Düzce Üniversitesi Bilim ve Teknoloji Dergisi

Characterization of Thermochromic Pigments as Coating Materials

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ABSTRACT

In this study, thermochromic coatings were produced using thermochromic pigment and polyvinylpyrrolidone (PVP). It is aimed to develop innovative materials that will reduce external dependence, increase international competitiveness and support energy efficiency. The particle size of the thermochromic pigments and TG/DTA analyzes were carried out. Particle size of thermochromic pigments that change color at 33°C green, black at 45°C, and blue at 65°C were measured as 2.483 µm, 6.227 µm and 3.671 µm, respectively, according to the particle size d (50) values. The color change of thermochromic pigments with increasing and decreasing temperature was examined by infrared thermometer. When the surface temperature was elevated above the transition temperature, the pigments' and coatings' color turned to white. When it was cooled, the product returned to its original color. Characterization studies were carried out by X-ray diffraction analysis and scanning electron microscopy analysis techniques. It has been determined that the resulting blackness of the thermochromic pigment is due to the presence of iron. Furthermore, color of green and blue pigment is originated from copper in the content. As a result of the EDX analyzes made in blue and black coatings, boron oxide (B_2O_3) was detected. Conclusions showed that thermochromic pigments can be used in the production of energy saving thermochromic coated smart glasses.

Keywords: *Coating 1, Glass 2, Thermochromic Pigment 3, Characterization 4*

Termokromik Malzemelerin Kaplama Malzemesi Olarak Karakterizasyonu

ÖZET

Bu çalışmada, termokromik kaplamalar termokromik pigment ve polivinilpirolidon (PVP) kullanılarak üretilmiştir. Dışa bağımlılığı azaltacak, uluslararası rekabet gücünü artıracak ve enerji verimliliğini destekleyecek yenilikçi malzemelerin geliştirilmesi amaçlanmaktadır. Termokromik pigmentlerin tane boyutu ve TG / DTA analizi gerçekleştirilmiştir. 33.45 ve 65°C'de renk değiştiren termokromik pigmentlerin sırasıyla tane boyutu d (50) değerlerine göre 2.483 µm, 6.227 µm, 3.671 µm olarak ölçülmüştür. Termokromik pigmentlerin artan ve azalan sıcaklık ile renk değişimi infrared termometre ile incelenmiştir. Yüzey sıcaklığı geçiş sıcaklığının

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üzerine çıkarıldığında pigmentlerin ve kaplamaların rengi beyaza dönmüştür. Soğutulduğunda ise ürün orijinal rengine geri dönmüştür. Karakterizasyon çalışmaları X-ışını kırınım analizi ve taramalı elektron mikroskobu analiz teknikleri ile gerçekleştirilmiştir. Termokromik pigmentin siyahlığının demirin varlığından kaynaklandığı tespit edilmiştir. Ayrıca, yeşil ve mavi pigmentin rengi içeriğindeki bakırdan kaynaklanmaktadır. Mavi ve siyah kaplamalarda yapılan EDX analizi sonucunda bor oksit (B_2O_3) tespit edilmiştir. Sonuçlar, termokromik pigmentlerin enerji tasarrufu sağlayan termokromik kaplamalı akıllı camların üretiminde kullanılabileceğini göstermiştir.

Anahtar Kelimeler: *Kaplama 1, Cam 2, Termokromik pigment 3, Karakterizasyon 4*

I. INTRODUCTION

In the buildings, a significant portion of the energy which consumed to provide heat comfort is lost from the windows. Intelligent coatings, thin films with spectral selective properties on the glass surface are an innovative solution for this problem. Thermochromic coatings are good candidates to solve this problem. Intelligent windows coated with thermochromic materials change their color and optical properties in response to temperature changes. M. Kamalisarvestani et al. showed effect of this type of coating in their study. They also showed that effect of coating addition and it is detailed with different dopant such as tungsten, fluorine, gold nanoparticles to the vanadium dioxide coating. By adding the right additives, the transition temperature can be reduced and visible light transmission can be increased. Each additive substance causes special effect on the coating. Tungsten reduces transition temperature; gold nanoparticles cause more beautiful film colors and fluorine enhances visible light transmission. Titanium dioxide imparts self-cleaning properties to films [1].

