ANADOLU ÜNİVERSİTESİ BİLİM VE TEKNOLOJİ DERGİSİ –A
Uygulamalı Bilimler ve Mühendislik

ANADOLU UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY –A
Applied Sciences and Engineering
Cilt/Vol.: 13-Sayı/No: 2 : 135-142 (2012)

ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

NANO-SIZED PIGMENT APPLICATIONS IN İZNİK TILES

Esin GÜNAY [1], Meryem SARIGÜZEL [1], Bayise KAVAKLI VATANSEVER [1], Ayşen KILIÇ [1], Şenol YILMAZ [2], Işıl AKBAYGİL [3]

ABSTRACT

Traditional İznik tiles are known as "unproducable" due to its high quartz content. İznik tiles contain four different layers as "body, engobe (slip), decors and glaze" and each one has some different starting materials. Recent studies have showed that the production techniques and the particle size of pigments are important parameters in development of colours. TUBITAK MRC and İznik Foundation carried out an experimental work to improve and understand the effects of nanotechnology application to İznik tiles. High quartz content was kept as it is and pigments were applied in decoration as nano-sized pigments.

İznik tiles were produced and comparison was carried out between traditional and modern İznik tiles in colour and brightness. Characterization techniques were used in order to understand and compare the results and also the effects of nano-sized pigments to İznik tiles.

Keywords: İznik tiles, Nano-sized pigments, Traditional pigment

[1,] TUBITAK MRC Materials Institute, 41470, Gebze, Kocaeli, Turkey.
esin.gunay@tubitak.gov.tr, meryem.sariguzel@tubitak.gov.tr, bayise.kavakli@tubitak.gov.tr, aysen.kilic@tubitak.gov.tr
[2,] Sakarya University, 54187, Serdivan, Sakarya, Turkey.
symaz@sakarya.edu.tr
[3,] Iznik Foundation, 34337, Etiler, İstanbul, Turkey.
isilakbaygil@iznik.com

Recieved: 31 January 2012; **Revised:** 12 September 2012; **Accepted:** 18 September 2012

İZNİK ÇİNİLERİNDE NANOMETRE BOYUTLU PİGMENT UYGULAMALARI

ÖZ

Geleneksel İznik çinileri, bileşimlerinde bulunan yüksek kuvarstan dolayı "üretilmesi imkansız seramik" olarak bilinmektedir. İznik çinileri; "masse, astar, dekor ve sır" olarak adlandırılan ve her biri ayrı başlangıç malzemelerine ve hazırlanma tekniklerine sahip 4 farklı tabakadan oluşmaktadır. Son çalışmalar, seramiklerin renklerinde, üretim tekniklerinin ve pigment tane boyutlarının önemli parametreler olduğunu göstermiştir. TÜBİTAK MAM ve İznik Vakfı, İznik çinilerine nanoteknoloji uygulamalarının etkisini anlayabilmek için deneysel çalışmalar gerçekleştirmiştir. Yüksek kuvars içeriği değiştirilmeden, dekor aşamasındaki pigmentlerin boyutu nano boyuta indirgenmiştir.

Geleneksel ve modern İznik çinileri üretilmiş, renk ve parlaklık özellikleri açısından karşılaştırılmıştır. Nanometre boyutlu pigmentlerin İznik çinilerine etkisinin anlaşılması ve karşılaştırma için karakterizasyon teknikleri kullanılmıştır.

Anahtar Kelimeler: İznik çinileri, Nanoboyutlu pigment, Geleneksel pigment.

1. INTRODUCTION

Traditional İznik tiles are known as "unproducable" due to its high quartz content and composition and its unique processing steps. İznik tiles contain four different layers as "body, engobe (slip), decors and glaze" and each one has different starting materials and preparation techniques. Although there are many different colours in İznik tiles; coral red, turquoise blue and emerald green are the most characteristic colours. Recent studies have showed that the production techniques and the particle size of pigments are important parameters in the colours of İznik tiles (Miras, 2008).

