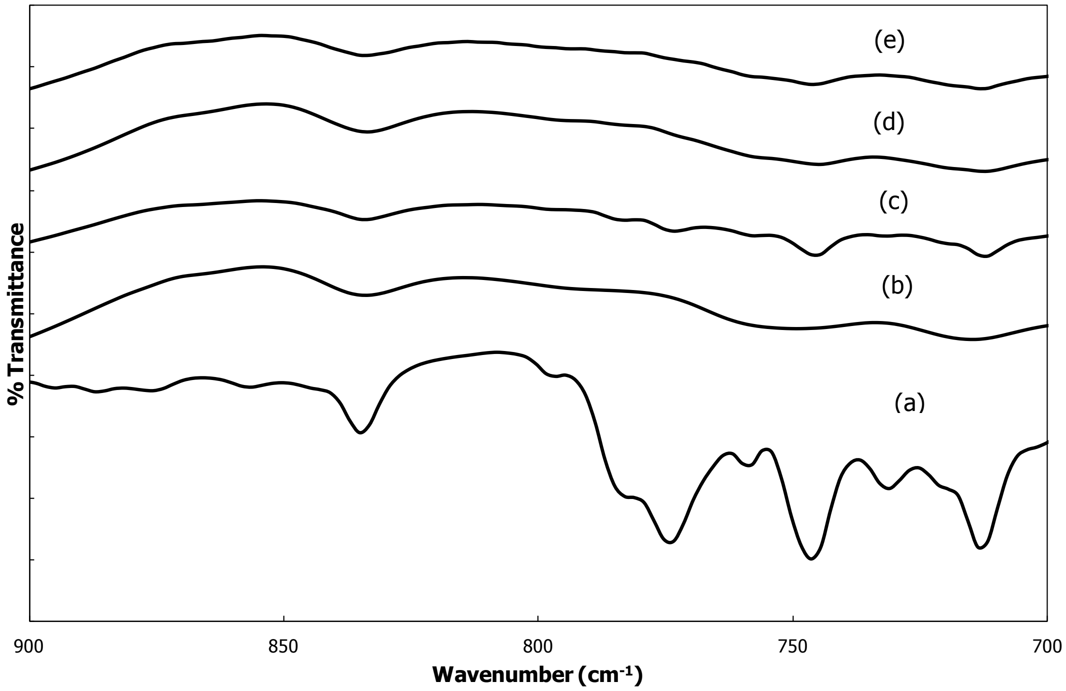


Figure 4.16 FT-IR spectra of ZnPcMT pigments between 700- 900 cm-1. Deposition after different time intervals at 120 °C (a) ZnPc, (b) MT, (c)½ hour, (d) 1hour, (e) 2 hours.

Peak analysis was also conducted to see the change in deposition with deposition time. CorelDRAW program was used and changes in the heights of the peaks were measured. C-C stretching in isoindole appeared at 1332 cm^{-1} was chosen as standard and changes in its heights at different time intervals were measured. Figure 4.17 shows the FTIR spectrum of ZnPcMT that was prepared at half an hour and the Figure 4.18 represents the results of CorelDRAW. Same analysis was performed for all time intervals and their figures represented in Appendix D. Table 4.2 shows the change in the ratio of the peaks in all cases. Also, with obtained ratios of the heights that are calculated according to results of CorelDRAW, heights of (c) peaks were recalculated by keeping the height of (a) peak constant at 35.07. Percentage of drops was calculated with Eqn. 1, first value was taken as 7.08 and their results were also shown in Table 4.2. Results indicate that, the height of the peak decreases with increasing time that means deposition becomes less favorable with increasing time.

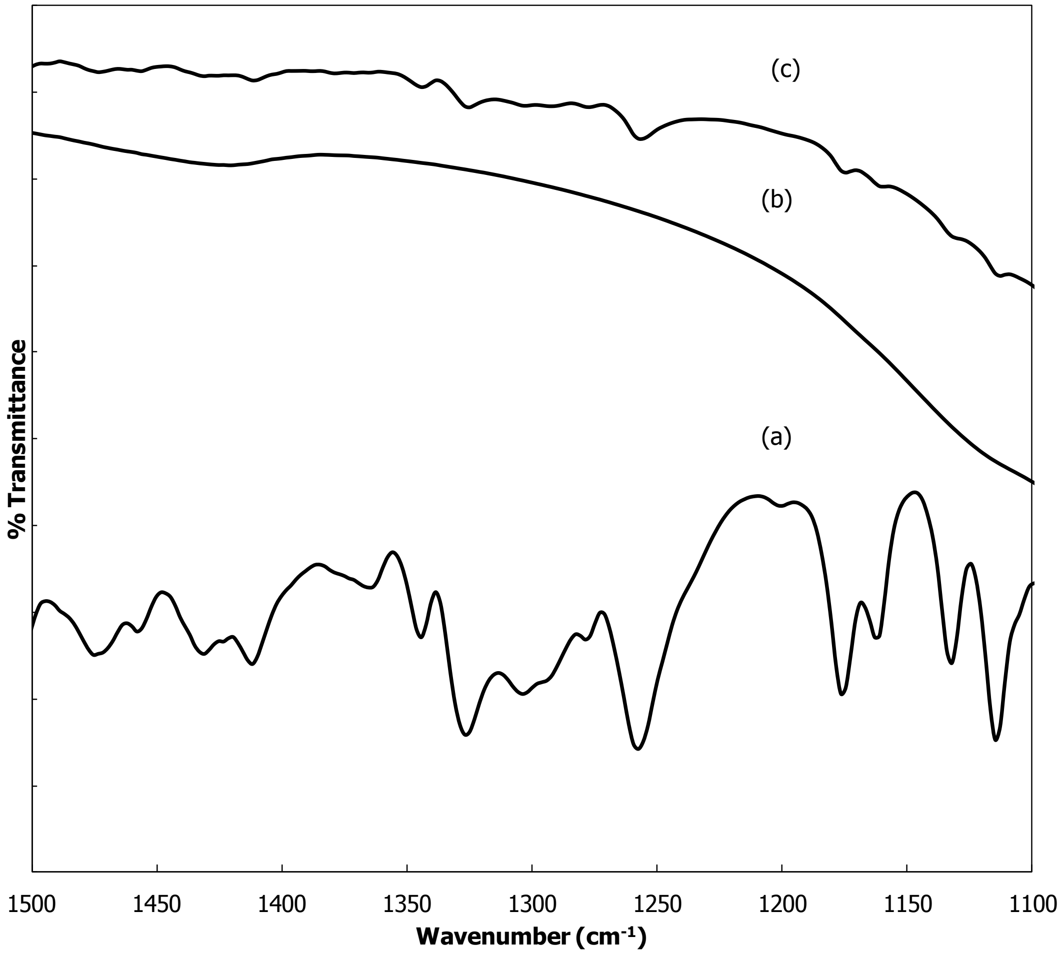


Figure 4.17 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c) ZnPc at ½ hour.

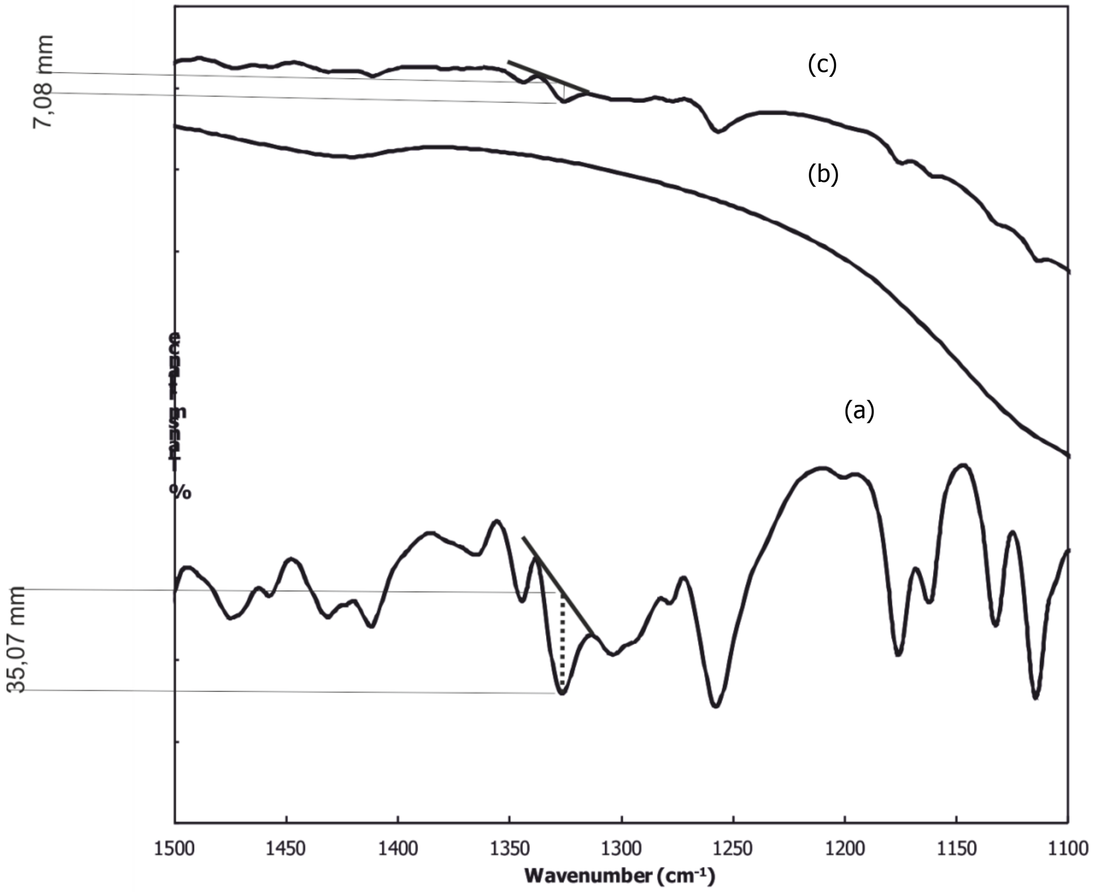


Figure 4.18 CorelDRAW results of peak analysis of ZnPcMT pigment at ½ hour (a) ZnPc, (b) mica titania, (c) ½ hour.

Table 4.2 Changes in the ratio of the peaks at different time intervals.

	Ratio of the peaks	**Height of c peaks**	**% drop**
½ hour	35.07/7.08= 4.95	35.07 / 4.95 = 7.08	0.00
1 hour	27.99/3.09=9.06	35.07 / 9.06 = 3.87	45.33
2 hour	27.02/2.26=11.96	35.07/11.96=2.93	58.62

4.3.2 FT-IR Analyis of TNZnPc Pigment

Combination pigment experiments were performed for TNZnPc at the conditions specified for ZnPc experiments; the temperature was kept constant at 120 °C, and time was set as ½ hour. However, most of the peaks belonging to TNZnPc pigments could not be seen in this case. To observe the effect of the amount of TNZnPc on the deposition, the experiments were repeated with different amounts, and the results are given in Figure 4.19 and Figure 4.20. The FTIR results are not sufficiently evident to prove that deposition of TNZnPc on MT is achieved. Peaks at 1340 cm^{-1} and 1540 cm^{-1} that belongs to the N-O stretching are not seen in all cases.

