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PREPARATION OF BLUE VITREOUS PAINT FROM CO_3O_4 NANOPARTICLES FOR APPLICATION ON STAINED GLASS AT LOW TEMPERATURES AN EXPERIMENTAL

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Abstract:
One of the most important problems facing the restorer in stained glass restoration is the completion of missing glass pieces to which vitreous paints containing metal oxides were applied that require a high temperature for installation, starting from 550 °C and increasing according to the colored oxide nature and the smelter used. The present paper discusses the preparation of blue vitreous paint for nanoparticles Co_3O_4 to improve its thermal and color properties. It compares the color prepared from the cobalt nano oxide Co_3O_4 and cobalt oxide CoO mainly used to color the glass blue since the pharaonic periods. Examination and analysis methods, i.e., XRD, FTIR, SEM, EDX, and TEM, were used in characterizing the cobalt nano oxide. STEM, SEM, and stereo microscope were used to study the prepared color samples. Results showed that the particles size of the prepared Co_3O_4 of 0.78 nm gave an excellent blue color when applied to the glass at a temperature of 620 °C compared to the color resulting from CoO, which was installed at a temperature of 700 °C according to mixing rates. That paved the way for reducing the proportion of the smelter in the color mixture to increase color resistance to weathering deterioration factors, especially moisture.

1. Introduction

The loss of glass pieces, especially those with painting, is one of the most important manifestations of damage to stained glass; thus, it is necessary to complete the missing glass pieces with all colored details on them. In the past, cold colorants, including oil colors, were used in color completion and exposed over time to drying and tearing, then peeling and loss from the surface of the glass, especially stained glass, due to its permanent and direct exposure to the external factor of damage. Furthermore, this completed layer of colors turns with time to black and works to contain dust and dirt, which sometimes causes a separation of the original color layer [1]. Frodl-Kraft [2] reported the restoration method known as Zettler, which was applied for the first time in 1917 in the restoration of the Church of St. Sebalclo in Germany. In this method, the damaged colors are re-melted by heating up to a temperature that may reach 550 ^{o}C, the damaged drawing is covered with a layer of glass powder with a colorless smelter, and the pieces are heated at a low temperature from 400 ^{o}C to 550 ^{o}C. Frenzel [3] argues that this method is harmful to the old glass pieces that become dark after the reheating process, especially pieces with a high level of Fe and Mn, and the blue glass becomes black. It also affects and exposes the cohesion of the color layer to damage faster [4]. Accordingly, specialists in the field of stained glass restoration tended to use Maimeri colors for pieces with old, damaged colors. Nonfarmale [5] mentioned the use of the international restoration colors Maimeri brand in the color completion of a window of the Church of Saint Giovanni in Italy to get a slice as thin as possible to reduce any trace of tearing that can occur after drying over time. In most cases, the missing pieces were completed with white or transparent glass as a result of the difficulty of re-completing the painted pieces with modern ones with the same quality which distorted the appearance of the stained glass panels. Therefore specialists tended to complete the missing pieces completely by re-painting them on modern glass with thermal colors. Gad Al-Karim [6] and Al-Safty [7] used Mn and Fe oxides with ground glass in the processes of completing the missing pieces of the archaeological stained glass. Abdel-bakey [8] used silver stain, Fe, and Mn in the processes of completing the window of the main façade of the Palace of Rustam Pasha in Cairo. She also obtained several color degrees based on an experimental study of five metallic oxides (Fe, Mn, CoO, Cu & Ag) and a group of these oxides to complete the missing pieces of a stained glass ceiling in an archeological palace in Cairo [9]. Reyntiens defined vitreous paint as firable colors, finely ground glass with a metallic oxide that once fired on the glass, can be used permanently to shade or color stained glass pieces [10]. Therefore, they have the same structural, physical, and chemical properties of glass [11]. They can be mixed with either watery, alcoholic, or oily medium [12]. One of their most important features is that they melt at a low temperature (550 °C-750 °C) compared to glass (1200-1300 °C). If these colors are fired properly, they will become a permanent part of the glass surface [13] and will not be affected by weather factors, but will remain as long as the glass is [1]. CoO is one of the most famous and powerful colored oxides used in glass coloring throughout the ages [14]. There is no historical evidence about the beginning of using cobalt as a colored material in stained glass, but it can be seen in the medieval windows of the 12th century European churches [15]. It has three well-known polymorphs; the monoxide or cobaltous oxide (CoO), the cobaltic oxide and the cobaltosic oxide or cobalt cobaltite (Co_3O_4), [16]. Co_3O_4 is the final product that is formed when cobalt compounds are calcined at a temperature up to 500 °C in an atmosphere saturated with oxygen. Co_2O_3 absorbs oxygen in sufficient quantity and transforms to a higher oxide Co_3O_4, with no change in the network structure [17]. The quality and degree of the produced color depend heavily on thermal stability and Co^{+2} ion coordination, as deep blue in the glass appears when cobalt ion is surrounded by four oxygen ions forming a quadrant pyramid where Co^{+4} groups are formed [18]. The concept of nanotechnology depends on the fact that particles less than 100 nm in size give the material involved in their composition new properties because these particles show new physical and chemical concepts that improve the properties of the material, leading to new behavior based on the size of the particles [19]. The physical and chemical properties of nanomaterials, such as color, strength, rigidity, chemical activity, electrical conduction, and thermal properties vary [20]. For example, the normal melting degree for gold is 1064 °C, but nano gold melts at about 500 °C when the size of gold granules is 1.35 nm. The melting degree decreases when the size of gold grains decreases [21]. Thus, using Co_3O_4, helps reduce the temperature of instilling color on the glass surface, which is one of the most critical problems facing the restorer when completing the missing pieces with thermal colorants. In this study, Co_3O_4 was prepared by the Sonochemical and calcination method. Then, new glass samples were prepared, and the blue color produced from nano-cobalt oxide was applied to three samples to get blue at a temperature from 600 °C to 620 °C. Producing four cobalt dioxide samples is commonly used to obtain the blue color at temperatures from 600 °C to 700 °C. After that, the samples were evaluated using different examination and analysis methods and compared with a modern standard sample of cobalt blue from Reusch International Co., the major company specialized in the production of colorants and stains used in the production and restoration of stained glass. The present study aims to obtain a blue glass color applied at a relatively low temperature while improving the properties of the produced color to be used in the processes of completing the missing glass pieces in archaeological stained glass panels.