Controlling the amount of solar energy entering the building, reducing the energy needs of buildings is a measure that can be taken to combat global warming. For this purpose, the windows are covered with special thin film which is effective on energy conservation. There are a lot of application for intelligent coatings, including greenhouses, sun protectors, housing, offices and automobile windshields. The development of such coatings provides environmental benefits leading to considerable savings in energy costs [2]. In other application area, it is possible to use thermochromic pigments in dye for coloring building. The shortcoming of existing building coatings is that they can't meet the color of building coating and the need to create a comfortable building environment from a thermal point of view. Therefore, cool tones in summer, warm tones in winter should be preferred to protection of inside temperature of building. However, present existing building coatings do not have these properties, and new building coatings that can be colored reversibly at different seasons should be developed. Materials that have thermochromic properties should be preferred to create a thermally comfortable building environment. To this aim it is generally considered to be a comfortable temperature of 18-20°C. For this reason, to achieve this it is necessary to develop a technology that can change the optical properties of the material according to the external temperature and solar radiation levels. Thermochromic coatings change their color as the temperature increases, turning them from darker tones to lighter tones. By controlling the amount of heat that flows into the building with thermochromic glass coatings, cooling loads for air-conditioned buildings are reduced. This system supply more comfortable thermal conditions without air conditioning. To create a thermally comfortable building environment it is necessary to use materials that change color with heat [3-5].

Use of intelligent coatings based on thermochromic materials is an effective way of reducing building energy consumption [6].

The studies in the literature include vanadium dioxide as an additive. Vanadium dioxide thin films demonstrate transition property from metal phase to semiconductor phase or from semiconductor phase to metal phase at certain temperatures. The phase transition temperature of VO_2 is 68°C. This temperature is too high a temperature to be applied in the building of the VO_2 thin film-based coating. By doped with transition metal ions such as tungsten, temperature can be lowered significantly. Furthermore low luminous transmittance and poor solar modulation of VO_2 based thermochromic windows limit practical applications [7-12].

The optical properties of glasses are changed by using thermochromic pigments in coating applications. Thermochromic behavior and color can be adjusted by mixing thermochromic pigments [13]. When the thermochromic pigment is added to the formed coatings it provides absorption of solar energy in winter [3]. It also provides selective transmission of infrared radiation in response to ambient temperature. However, polyvinylpyrrolidone (PVP, K90) is added as a supporting, binder and anti-cracking agent for film formation [14-17]. Given the disadvantages of VO_2-containing coatings, we need thermochromic pigments for coating applications.

Transition is provided by the thermally reversible transformation of the molecular structure of the pigments. This process can be explained by changing on organic leko dye mixtures, which are the three main components. First one is called as color former which is usually a cyclic ester that determines the color of the final product. Second one is color developer which is a weak acid that imparts a reversible color change to the thermochromic material and is responsible for the color intensity of the final product. The medium is solvent. It is usually an alcohol or an ester and its melting point of controls the transition temperature at which the color change occurs. Encapsulation method is used for protection of thermochromic properties in microcapsules smaller than 15 μm. This process protects thermocromic system and surrounding chemicals from weather and oxidation [18-21].

Many methods can be used to prepare thermochromic films. Among them, sol-gel method is preferred most because of its low cost, low annealing temperature and ease of application [22]. By the developments in technology, significant developments have been also observed on intelligent glasses with superior technical and aesthetic qualities. The production of dynamic temperature intelligent glasses, which can automatically respond to environmental conditions, is among the primary research topics of today's glass industry. Among the many different intelligent glass systems, thermochromic glasses are predominant due to their structural simplicity and multifunctionality. Additionally, this type of glasses has superior handling characteristics compared to other glass types due to their automatic response to changing temperatures. These properties are the most important reason for use of them on all climates, every day of the year, and every hour of the day. Thermochromic coatings can reduce the cooling expenses by applying to exterior surfaces in hot weather conditions. There is very high attraction on production of color-changing thermochromic coatings in recent years. Within the scope of this study, thermochromic pigments that control the light and heat energy by changing their optical properties depending on the changing temperature were characterized to produce a new generation of thermochromic intelligent glasses.