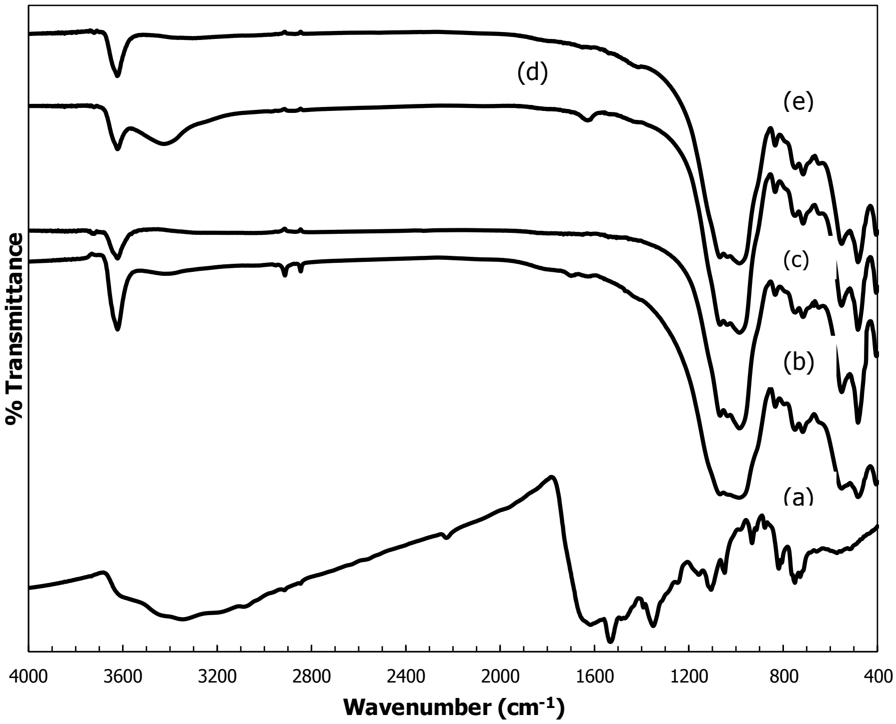


Figure 4.19 FT-IR spectra of TNZnPc pigment at 120°C, (a) TNZnPc, (b) mica titania, (c) P16, (d) P17, (e) P18.

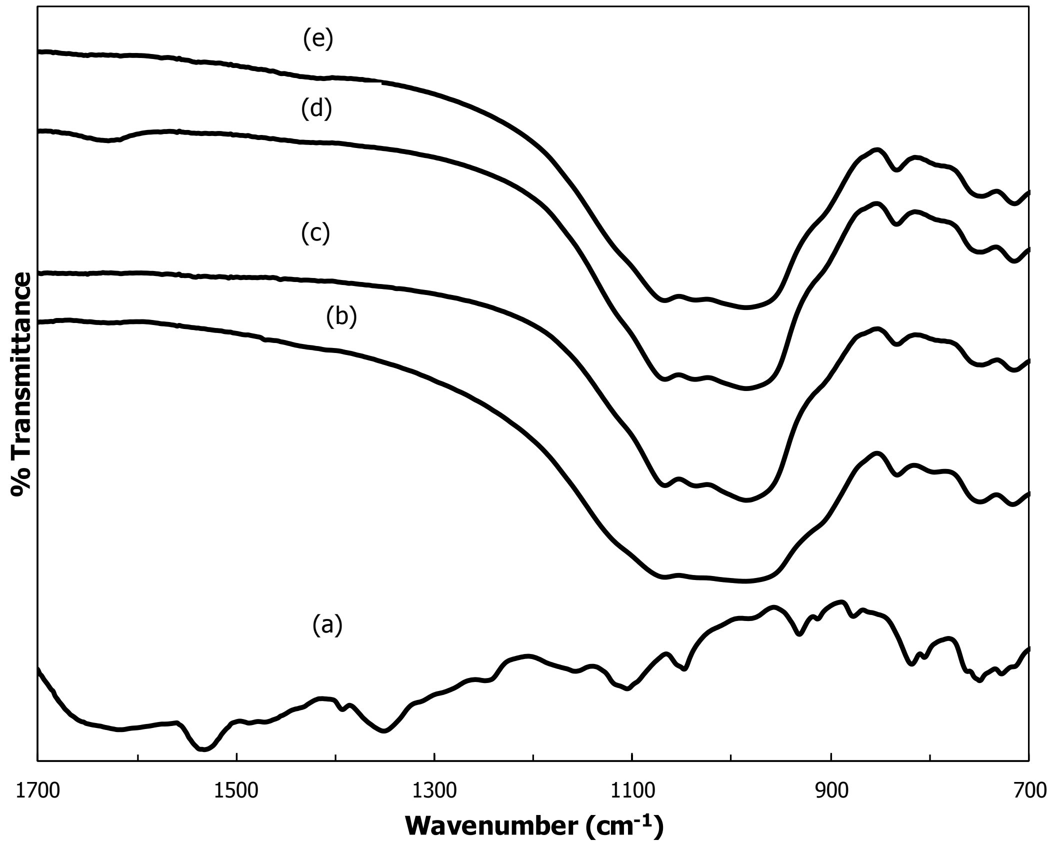


Figure 4.20 FT-IR spectra of TNZnPc pigment between 1700-700 nm at 120°C, (a) TNZnPc, (b) mica titania, (c) P16, (d) P17, (e) P18.

4.3.3 SEM Results of ZnPcMT Pigments

Figure 4.21 shows the SEM micrographs of ZnPcMT pigment samples coated at different temperatures. These SEM micrographs indicate that, ZnPc pigment was not deposited in the form of rod- like crystals on mica-titania surface that is seen in CuPc case. Only TiO_2 crystals could be noticed from the surface. Mica has platelet structure and the ZnPc molecules may take place between these platelets and because of that these SEM micrographs are not enough to say that deposition was achieved successfully.

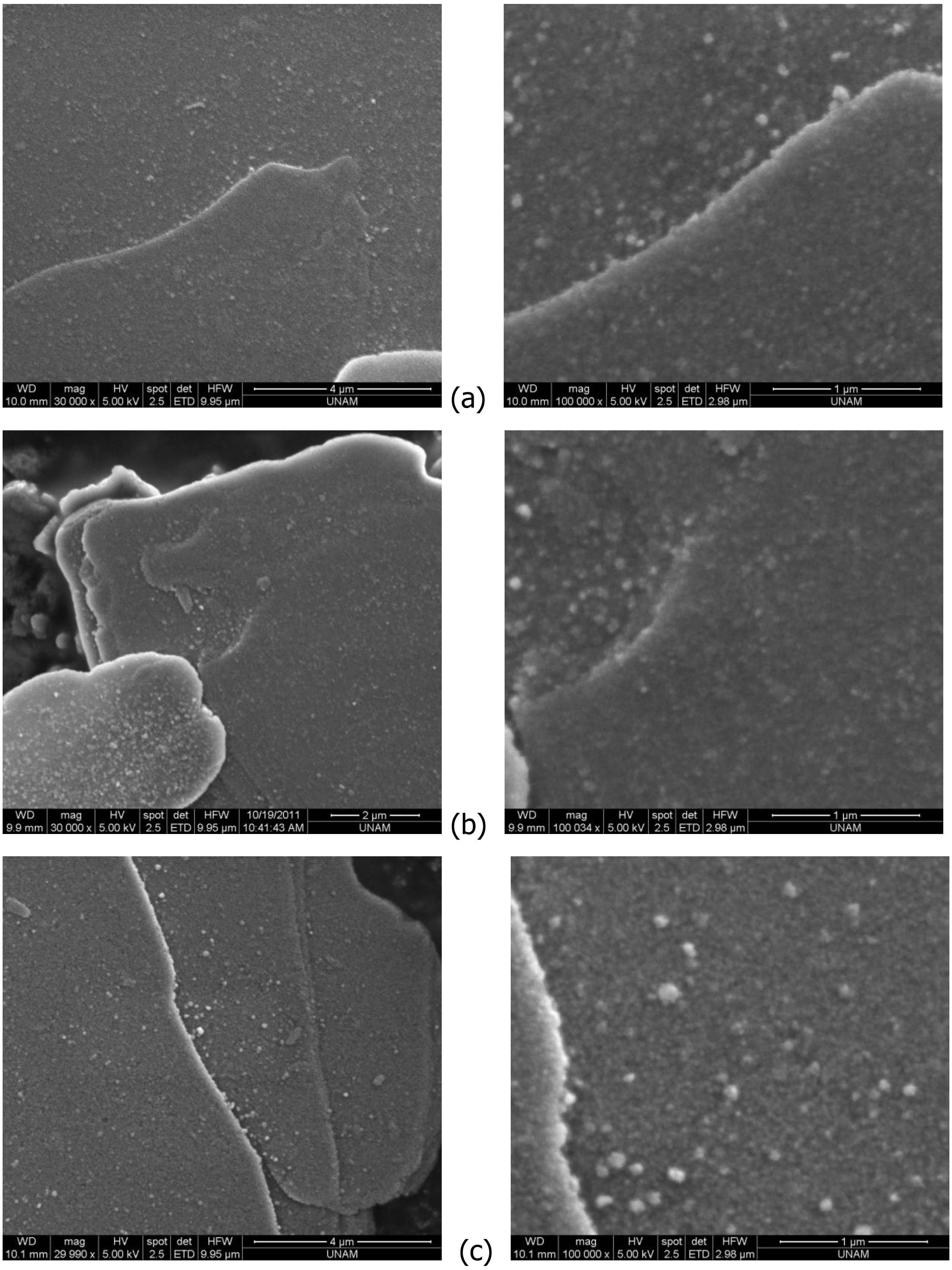
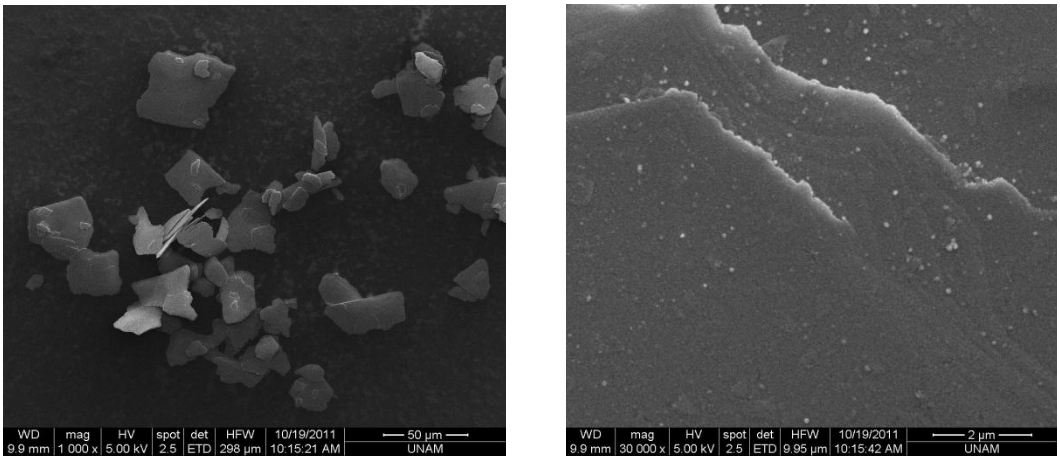


Figure 4.21 SEM micrographs of ZnPcMT of (a)P2, (b) P3, (c)P4.