Ceramic stains are obtained from many metal oxides and used under glaze, over glaze and in glaze. Al_2O_3 and SiO_2 are the most important compounds in almost all stains. Ceramic pigments are distinguished from colouring oxides by dispersing well in glaze due to their small particle size. In composition of ceramic stains, colouring oxides can be used either individually or as a combination of a few oxides. Most important factors affecting the stability and performance of colouring are the composition of glaze, firing temperature and furnace atmosphere (Arcasoy, 1983).

Ceramic pigments have a wide field of application in glaze and ceramic industry. In recent years, there have been major advances in the production of ceramic pigments with sol-gel technology (Antonic et al. 1997). Ceramic pigment production with traditional method is provided by the calcination of metal oxides at high temperatures. However, pigment production in this method has many disadvantages. Among these; colouring agents loose their stability because of high temperature, reduction in colour performance occurs, energy loss and environmental problems (with use of heavy metals) should also be considered (Ishbel, 1997). In sol-gel method, thermally stable and high colour performance pigments can be obtained at lower temperatures (Balogh, 1997). However, sol-gel method is expensive and takes a long time.

Nano pigments are organic or inorganic substances, insoluble, chemically and physically inert into the substrate or binders. Although, particle sizes in the 100-200 nm range are required in the manufacturing practice, nano pigments have recently gained a wide range of industrial applications. For example, mica-based pigments (particle size ~20 nm) with pearlescent effect are used in cosmetics, automobile coatings, plastics, etc (Cavalcante et al. 2009).

The ceramic pigments with particle sizes in nano scale are commercially potent in pigment industries, because of their high surface area

which assures higher surface coverage; higher number of reflectance points and hence maximum scattering; and small particle for uniform dispersion by homogeneous mixing with the binders in stain formations, which enhances the mechanical strength; and small particle uniform dispersion by homogeneous mixing with the binders in stain formations, which enhances the mechanical strength of the stain after drying (Biswas, 2007).

In this study, İznik tiles were produced and comparison was carried out in between traditional and nano-sized stain decoration. Colour and gloss measurements were performed to improve and understand the effects of nanotechnology (nano-sized pigments) to İznik tiles.

2. METHODS

In preparation of three layers (body, engobe and glaze) of four layered İznik tiles; glass, grog, feldspar, zirconium silicate, zinc oxide and frit were used. Six different pigments were used in the preparation of stain mixtures used in decoration. Yellow, green, red, cobalt blue pigments and copper oxide were used. Clay, frit and quartz were also used to obtain main İznik colours of turquoise, green, cobalt blue and red. The top layer glaze was prepared by mixing frit and water.

Quartz based dry pressed body in the form of plates was engobed and bisque firing was performed. Stains were prepared with traditional and nano-sized pigments reduced to nano size by introducing mechanical crushing with Franco Gabrielli Technology model jet mill for 5 minutes. Traditional and nano-sized stains were applied with brush for decoration. After drying the decored plates, alkali lead glaze was used for glazing. Glost firing was performed at 950ºC for 20 minutes.

Particle size analysis of pigments and stains were measured with Malvern Mastersizer-X particle sizer, water used as dispersant and Malvern Zetasizer Nano ZS 3600 equipment, water used as dispersant and Igepal used as additive.

Microstructure of nano-sized pigments was examined by JEOL 2100 HRTEM model High Resolution Transmission Electron Microscope and Energy Dispersive Spectrometer with semi-quantitative micro-analytical method.

Gloss measurements of final products (İznik tiles) were performed with Erichsen Picogloss 503 model Glossmeter according to the "ASTM D523-08 Standard Test Method for Specular Gloss" standard.

X-rite Portable SP64 Sphere Spectrophotometer was employed for determining the chromatic coordinates (L*, a* and b* values-CIE L*a*b*) of the final products (İznik tiles) according to ASTM E313-05 standard. Furthermore, another colour space CIE L*c*hº was used for indicating the chroma (saturation) and hue angles.

3. RESULTS AND DISCUSSION

3.1 Particle Size Analysis of Pigments and Stains

Particle size analysis (D_{50}) of traditional and nano-sized pigments used in stains on the decoration of İznik tiles are given in Table 1. Average grain sizes of traditional and nano-sized pigments were between 2.78-13.06 μm and 37.1-114 nm, respectively.

For the preparation under glaze stains; quartz, frit, transparent glaze, clay and glass raw materials were also used beside pigments. Particle size analysis results of traditional and nanometersized stains are given in Table 2.