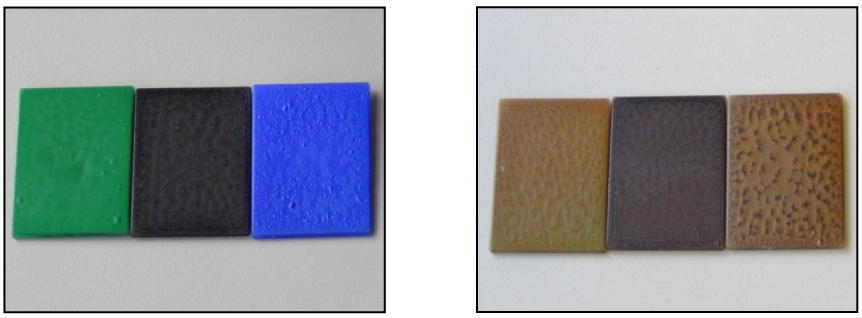
II. EXPERIMENT

A. MATERIALS

Thermochromic pigments supplied by Hali Chemical Co., Ltd. Company consist of thermochromic microcapsule powders. Polyvinylpyrrolidone (PVP, K 90, average molecular weight: 360.000, Tokyo Chemical Ind. Co., Ltd.) was used as binders in the study. 2-propanol was obtained from Merck, USA and quartz lamellas were purchased from Science-Med Ltd. Microencapsulation that protects the system from weathering, oxidation acts as a barrier between thermochromic system and surrounding chemicals. Thermochromic pigments that brought from China non-toxic, non-hazardous, odorless, harmless product with heat and solvent resistance (Figure 2.)

B. PREPARATION OF COATING

Primarily, quartz lamellas (25mm x 25mm) were cleaned in ultrasonic bath for 30 minutes in acetone, ethanol and pure water, respectively. Then they were dried for 10 minutes. 4 g of polyvinylpyrrolidone and 40 ml of 2-propanol were mixed and left to stand for 2 days to completely dissolve in each other. Then 2 g of thermochromic pigment were added and mixed. The mixture which was allowed to aging for one more day was applied by scraper onto the quartz lamella. The formed samples were subjected to heat treatment at a temperature of 150°C to 250°C in the vacuum chamber and the furnace at an increasing temperature of 10°C. Figure 1 shows the heat-treated coatings at 200 and 250°C with a heating rate of 25°C/min.



(a) **(b)**

Figure 1. *Heat treated coating samples* ***(a)*** *200°C, 30 min.* ***(b)*** *250°C, 30 min.*

C. EXPERIMENTAL TECHNIQUE

This work is focused on development of thermochromic coatings by using thermochromic pigments. For this purpose, characterization of pigments was carried out. Digital Microscope photo of thermochromic pigments were taken with a 1000X8 LED 2MP USB microscope. A contactless laser gun infrared IR thermometer GM320 was used to determine the color change temperatures of the pigments. Rigaku MiniFlex 600 brand X-ray diffractometer (XRD) was used in the analysis of the phases of the thermochromic pigments. Surfaces of the samples were scanned in 2θ angle with a scan speed of 1°/min between 10-50° to complete the measurements. Particle size distribution analysis of thermochromic pigments was performed using Malvern, Mastersizer 2000 laser grain size meter. The

color measurements were made using the Konica Minolta CM 2300D spectrophotometer. Thermogravimetric (TG/DTA, Netzsch STA 449F3 brand) analyzes of color-changing thermochromic pigments at 33°C, 45°C and 65°C were made with Netzsch STA 449F3 brand. Microstructural analyzes were carried out using the Zeiss Supra 50 VPTM model SEM for gold coated samples to ensure conductivity without charging. Elemental analyzes of thermochromic coatings were determined using an energy-dispersive X-ray (EDX) device.