4.3.4 SEM Results of TNZnPcMT Pigments

In Figure 4.22, the SEM micrographs of P18 are given. FTIR results do not provide enough evidence to conclude that deposition was not obtained in TNZnPc on mica- titania. Therefore, SEM micrographs were also taken for TNZnPc pigments. Similar to ZnPc case, TNZnPc pigment did not form rod-like crystalline structure on the substrate and only TiO_2 crystals could be noticed from the surface even at high magnifications.



(a) (b)

Figure 4.22 SEM micrographs of P18; (a) left (× 1000 magnification), (b) right (× 30000 magnification).

4.3.5 Elemental Analysis of Combination Pigments

To verify that ZnPc and TNZnPc pigments has deposited on mica-titania surfaces elemental analysis was also conducted. The effect of the amount of phthalocyanines on combination pigments, and also of the deposition temperature was also investigated by elemental analysis based on nitrogen. Nitrogen amounts of combination pigments were analyzed, and these nitrogen amounts were used to calculate the amount of zinc phthalocyanines that were deposited on mica- titania surfaces. As mentioned in experimental part, these combination pigments were prepared by adding 0.6 g mica titania pigment into the specified amount of ZnPc/ TNZnPc. The results are tabulated in Table 4.3. They show the percentage of nitrogen amount of combination pigments and the calculation of mass in percentage phthalocyanine was given in Appendix B. The deposition increases with temperature at all loadings except for 0.08 g ZnPc case at 120°C. When the temperature was kept constant, deposition increases with the initial loading amount of ZnPc.

Table 4.3 Mass percents of N and ZnPc pigments on mica-titania.

Sample Name	N % (mass)	Phthalocyanine (%)
0.04ZnPc_DMF_50 (P2)	0.00*	0.00*
0.04ZnPc_DMF_90 (P3)	0.67	3.45
0.04ZnPc_DMF_120 (P4)	0.68	3.51
0.08ZnPc_DMF_50 (P7)	1.52	7.84
0.08ZnPc_DMF_90 (P8)	1.54	7.94
0.08ZnPc_DMF_120 (P9)	1.27	6.55
0.16ZnPc_DMF_50 (P10)	1.80	9.28
0.16ZnPc_DMF_90 (P11)	2.27	11.70
0.16ZnPc_DMF_120 (P12)	2.46	12.68

* trace

In the case of TNZnPcMT pigments, the elemental analysis showed that no nitrogen was present in all samples. It means that the deposition of tetra nitro phthalocyanines on mica-titania was not accomplished. It could be due to the charge of the nitro groups at the periphery of the phthalocyanine.

4.3.6. Fluorescence Spectroscopy of ZnPcMT

As mentioned before, ZnPc has fluorescence property and it can be affected by different substituents or by different solvents. In our study, ZnPc pigments are combined with mica-titania pigment to observe whether it enhances or diminishes mica-titania's fluorescence effect. The samples for analysis were prepared as solid pellets (using KBr) since ZnPcMT is insoluble in most common solvents.

Figure 4.23 gives the fluorescence spectrum of combination pigments of P2, P3 and P4. Deposition at low temperature was not effective and at 50 °C flureoscence of mica-titania is not affected from phthalocyanine compounds. Elemental analysis has already shown that the amount of phthalocyanine that was deposited on mica-titania surface is so small. Therefore, intensity of the combination pigment is greater than the intensity of mica-titania itself. In this case, fluroescence effects of the both of pigments, ZnPc and mica-titania were observed. With the increasing temperature, amount of deposited ZnPc was also increases and at 90 °C, a layer forms on the surface. Because of this layer formation, ZnPc inhibits the effect of mica-titania. In some process, some of the radiation emitted by a material is absorbed by the material itself and in the case of ZnPc, similar result is seen. When the layer becomes thicker on mica-titania surface, ZnPc molecules absorb their radition and at 120 ^{o}C, they directly prevent the effect of MT.

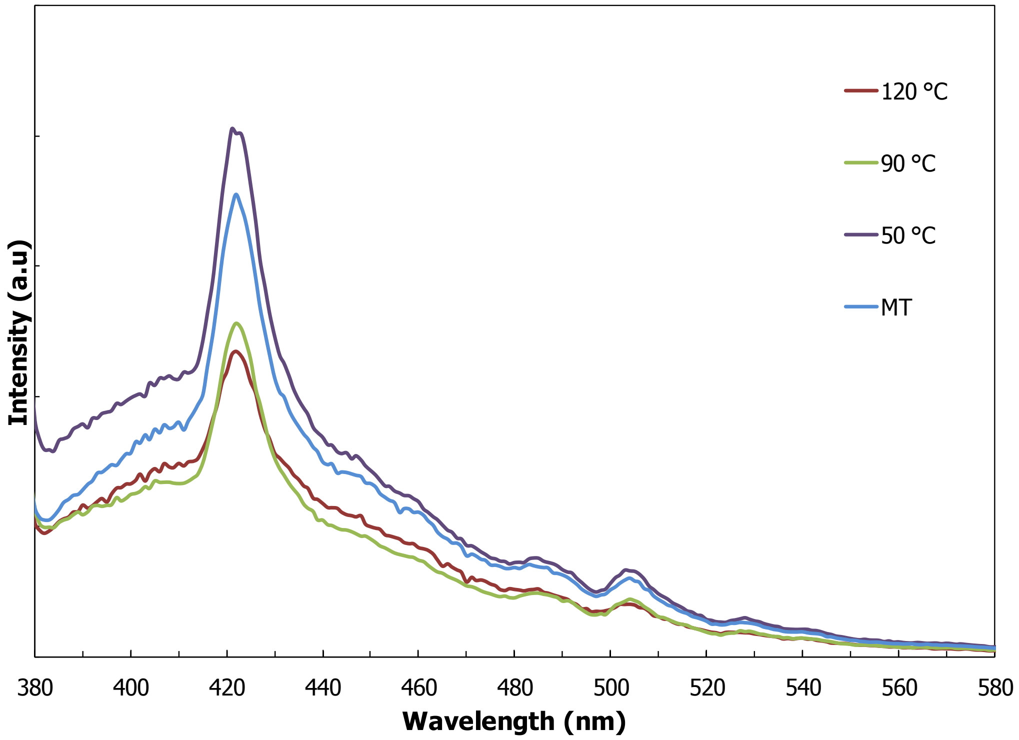


Figure 4.23 Fluorescence spectra of combination pigments with weight ratio of 0.067 (ZnPc/ MT) at different temperatures.

Figure 4.24 shows the fluorescence spectra of combination pigments P7, P8 and P9. These results are coincide with the elemental analysis results, it is seen that the amount of phthalocyanine deposited at 120 °C is less than that of at 90 °C. With the increasing amount of deposited ZnPc on mica-titania surface, layer of ZnPc becomes thicker and because of their interaction with each other, phthalocyanine molecules desorp from the mica-titania surface. Because of this desorption, mica-titania effect becomes compatible with the effect of phthalocyanine.

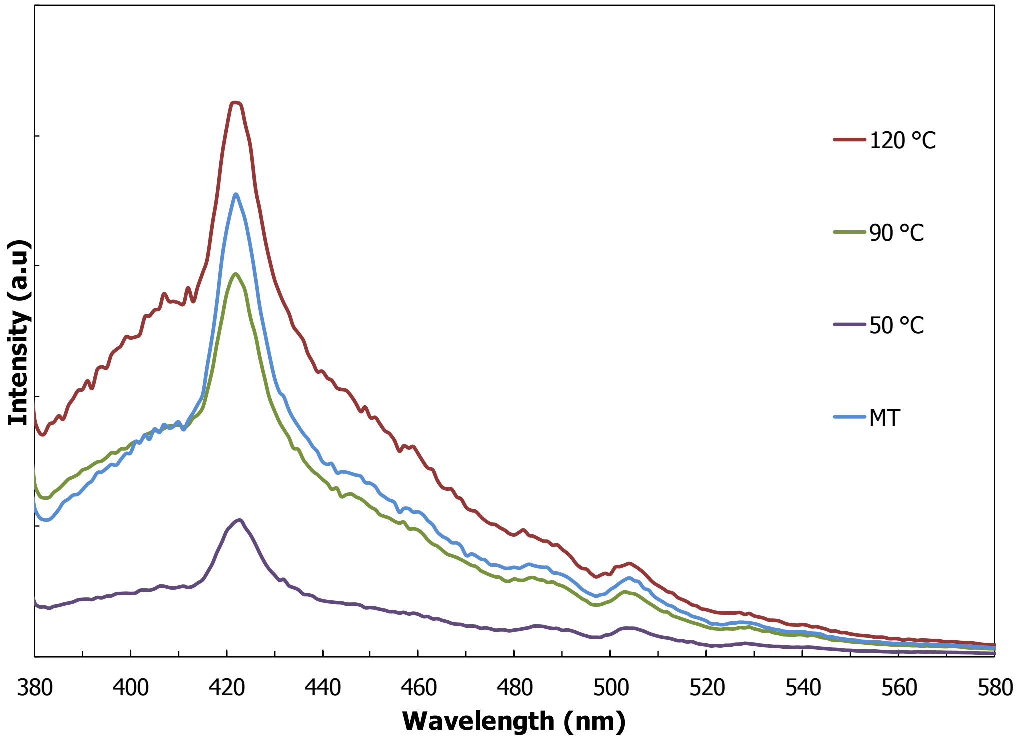


Figure 4.24 Fluorescence spectra of combination pigments with weight ratio of 0.133 at different temperatures.

The fluorescence spectra of combination pigments of P10, P11 and P12 is given in Figure 4.25. Similar results were also obtained in the case of 0.067 (w/w). The increase in the temperature enhances the deposition of phthalocyanine molecules on mica-titania surfaces, however, this results in a negative input i.e., phthalocyanine inhibits the fluorescence effect of MT.