For traditional under glaze stains; average grain sizes were between 3.04-3.54 μm and nanometersized paints were between 36.4-129 nm. Micron sized particles were also observed in both nanometersized pigments and stains.

Table 1. Particle size analysis of traditional and nano-sized pigments

Pigment Code	50 % (µm)	
	Traditional	Nano
Black (for contour)	2.78	-
Turquoise (Cu_2O)	4.84	0.0371
Green	6.86	0.0871
Cobalt blue	7.98	0.0365
Yellow	8.01	0.0951
Red	13.06	0.1140

Table 2. Particle size analysis of traditional and nano-sized stains

Stain Code	50 % (µm)	
	Traditional	Nano
Turquoise	3.54	0.0676
Green	3.11	0.0514
Cobalt blue	3.20	0.0364
Red	3.04	0.1290

3.2 High Resolution Electron Microscope (HRTEM) Studies of Nano-Sized Pigments and Nano-Sized Stains

Microstructural characterization of nano-sized pigments and nano-sized stains were carried out by High Resolution Transmission Electron Microscope and Energy Dispersive Spectrometer. The results are given in Figures 1 and 2.

Particle size analysis results supported by TEM photographs showed that traditional micron sized pigments can be ground to nano size by mechanically. It has been shown that average grain size of stains prepared by using nanometersized pigments are also in nano scale. There were some differences in particle shapes of nano-sized stains because of the mechanical crushing effect.