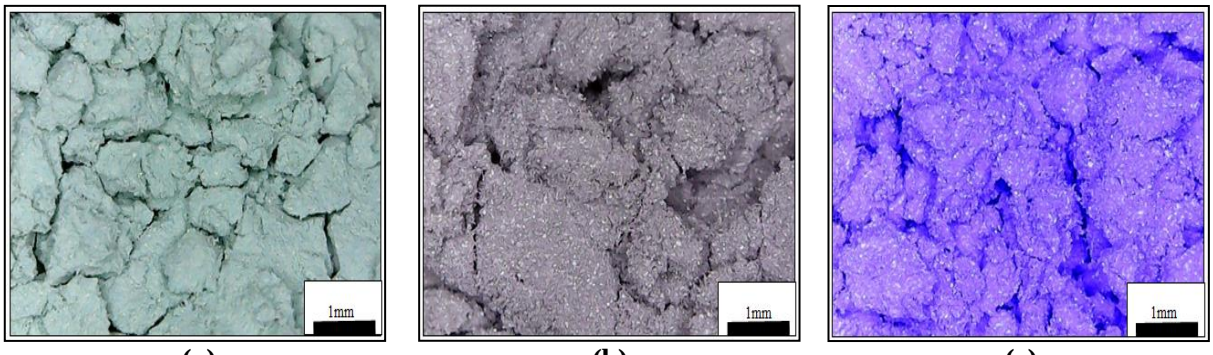
III. Results and Discussion

A. THERMAL AND PHYSICAL CHARACTERIZATION OF PIGMENTS

Figure 2 shows green, black and blue color thermochromic pigments photo images. Figure 3 shows images of thermochromic pigments of 33°C green, 45°C black and 65°C blue, taken with 1000X8 LED 2MP USB Digital Microscope.

(a) **(b)** **(c)**

Figure 2. *Color changing at* ***(a)*** *33°C green,* ***(b)*** *45°C black,* ***(c)*** *65°C blue thermochromic pigment*



(a) **(b)** **(c)**

Figure 3. ***(a)*** *33°C green,* ***(b)*** *45°C black,* ***(c)*** *65°C blue thermochromic pigment 1000X8 LED 2MP USB*

A heating method was used to determine and correct the color change temperature of the pigments. Heating pigments above a certain temperature a color change occurred to a lighter color than a darker color. Infrared thermometer was used to check whether the thermochromic pigments change color at the specified temperature. It was determined that the color change temperature of the green color

thermochromic pigment is not a specific point. The thermochromic pigment color change temperature range is usually 4-6°C, whereas this value is determined as 7°C for green color pigments. In the case of black and blue pigments, the temperature change range couldn't be detected. The color change of the thermochromic pigments with increasing and decreasing temperature was examined by infrared thermometer and the color change of the pigments with increasing temperature was shown in Figure 4.

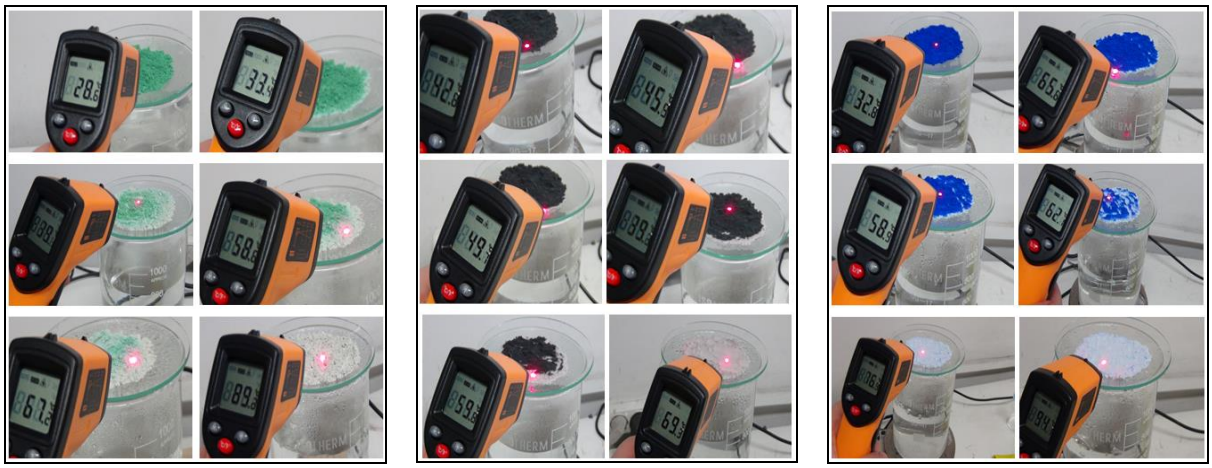
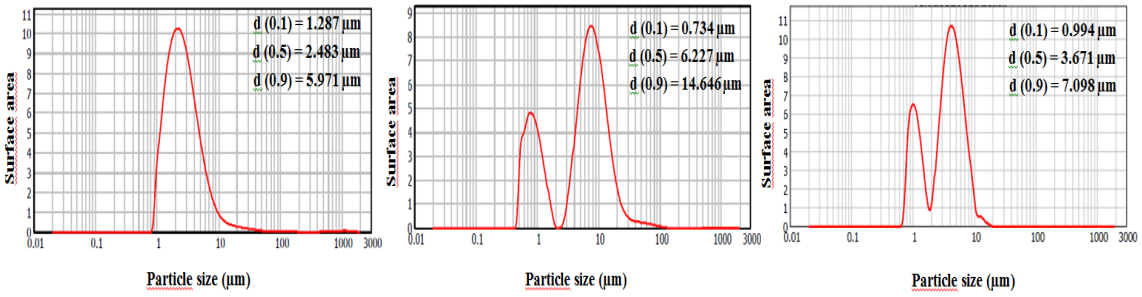