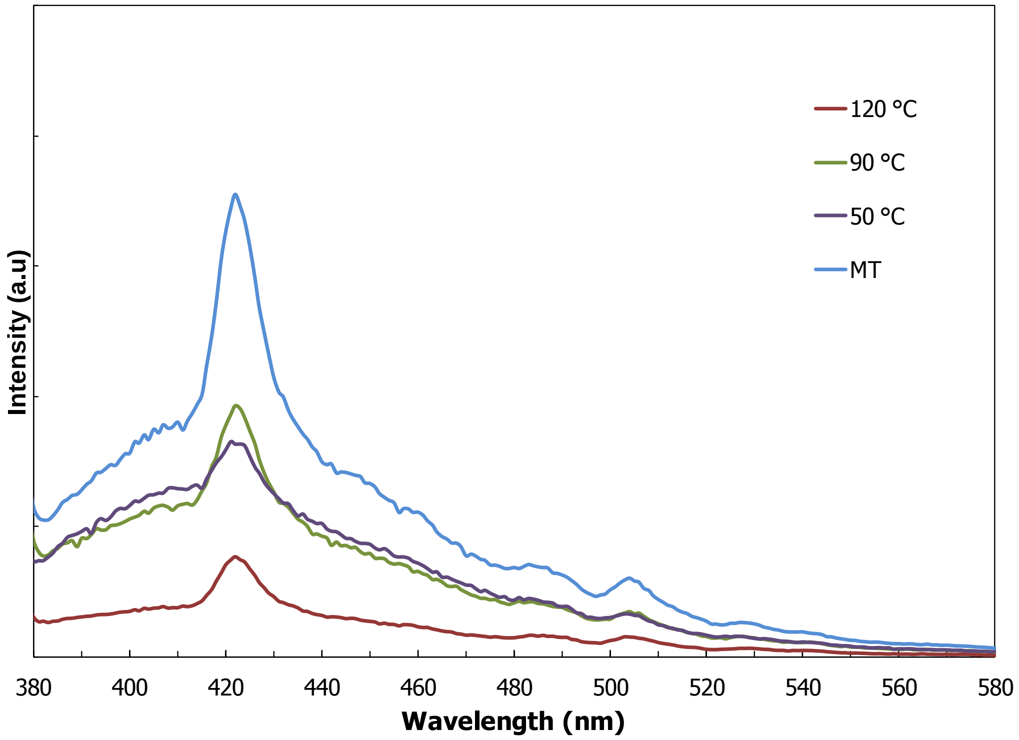


Figure 4.25 Fluorescence spectra of combination pigments with weight ratio of 0.267 at different temperatures.

Figure 4.26 shows the effect of phthalocyanine concentration on flureoscence effect. Generally, it is expected that fluorescence intensity should increase with the concentration of material. However, in our case different result was obtained. The flureoscence intensity decreased with the increasing concentration. It can be explained with the aggregation of phthalocyanine molecules, i.e. when the amounts of ZnPc molecules increase their interaction between them becomes stronger and they start to aggregate. As a result of this ,they absorb the radiation emitted in the solution; this is a kind of self-absorption phenomenon.

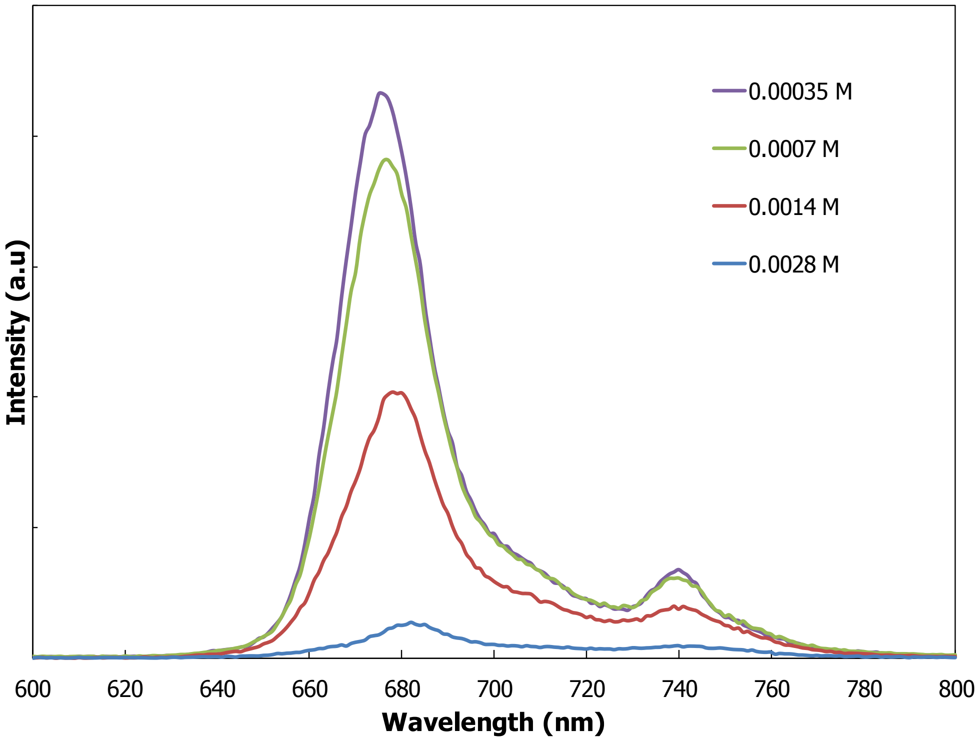


Figure 4.26 Fluorescence spectra of ZnPc samples having different concentrations.

4.3.7 Optical Properties of Paints Manufactured with Combination Pigments

Alkyd based formulations of combination pigments were prepared and their color and gloss properties were investigated. The paint that contains only mica-titania pigment was chosen as standard and the comparisons were made with reference to this sample.

To characterize color properties of paints, L*a*b values of the samples were taken into the consideration. The L parameter is used to show the lightness of the paint while a* is for redness and b* for the yellowness. Positive ‘a’ values show that paint is redder than the sample; negative values are indications of the greenish samples. Similarly, positive 'b' values show that paint is yellower than the sample; negative values are indications of the bluish samples. dL*, da* and db* indicate the difference between the sample and the standard. Table 4.4, 4.5, and 4.6 list the values for each ZnPc samples. The comparative color properties of combination pigments based on different zinc phthalocyanine deposition at different temperatures are also shown in Figure 4.27.

Table 4.4 The L*a*b* values of paints of combination pigments at 120 °C.

Name of Sample	dL*	da*	db*	dE*
MT (Standard)	0.00	0.00	0.00	0.00
P4	-6.76	0.80	1.22	3.15
P9	-7.78	0.08	3.12	4.87
P12	-14.19	-0.52	5.33	8.76

Table 4.5 The L*a*b* values of paints of combination pigments at 90 °C.

Name of Sample	dL*	da*	db*	dE*
MT (Standard)	0.00	0.00	0.00	0.00
P3	-2.78	0.56	0.55	1.41
P8	-6.12	0.19	-0.69	2.59
P11	-10.55	-1.14	1.19	4.70

Table 4.6 The L*a*b* values of paints of combination pigments at 50 °C.

Name of Sample	**dL***	**da***	**db***	**dE***
MT (Standard)	0.00	0.00	0.00	0.00
P2	-6.75	0.85	-1.98	3.73
P7	-6.94	-0.63	-0.47	2.91
P10	-12.92	-0.94	1.50	5.62

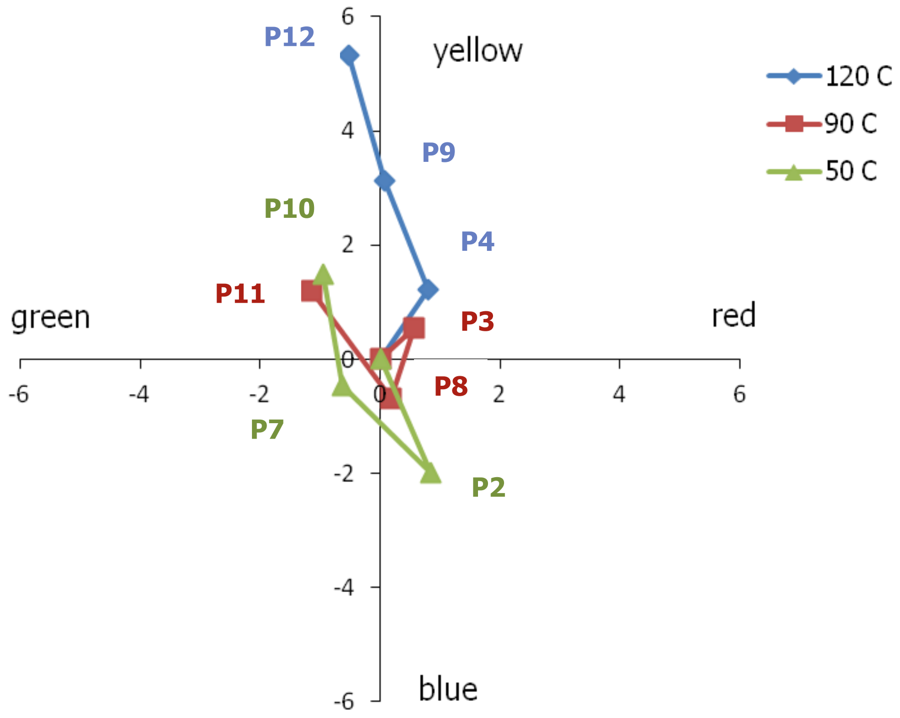


Figure 4.27 The comparative color properties of combination pigments based on different zinc phthalocyanine deposition at different temperatures.

MT pigment based paint is taken as reference and it is shown at the origin. With the increasing amount of ZnPc in the ZnPcMT pigments, yellow and green shift is seen in all cases.

CHAPTER 5

CONCLUSIONS

1. Unsubstituted zinc phthalocyanine (ZnPc) and tetranitro zinc phthalocyanine (TNZnPc) were synthesized by microwave irradiation using cheap precursors. They have fluorescent property.

2. The optimum deposition temperature was determined as 120 ^{o}C.

3. The optimum reaction time for deposition of ZnPc was determined as ½ hour.

4. Different amounts of ZnPc were deposited on mica-titania surfaces and it is observed that, with the increasing amount of ZnPc, the interaction between ZnPc particles increases and they desorp the surface of mica-titania pigment. The best result was obtained with P9 pigment.

5. TNZnPc pigments did not deposit on mica-titania pigment.

6. Rod-like micron sized crystal formation of CuPcMT pigments was not observed in ZnPcMT case.

7. High temperature provides enhancement in fluorescence intensity, however, the increase in the amount of ZnPc cause a decrease in intensity.

CHAPTER 6

RECOMMENDATIONS

1. Different precursors can be tried to synthesize substituted zinc phthalocyanines. Crystalline phases and surface morphologies of them on the mica-titania substrates can be investigated.