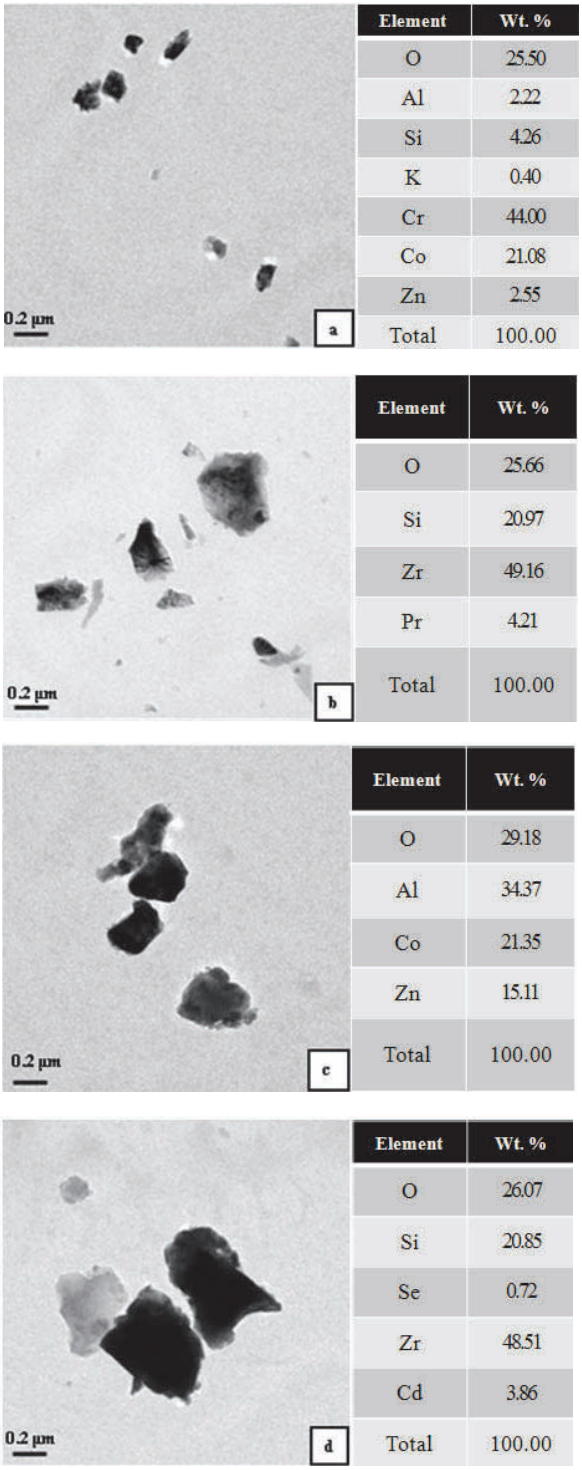

Figure 1. TEM images and EDX analysis of nano-sized pigments

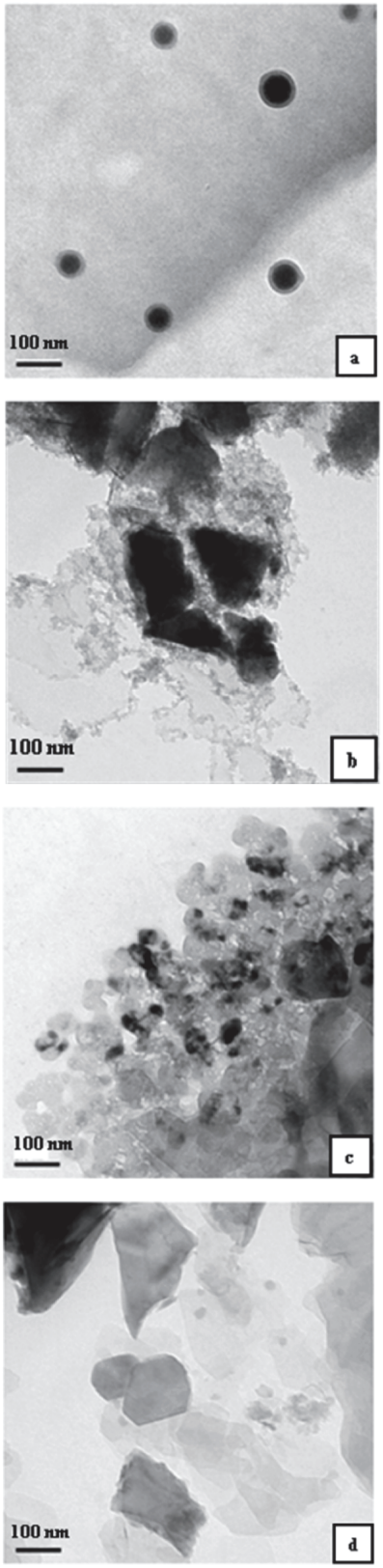

Figure 2. TEM images of nano-sized stains: (a) green, (b) turquoise, (c) cobalt blue and (d) red

3.3 Gloss Measurements

In this study, to obtain a clear differentiation over the complete measurement range from high gloss to low gloss, first measurements of all the samples were done at 60º; and then the evaluation was done according to the information below:

If gloss range is found between 10-70 gloss units (GU), the surface is accepted as semi gloss. If higher than 70 GU results found, then surface of the sample is accepted as high gloss. If lower than 10 GU measured, the surface of sample is accepted as low gloss.

According to the explanation above; for comparison of the glossiness results, 20 degree angle results should be used for high gloss surfaces, 60 degree results should be used for medium gloss surfaces, and 85 degree angle results should be used for low gloss surfaces.

The photos of the final products (İznik tiles) are given in Figure 3. Under normal conditions, a coating should cover the samle surface in equal thickness. On the other hand; İznik tiles are hand decorated by using a brush and followed by hand glazing. Because of this, it has been thought that the glossiness of a sample surface can change related to the implementer. Hence; glossiness measurement of the samples were performed both parallel and perpendicular direction (Table 3) to the brush to minimize the implementer effects in this study.

According to the results of measurements at 60º, İznik tiles were accepted as high gloss (>70 GU). With respect to the standard; glossiness comparison should be done at 20º for high gloss samples. It can be seen from Table 3 that the glossiness of İznik tiles improved by using nano-sized stains instead of micron sized stains.

3.4 Colour Measurements

In colour measurements of final products (İznik tiles), traditional stains were chosen as references. Colour measurement results of final products (İznik tiles) are given in Table 4.