Figure 4. *Color change of thermochromic pigments with increasing temperature*

B. CHARACTERIZATION OF PARTICLE SIZE

Because of agglomeration tendency, particle size measurement of thermochromic pigments was made by using isopropyl alcohol instead of water as dispersing agent. As seen in the Figure 4, the particle size distributions of the pigments were very wide, which was why the pigments tend to aggregate. The d_{10}, d_{50}, d_{90} values and particle size distribution were plotted in Figure 5.



(a) **(b)** **(c)**

Figure 5. ***(a)*** *33°C green,* ***(b)*** *45°C black,* ***(c)*** *65°C blue thermochromic pigment particle size distribution graph*

C. THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYZER (TG/DTA)

Using the TG/DTA controlled temperature program the temperature difference (ΔT) between the reference materials, the sample and the weight change of the sample were measured. Thermal degradation of the pigments was assessed by TG/DTA. TG/DTA analyzes were carried out in alumina crucibles at a heating rate of 10°C/min up to 1300°C. In this analysis, the weight change due to the

temperature increase, endothermic, exothermic reaction and thermal stability of pigments were investigated. The obtained TG/DTA thermal analysis results were given in Figure 6. When the graphs of all three pigments are examined, the maximum mass loss for the green pigment reaches 66.76 % at 200-400°C. The maximum weight loss was 67.02 % between 300-450°C for black pigment and 67.17 % between 200-420°C for blue pigment. Among these temperatures, large changes in the mass of the thermochromic pigments are observed. These changes are particularly sudden in the TG curve for the pigments. The temperatures at which the first weight loss occurs in the TG curves indicate that the physical water has been removed. The green color thermochromic pigment has a narrow and strong exothermic peak at 329.7 °C. The blue thermochromic pigment has a broad exothermic peak at 376.7°C, while the black thermochromic pigment has the strongest exothermic peak at 357.5°C.