2. Materials and Method

2.1. *Materials*

- Preparation of nano-sized cobalt oxides Co_3O_4 from their corresponding complexes by Sonochemical method and calcination to prepare the blue color.
- Seven glass samples were prepared: three Co_3O_4 and four CoO.

2.1.1. Preparation of Co_3O_4 nanoparticles

In the preparation of Co_3O_4 nanoparticles from $Co(NO_3)_2.\ 6H_2O$ by the Sonochemical method and calcinations, fig. (1), 20 ml of a 0.1 M solution of metal salt [$Co(NO_3)_2.\ 6H_2O$ 1.45] in EtOH was positioned in a large-density ultrasonic probe, operating at 24 kHz with a maximum power output of 400 W. Into this solution, 20 mL of a 0.1 M solution of the imine ligand was added dropwise. The obtained precipitate of cobalt complex was filtered off, washed with ethanol, and then dried in air. Nano-sized cobalt oxide was prepared by the calcination of the obtained cobalt complex in the air at 500 ºC with a heating rate of 10 °C min^{-1} for 1.5 h**.** The resulting cobalt oxide was washed with ethanol and dried in a desiccator[(*)]

Figure (1) Shows the preparation of Co_3O_4 nanoparticles (*after, Abdel Rahman, et al, 2017*) [22].

2.1.2. Sample preparation

Color samples were prepared through the following steps: **1)** Pieces of transparent glass 3 mm thick with a 2 cm×2 cm area were equipped to be used as a glass substrate for color samples. **2)** Glass powder was used from the same glass substrate, which was analyzed to identify its components using EDX, tab. (1). **3)** Color samples were prepared as shown in tab. (2), which shows the mixture ratios and the temperature of the installation. **4)** Arabic gum was used as a bonding material and water as a mixing medium [12]. **5)** Firing was done in an oxidized atmosphere with temperature stabilized for 20 minutes, except for sample B4, which was stabilized for 30 minutes. Results in fig. (2) show samples A1, A2, and A3 of Co_3O_4; samples B1, B2, B3, and B4 of CoO; and the standard sample.

Table (1) Results of EDX analysis of glass powder.

Element	O	Na	Mg	Al	Si	Pb	K	Ca	Ti	Mn	Fe	Zn
Weigh %	5.0	8.3	1.6	2.5	61.8	3.1	6.3	7.2	1.3	0.8	0.9	1.2

Table (2) Mixture ratios and the temperature of the installation.