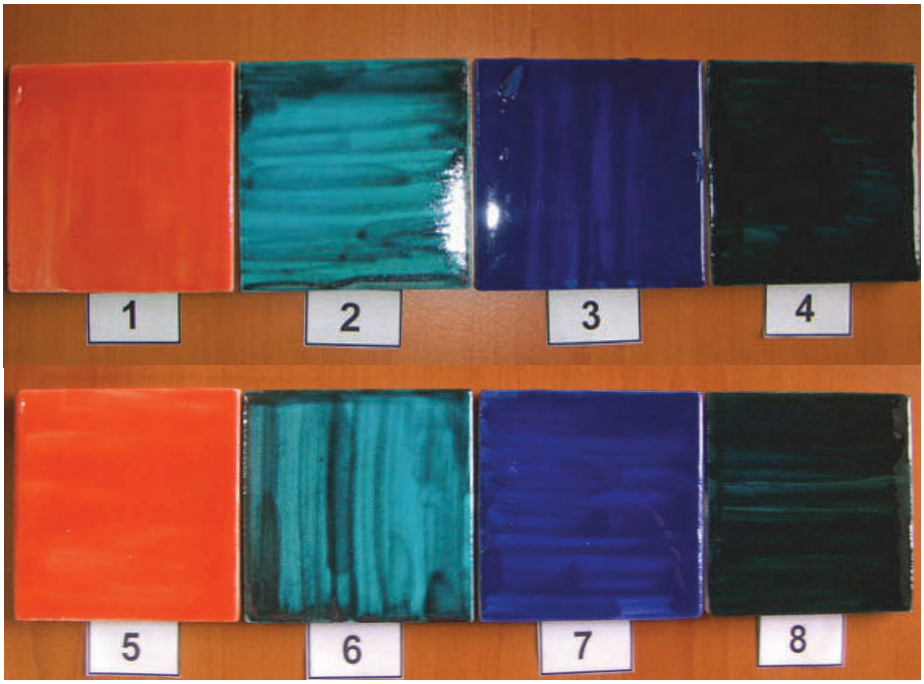

Figure 3. Final products (İznik tiles) (In 1-2-3-4 coded samples traditional stains were used, in 5-6-7-8 coded samples nano-sized stains were used.)

Table 3. Gloss measurements of the final products (İznik tiles)-parallel and perpendicular to the brush trace of stain (values are given in gloss units) (average of 6 measurements)

Plate No	Parallel			Perpendicular		
	20°	60°	85°	**20°**	60°	85°
1-Nano red stain	**113**	113	99.7	**113**	113	99.7
2-Nano turquoise stain	**80.5**	121	95.8	**60.7**	110.2	94.3
3-Nano cobalt blue stain	**91.8**	114	97.4	**68.7**	80.4	72.1
4-Nano green stain	**110**	115	100.2	**85.56**	113.1	97.8
5-Traditional red stain	**69.4**	113	95.3	**68.5**	105.46	88
6-Traditional turquoise stain	**77.6**	109.8	92.6	**59.7**	106.8	81.8
7-Traditional cobalt blue stain	**69.4**	114.2	88.4	**39.4**	77.7	69.6
8-Traditional green stain	**66.2**	113	92.7	**43.2**	93.9	74.2

Colour measurement results are also shown in coordinate system (Figure 4). As standards, traditional stains were placed at the center. The nano colour values were placed according to the ΔL, Δa, Δb values. ΔL, Δa, Δb were obtained from the difference between the sample (nano) and reference (traditional) values.

In all colour measurements (red, cobalt blue, green and turquoise) the Δh and ΔC values are positive, so it shows that nanometersized paints are more vivid and glossy than traditional one.

4. CONCLUSION

İznik tiles were produced with both traditional and nanometersized stains in decor stage. The colours and glossiness of traditional micron sized and modern nanometersized painted tiles were compared to understand the effects of nanometersized pigment usage.

Results of the gloss measurements showed that more glossy surfaces were obtained with nano-sized stains by both parallel and perpendicular to the brush trace.