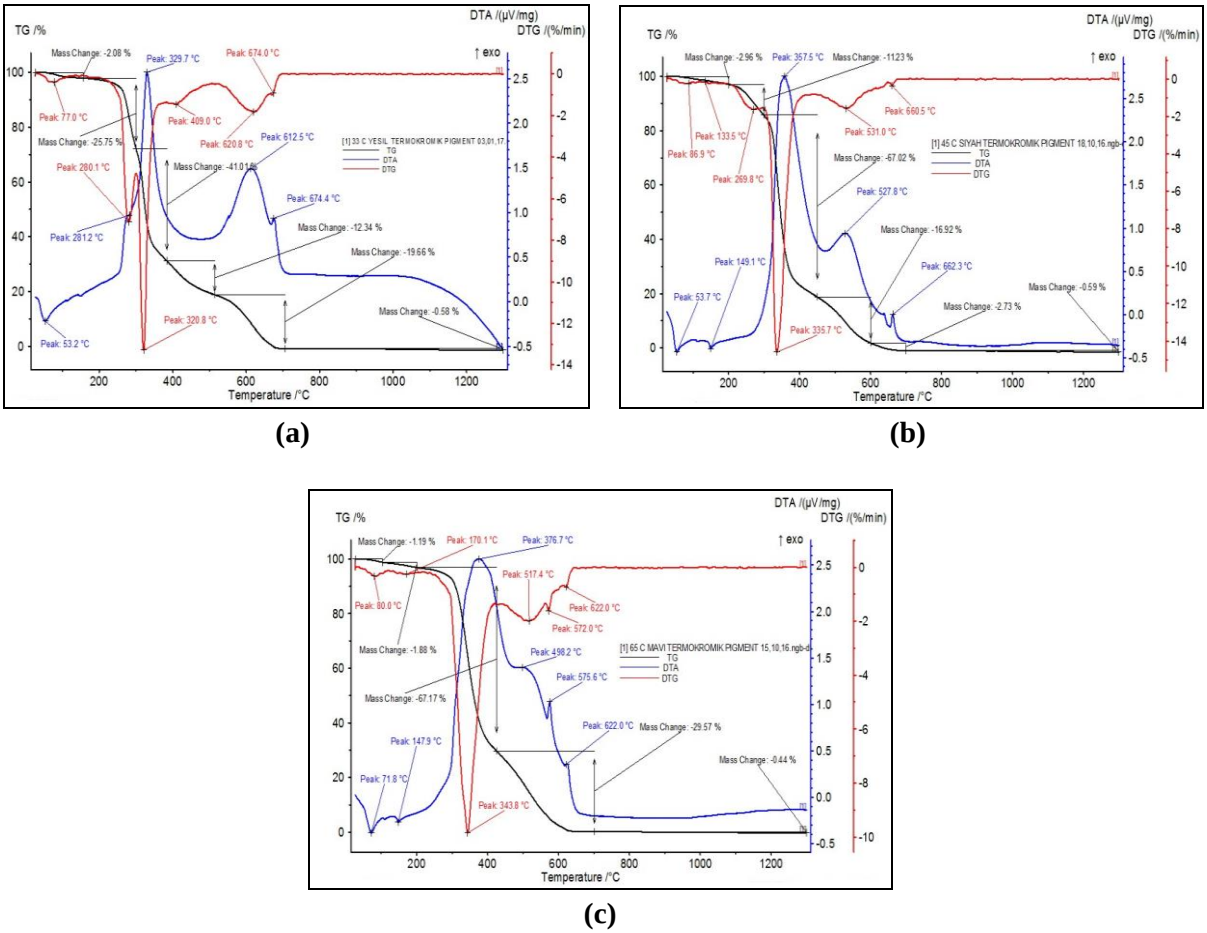


Figure 6. *TG-DTA chart of* ***(a)*** *33°C green,* ***(b)*** *45°C black,* ***(c)*** *65°C blue thermochromic pigment*

D. PHASE CHARACTERIZATION

XRD patterns of thermochromic pigments are given in Figure 7. Green color thermochromic pigment X-ray diffraction results show that the pigment has methyl stearate, copper chloride ethylene diammine and TNB phases. The black pigment has been found to have cetyl alcohol and magnetite phases. Cetyl alcohol, poly (6-hydroxybenzoic acid) ester and melanothallite phases were detected in blue pigment. XRD experiment indicate that copper (II) oxychloride is known as melanothallite.