2. New washing and purifying steps can be developed.

3. ZnPc and TNZnPc can be dispersed in different solvents for deposition on mica- titania.

4. Different paint formulations can be made and their paint properties can be studied.

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APPENDIX A

STRUCTURAL FORMULAS OF USED MATERIALS IN THE EXPERIMENTS

Table A.1 List of chemicals

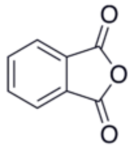
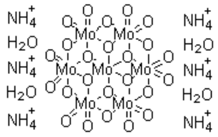
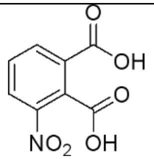
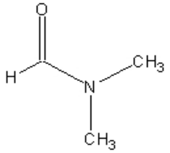
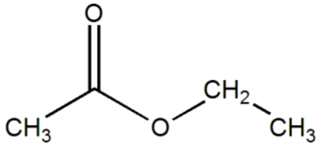
Chemical	Chemical Formula	Structural Formula
Phthalic anhydride	$C_6H_4(CO)_2O$	
Zinc chloride	$ZnCl_2$	-
Ammonium heptamolybdate	$(NH)_4Mo_7O_{24}.4H_2O$	

Table A.1 List of chemicals (continued)

3- nitrophthalic acid	$O_2NC_6H_3\text{-}1,2\text{-}(CO_2H)_2$	
Dimethylformamide	$(CH_3)_2NCHO$	
Ethyl acetate	$CH_3COOCH_2CH_3$	

APPENDIX B

FT-IR SPECTROSCOPY RESULTS FOR COMBINATION PIGMENTS

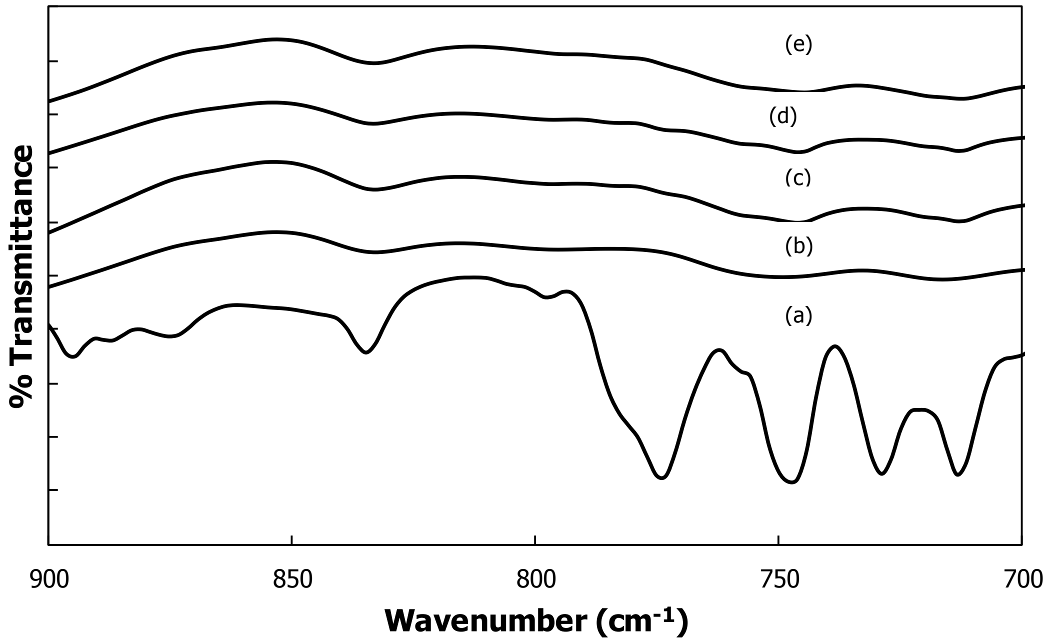


Figure B.1 FT-IR spectra of 0.04 g ZnPc pigment (a) ZnPc, (b) mica-titania, (c) 50°C, (d) 90°C, and (e) 120°C.

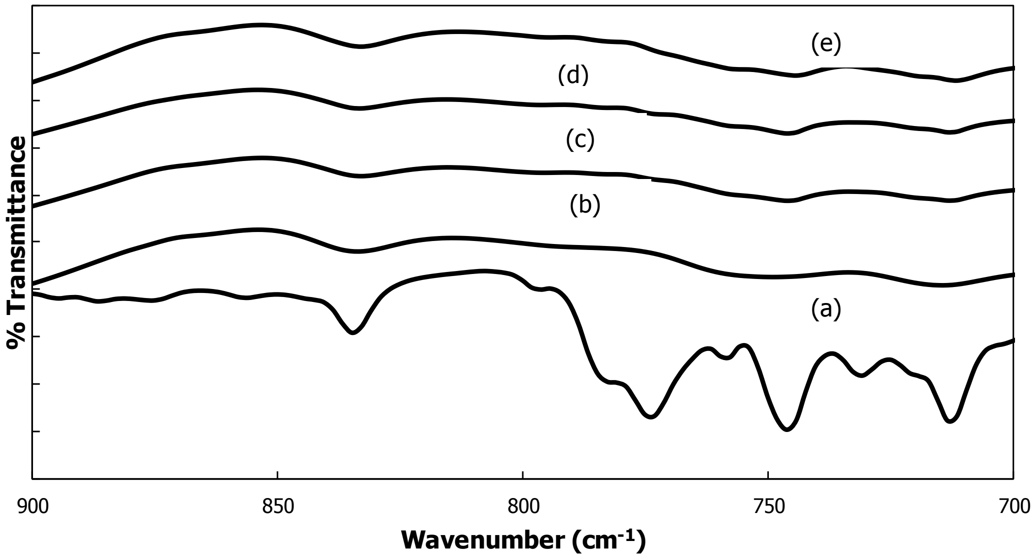


Figure B.2 FT-IR spectra of 0.08 g ZnPc pigment (a) ZnPc, (b) mica-titania, (c) 50°C, (d) 90°C, and (e) 120°C.

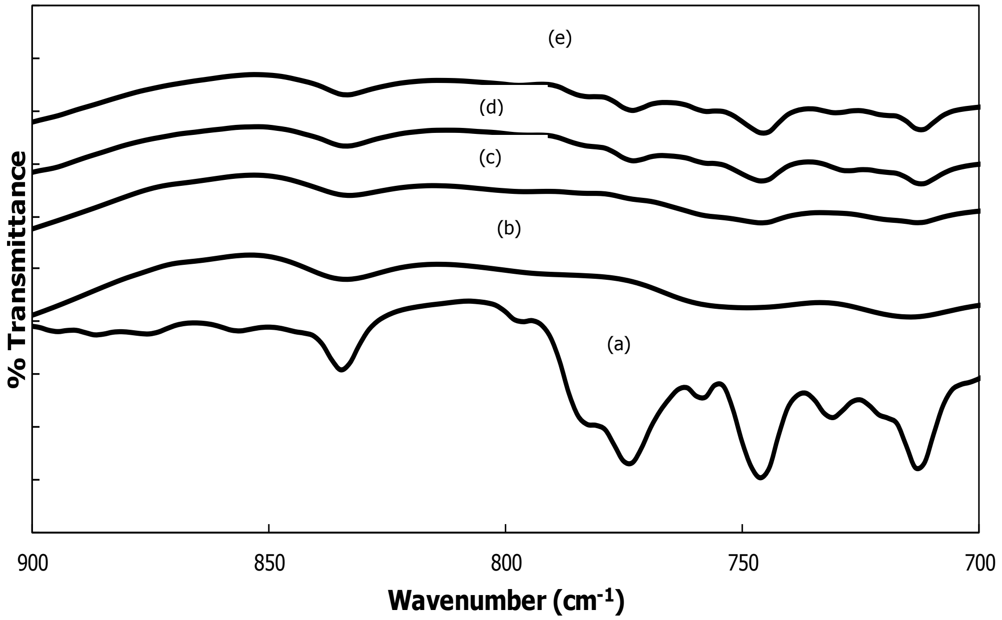


Figure B.3 FT-IR spectra of 0.16 g ZnPc pigment (a) ZnPc, (b) mica-titania, (c) 50°C, (d) 90°C, and (e) 120°C.

APPENDIX C

ELEMENTAL ANALYSIS RESULTS OF COMBINATION PIGMENTS

To determine the amount of zinc phthalocyanines and tetra nitro zinc phthalocyanines that deposited on mica- titania surface elemental analysis was performed. Results of analysis are given in Table B.1.

To calculate the amount of phthalocyanines on mica- titania surfaces, molecular weight of the zinc phthalocyanine and the amount of nitrogen in it were used. 1 mol ZnPc is 577.38 g and it contains of 112 g nitrogen.

$$\% \text{ ZnPc} = \frac{\% \text{ amount of N in the Sample* Molecular Weight of ZnPc}}{\text{Nitrogen Amount in ZnPc}}$$

% ZnPc = 1.52*577.38/112 = 7.84 %

Table C.1. Amounts of % N in combination pigments at different temperatures.

Sample Name	**N % (mass)**	**Phthalocyanine (%)**
0.04ZnPc_DMF_50 (P2)	0.00*	0.00*
0.04ZnPc_DMF_90 (P3)	0.67	3.45
0.04ZnPc_DMF_120 (P4)	0.68	3.51
0.08ZnPc_DMF_50 (P7)	1.52	7.84
0.08ZnPc_DMF_90 (P8)	1.54	7.94
0.08ZnPc_DMF_120 (P9)	1.27	6.55
0.16ZnPc_DMF_50 (P10)	1.80	9.28
0.16ZnPc_DMF_90 (P11)	2.27	11.70
0.16ZnPc_DMF_120 (P12)	2.46	12.68