Table 4. CIE L*a*b* and L*C*h° colour coordinates of final products (İznik tiles)

		Traditional	Nano	Delta
Red	L*	46.06	49.53	3.47
	a*	33.67	36.11	2.44
	b*	18.47	24.93	6.46
	C*	38.41	40.80	2.39
	h°	28.74	30.04	1.3
Cobalt blue	L*	34.69	38.00	3.31
	a*	9.68	13.51	3.83
	b*	-25.76	-32.13	-6.37
	C*	27.52	34.16	6.64
	h°	290.59	291.88	1.29
Green	L*	34.16	35.67	1.51
	a*	-6.87	-9.27	-2.4
	b*	0.48	2.15	1.67
	C*	6.88	9.30	2.42
	h°	169.93	175.84	5.91
Turquoise	L*	56.33	65.99	9.66
	a*	-29.96	-30.33	-0.36
	b*	-13.94	-14.71	-0.77
	C*	33.05	33.71	0.66
	h°	204.96	205.87	0.92

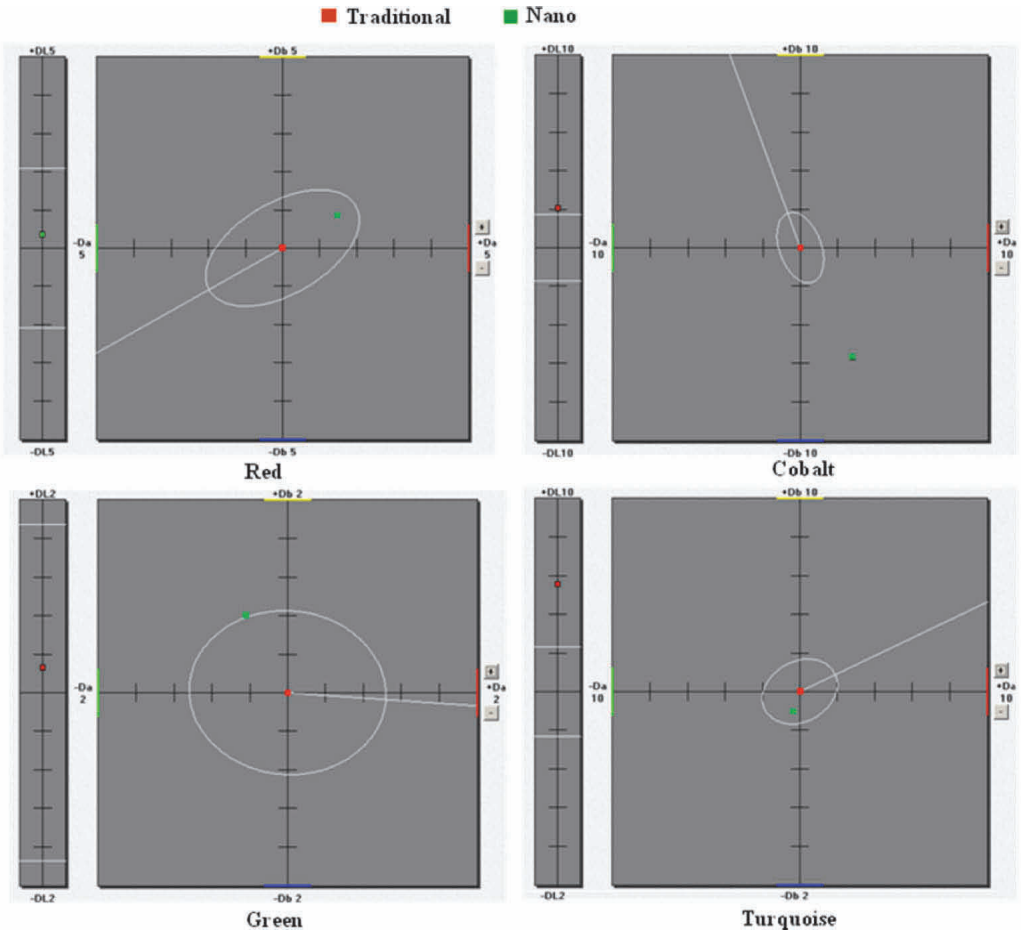

Figure 4. Colour measurement results in coordinate system

For four main colours used in İznik tiles (red, cobalt blue, turquoise and green), the colour performance of tiles affected by using nano-sized stains positively. İznik tiles decored with nano-sized stains were more vivid.

ACKNOWLEDGEMENT

This research has been done as a part of the TUBITAK 1001 project titled "Advancing İznik Tiles (Our Cultural Heritage) to 21st century by Applying Nano-Science and Advanced Nano-Structured Materials-110M190". The authors are grateful to TUBITAK for financial support.

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