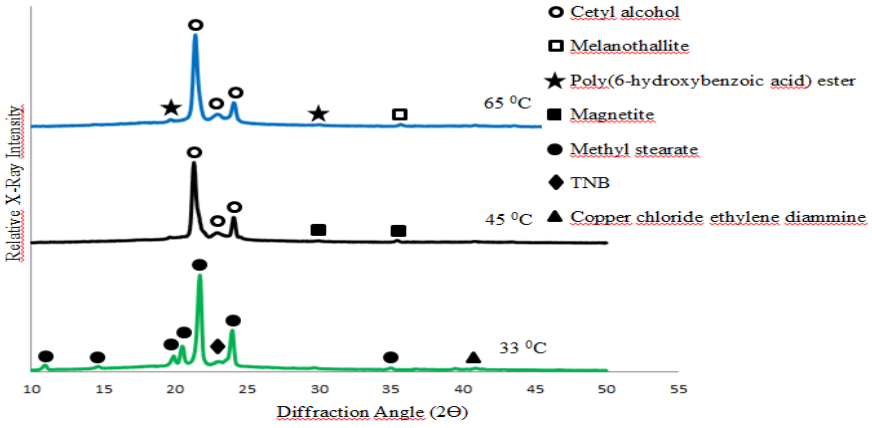


Figure 7. *XRD patterns of thermochromic pigments*

E. COLOR MEASUREMENT WITH SPECTROPHOTOMETER DEVICE

The color coordinates, CIELAB L * a* b * parameters and ΔE color difference for each thermochromic pigment sample were measured and the results were presented in Table 1. Figure 8 shows reflectance spectrum of thermochromic pigments measured between 400 nm and 700 nm wavelength.

Table 1. *Color values of thermochromic pigments 33°C green, 45°C black and 65°C blue*

Sample name	**L**	**a**	**b**	**ΔE*ab**
33°C Green thermochromic pigment	67.64	-22.92	9.99	0.35
45°C Black thermochromic pigment	45.42	-1.26	0.80	0.01
65°C Blue thermochromic pigment	47.17	16.41	-45.64	49.72

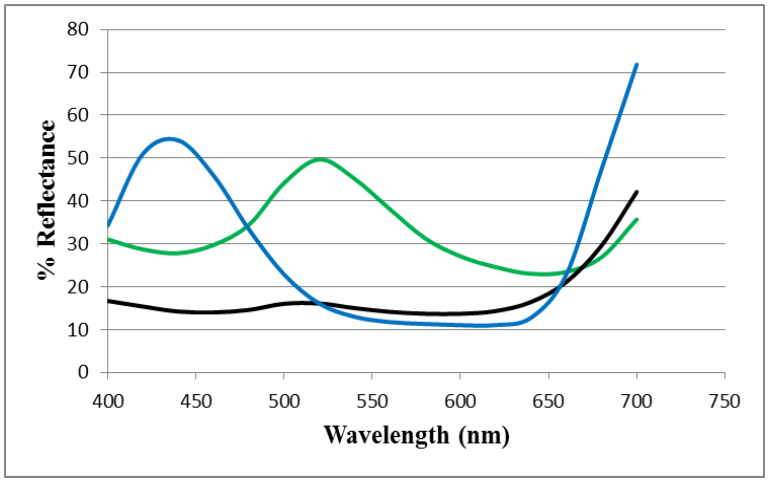


Figure 8. *Reflectance spectrum of thermochromic pigments*

From the results obtained in Table 1 and Figure 8, it was determined that the color difference of blue color thermochromic pigment is too much and the color difference of black color thermochromic pigment is very small. At temperatures exceeding 200°C, the pigments were irreversibly damaged and

the thermochromic properties of the coating deteriorated. It was determined that the color performance of the thermochromic coatings subjected to heat treatment for 30 minutes at 200°C was maintained. Color of coatings was deterioration in the vacuum drying-oven (190°C for 3.5 hours). Therefore, the heating time of the coatings should be reduced as much as possible. It has been found that high temperature and longtime heating damage the color performance of the coatings. As a result, thermochromic coatings have an unstable system, so color stability, heat resistance and aging resistance are not so strong. For this reason, the heat treatment temperature should be kept low while the thermochromic film receipt is being formed.

IV. CONCLUSION

There has been an increasing interest in the development of advanced materials applications such as thermochromic coating in the buildings in recent years. In this study, it has been shown that primarily thermochromic pigment coated glass can be obtained by scraper. In the second stage thermochromic coatings will be produced by adding appropriate thermochromic pigments into the appropriate binder system and other auxiliary components. This study aims to contribute to national energy saving by starting to produce a new high technology product with high added value in our country. In case of being successful of this work will contribute greatly to the national economy. This study is an important prototype for the development of next generation intelligent thermochromic glasses.

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