APPENDIX D

PEAK ANALYSIS RESULTS OF COMBINATION PIGMENTS

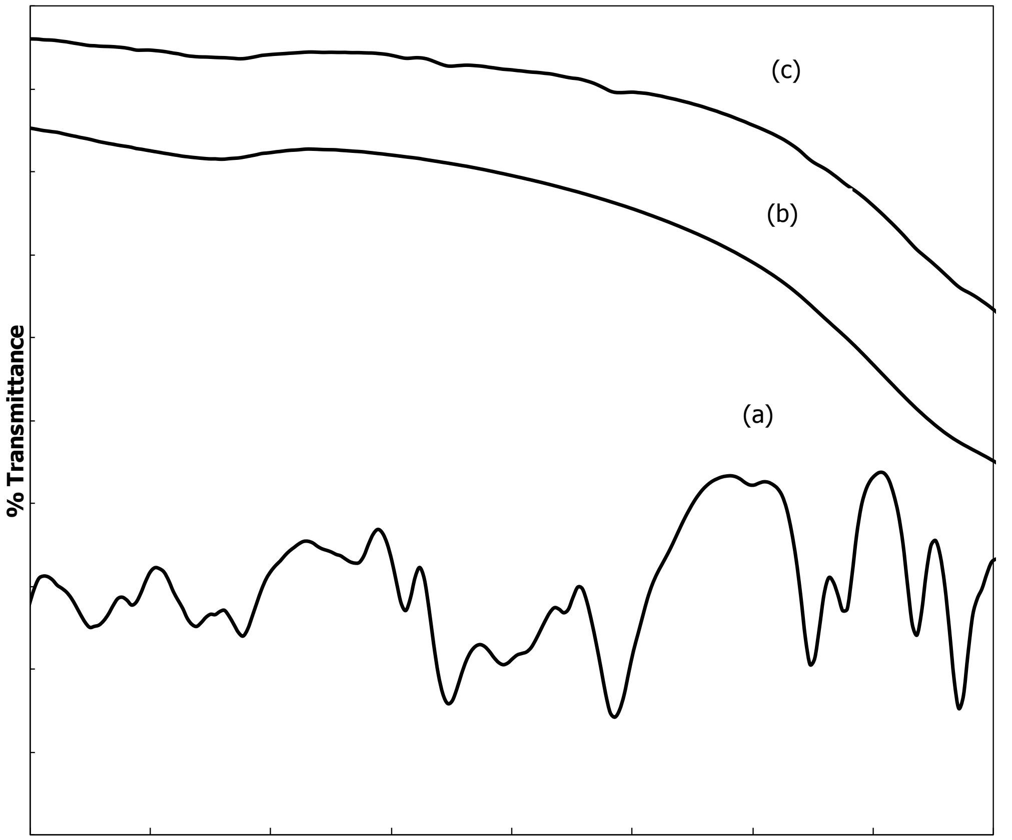


Figure D.1 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c) ZnPcMT at 25°C.

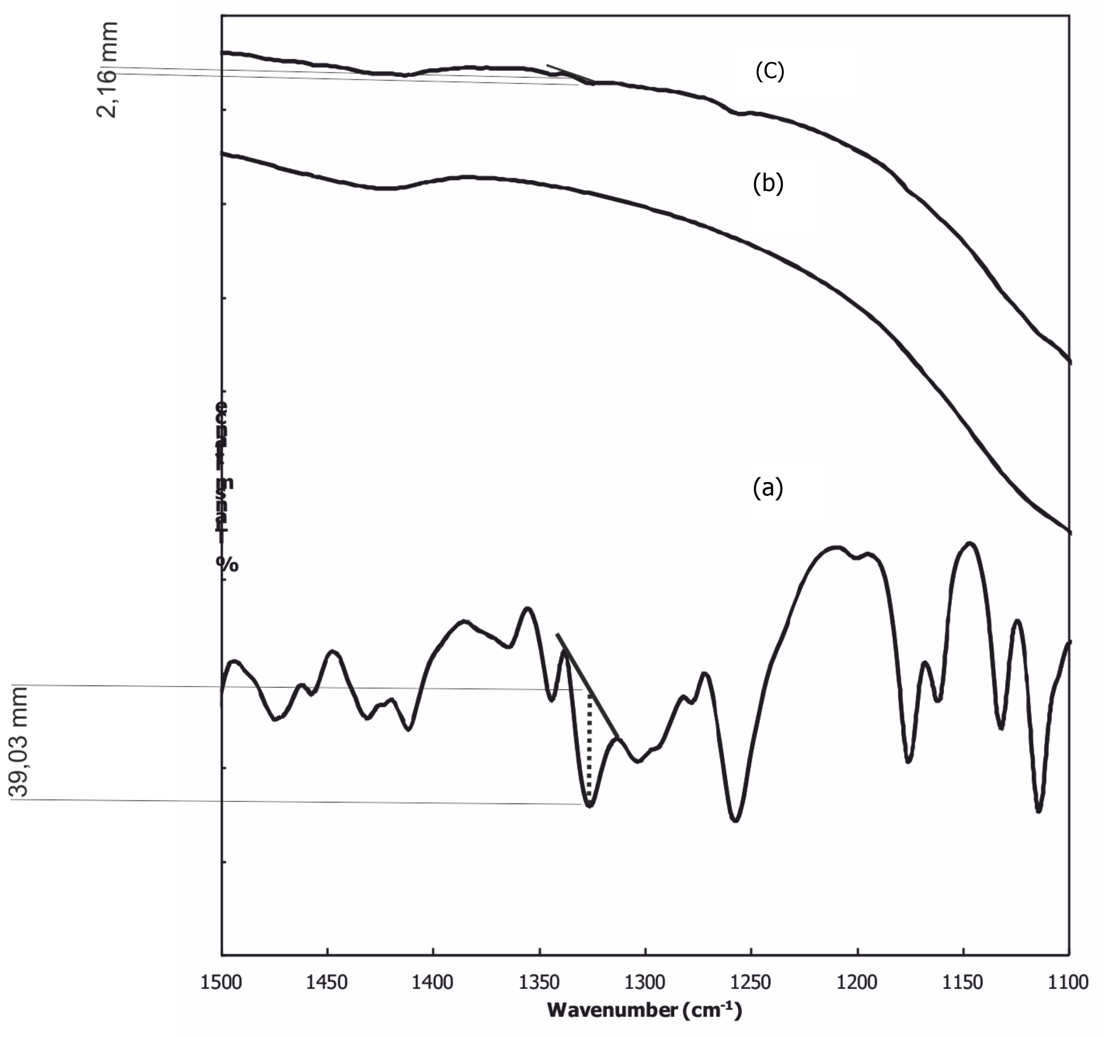


Figure D.2 CorelDRAW results of peak analysis of ZnPcMT pigment at 25 °C (a) ZnPc, (b) mica titania, (c) 25 °C.

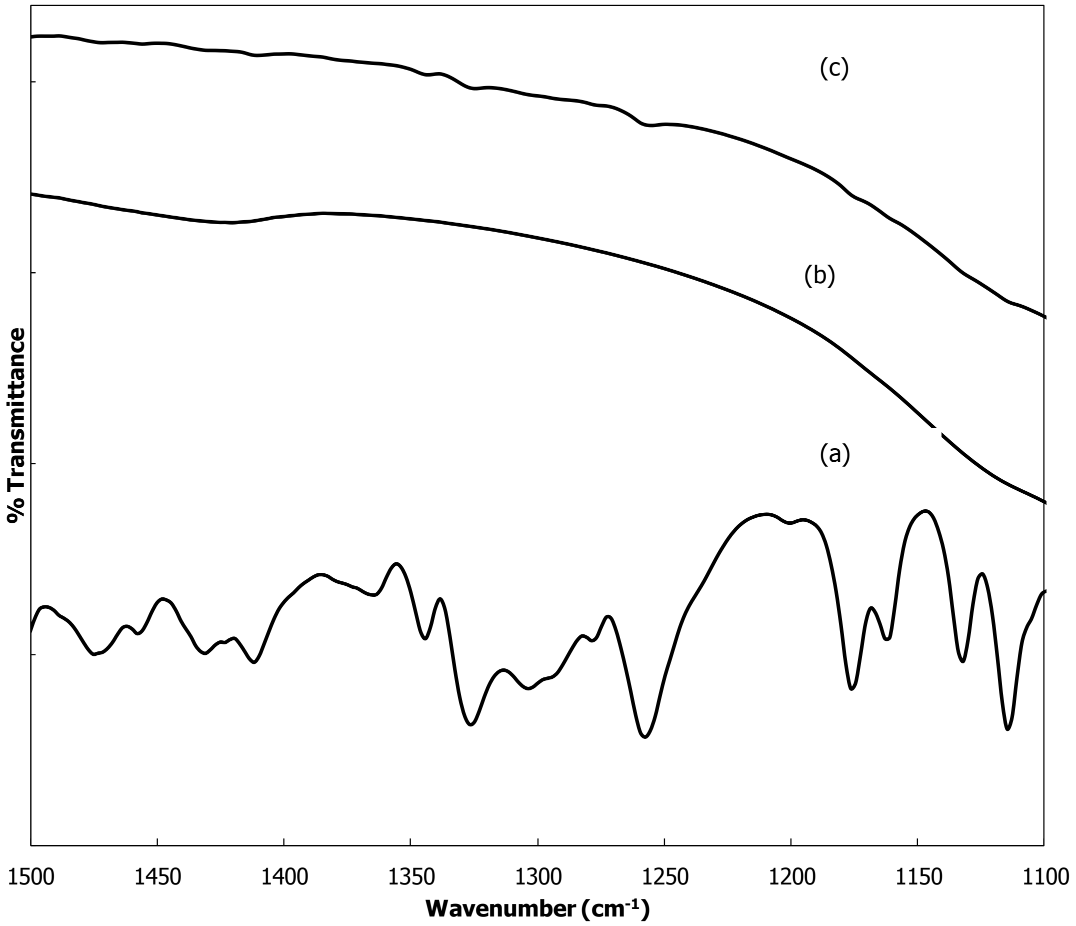


Figure D.3 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c) ZnPcMT at 50°C.

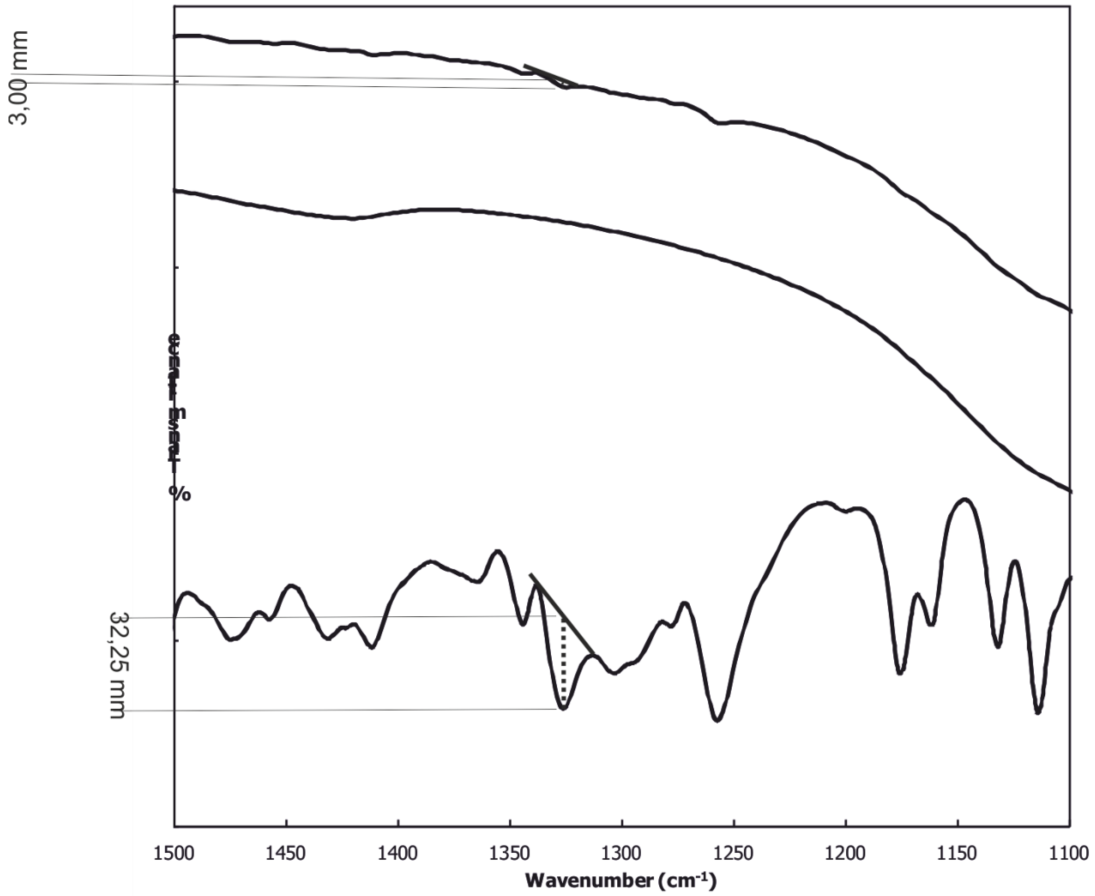


Figure D.4 CorelDRAW results of peak analysis of ZnPcMT pigment at 50 °C (a) ZnPc, (b) mica titania, (c) 50 °C.

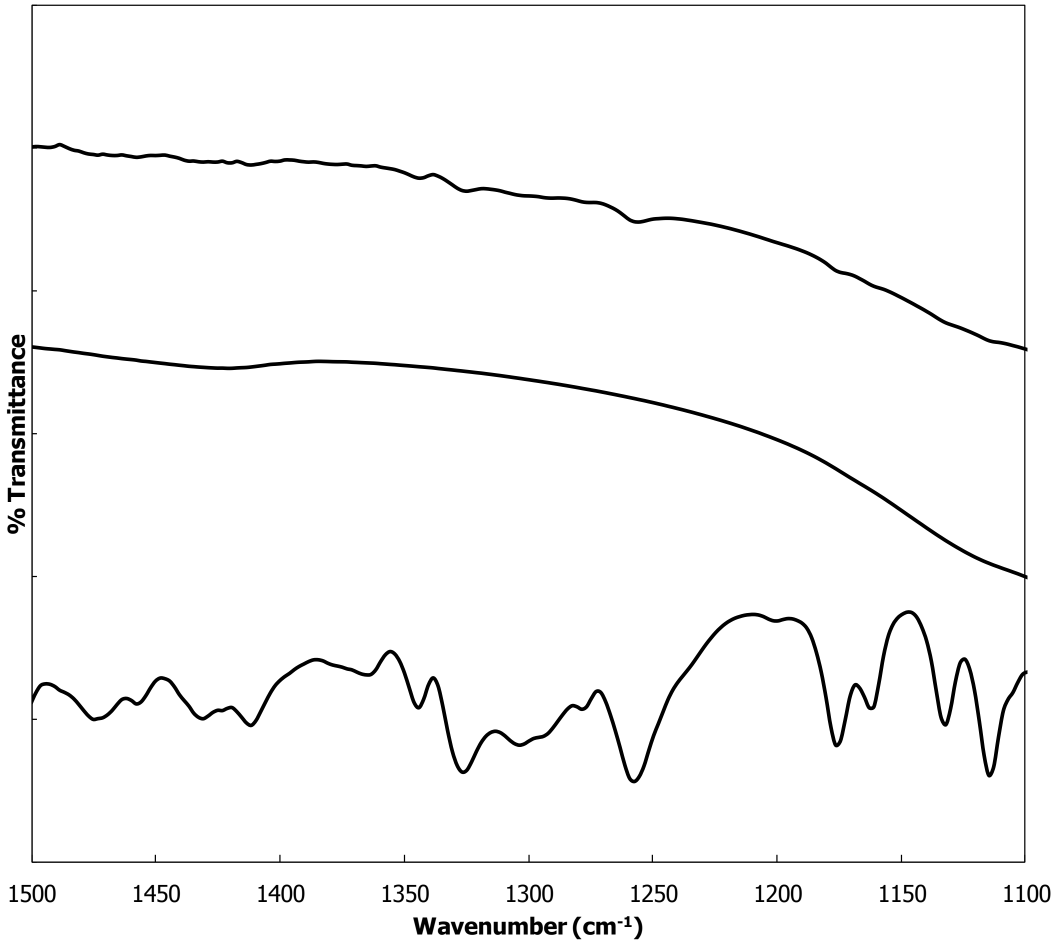


Figure D.5 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c) MT at 90°C.

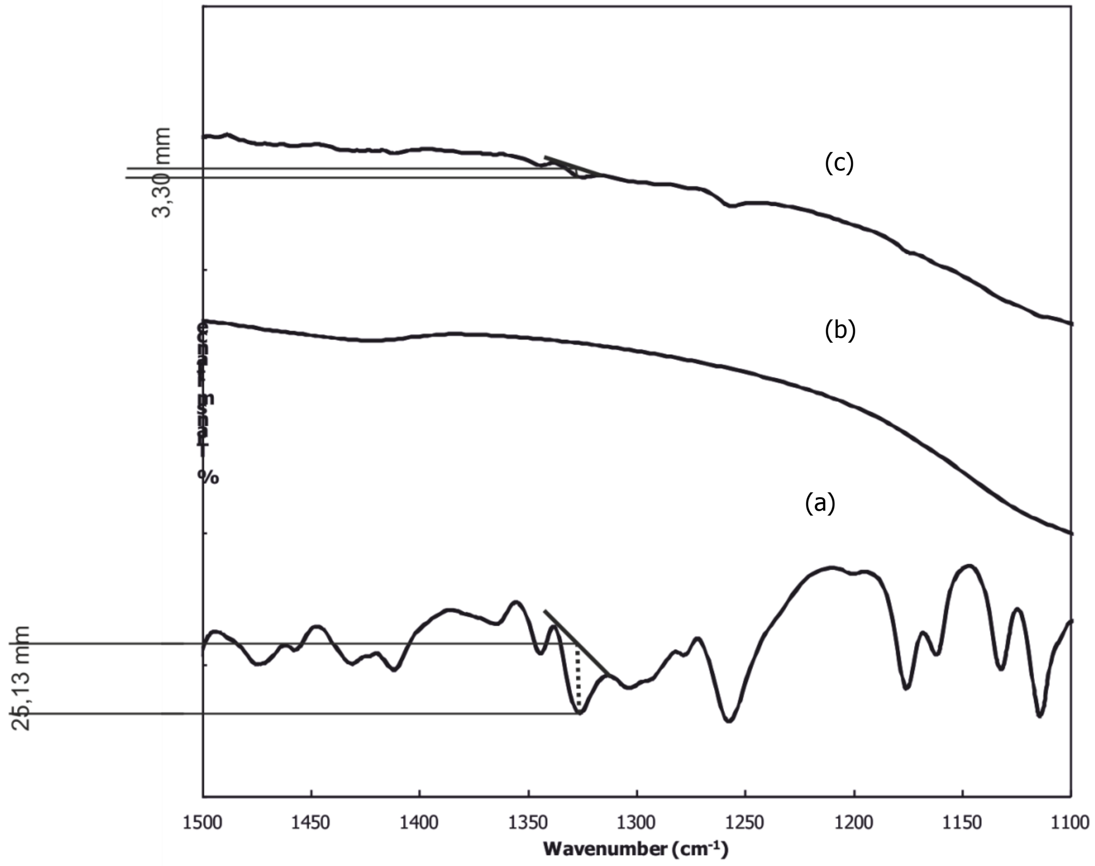


Figure D.6 CorelDRAW results of peak analysis of ZnPcMT pigment at 90 °C (a) ZnPc, (b) mica titania, (c) 90 °C.

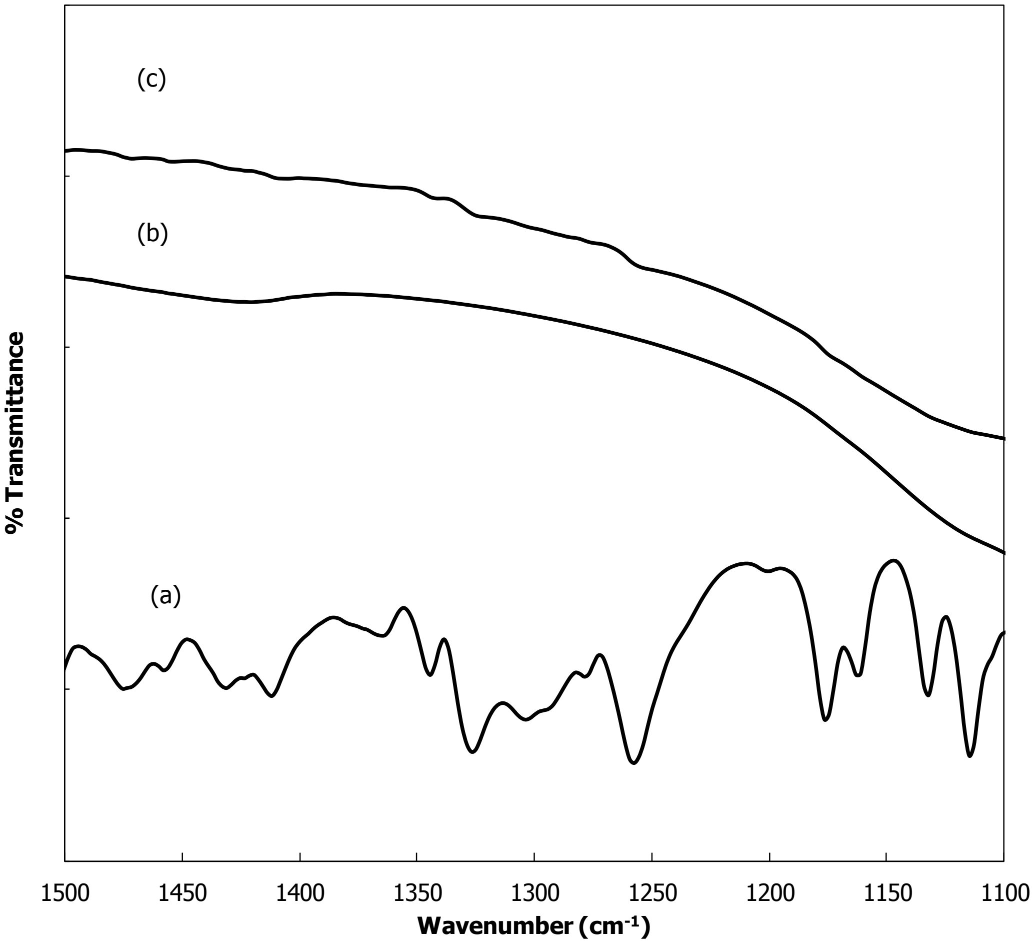


Figure D.7 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c)ZnPcMT at 1 hour.

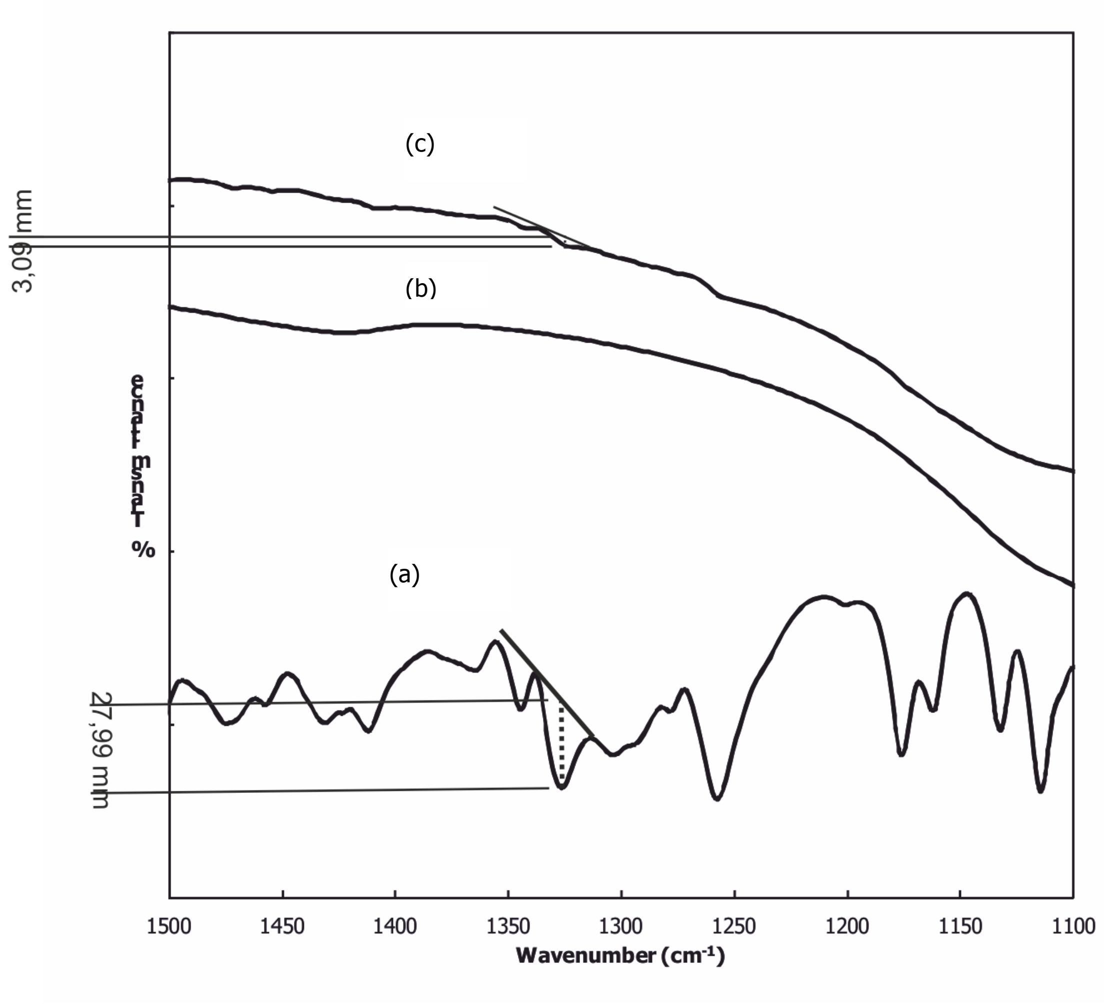


Figure D.8 CorelDRAW results of peak analysis of ZnPcMT pigment at 1 hour (a) ZnPc, (b) mica titania, (c) 1 hour.

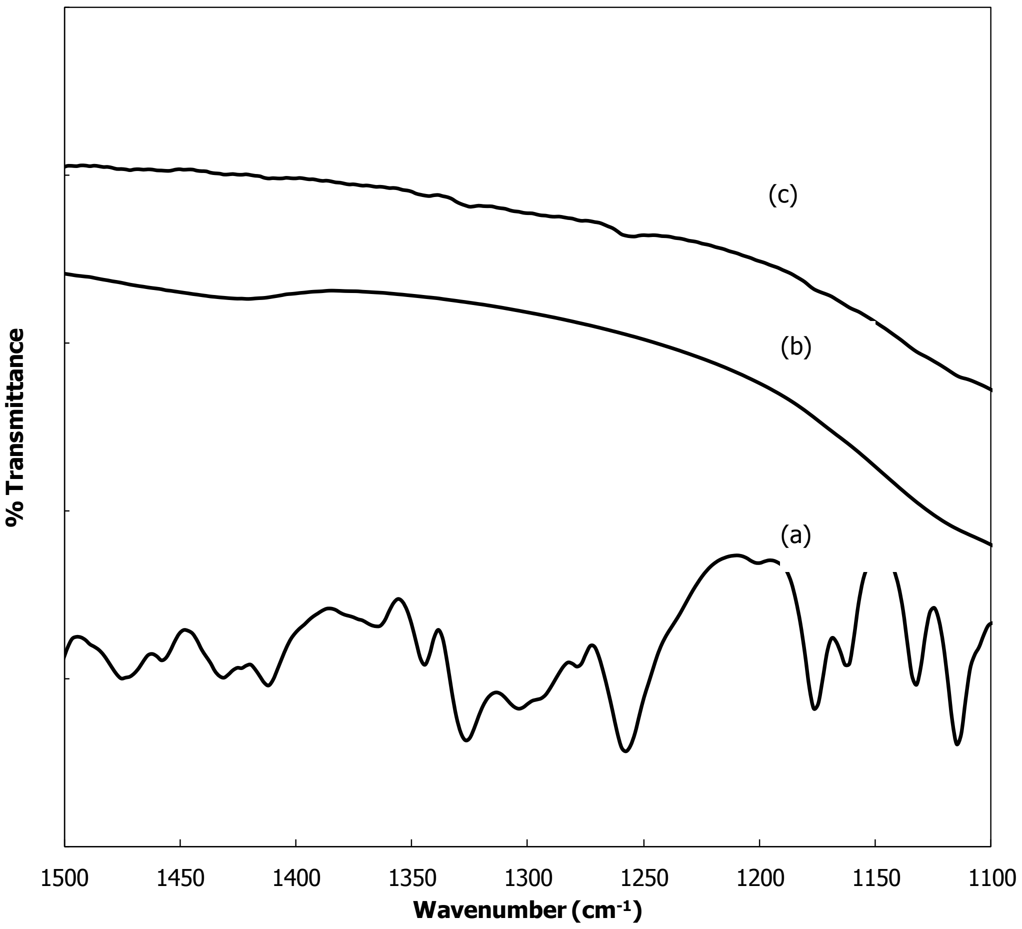


Figure D.9 FT-IR spectra of pigments (a) ZnPc, (b) mica titania, (c) ZnPcMT at 2 hours.

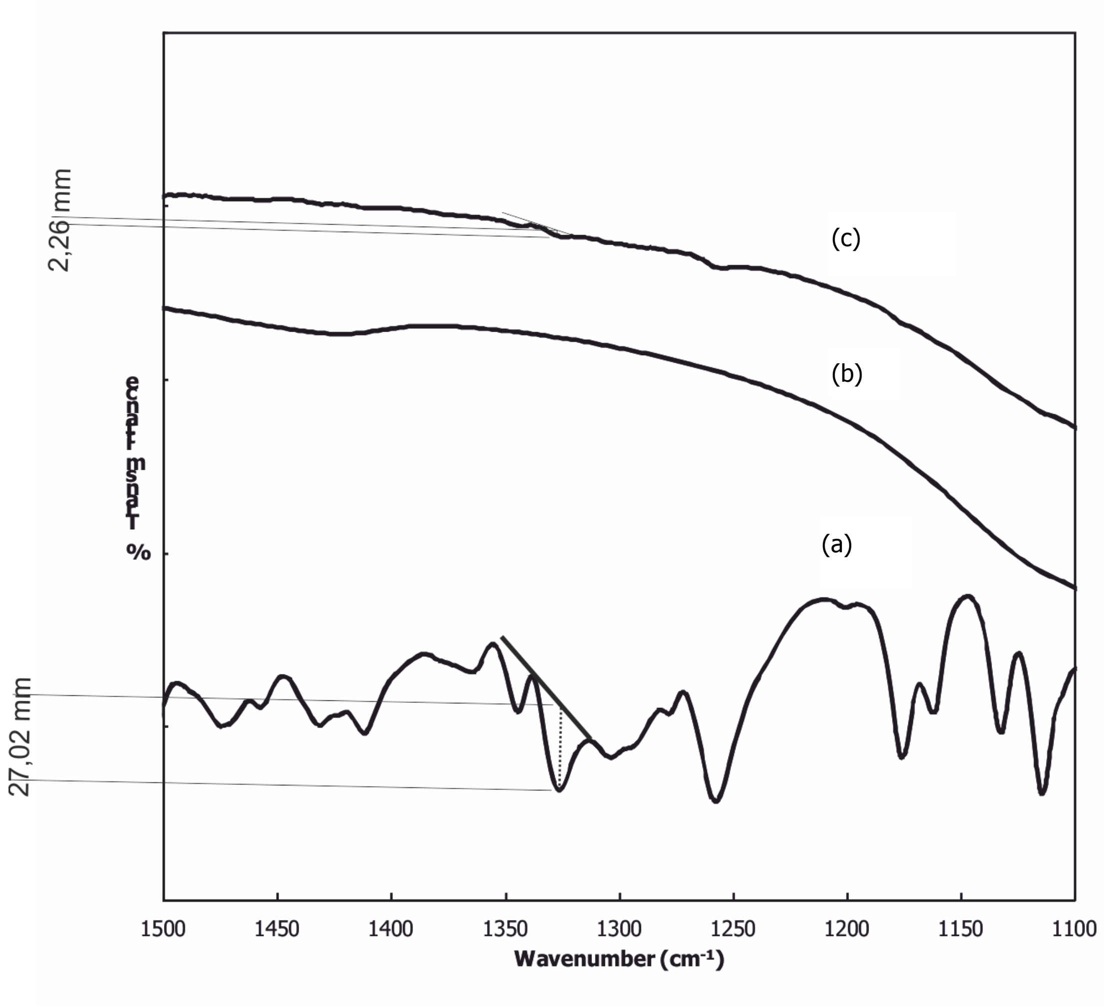


Figure D.10 CorelDRAW results of peak analysis of ZnPcMT pigment at 2 hours (a) ZnPc, (b) mica titania, (c) 2 hours.