Composition / Sample	Glass Powder %	Colored oxide %	$Na_2B_4O_7 10H_2O$	KNO_3	Na_2Co_3	Temp. °C
A1	60	Co_3O_4 3	20	10	10	600
B1	60	CoO 3	20	10	10	600
A2	60	Co_3O_4 2	20	10	10	620
B2	60	CoO 2	20	10	10	620
A3	70	Co_3O_4 2	15	7.5	7.5	620
B3	50	CoO 2	25	10	15	650
B4	60	CoO 2	20	10	10	700

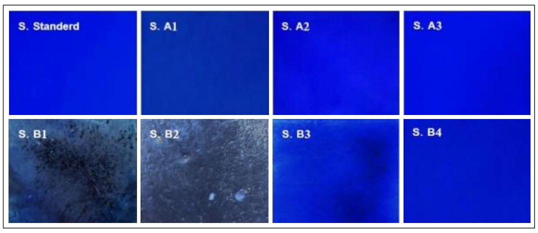


Figure (2) Shows the results of A1, A2 & A3 samples of Co_3O_4; B1, B2, B3, and B4 of CoO; and the standard sample.

2.2. *Methods*

- To examine and analyze Co_3O_4 nanoparticles powder, the structural and morphological characterizations were performed using XRD, FTIR, SEM, EDX, and TEM [23].
- A stereo microscope, SEM, STEM, and Automatic Colorimeter were used to examine blue samples resulting from the use of Co_3O_4 and CoO to study the morphological shape of the color layer on the surface of the glass and to clarify the defects and features of the color [24].

3. Results

3.1. *Analysis of the glass powder*

The results of analyzing the glass powder used for preparing the blue color listed in tab. (1) indicated Si (61.8%), which is a good percentage because of using Borax containing boron oxide to improve the appearance of the prepared color. They showed Na (8.3%) and K (6.3%), which is less than the natural content of alkali substances in the glass. A glass powder was to be used without a high percentage of alkali substances. Thus, percentages of (10-20%) of $Na_2B_4O_710H_2O$ – KNO_3 – Na_2Co_3 of the weight of the mixture should be added. The existence of Mn (0.8%) created balance with Fe (0.9%) as an impurity [6] in order not to affect the prepared color.

3.2. *Investigation of Co_3O_4*

The results of TEM, fig. (3); **a)** gives an overview of metal oxides, **b)** shows high magnification, **c)** shows a calculated histogram of the particle size distribution of Co_3O_4. Figure. (4) shows the pattern of FTIR spectral bands of the prepared metal oxides because the characteristic bands appeared in 655, 548. Figure. (5) shows the pattern of XRD and crystallographic parameters of the prepared metal oxides. The results show that the size of the crystals of the nanomaterial is 0.78 nm, and the crystal system is cubic. The results of SEM-EDX, fig. (6-a & b) show EDX pattern of and SEM image of Co_3O_4 nanoparticles, where, cobalt of 66.31% and oxygen of 33.19%.

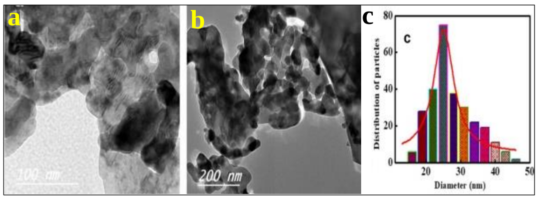
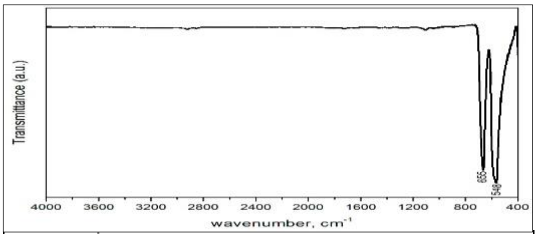
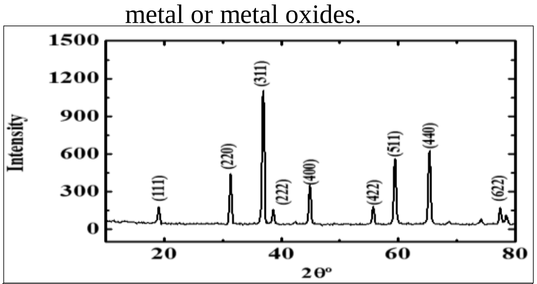


Figure (3) Shows TEM photomicrographs of the prepared CO_3O_4 **a.** overview, **b.** high magnification, **c.** calculated histogram of particle size distribution of Co_3O_4



Com.	(OH)	(C=N)	$(OH)_{bending}$	(M-O)
Co_3O_4	-	-	-	655.548

Figure (4) Shows FTIR pattern and spectral bands nanoparticles and crystal-of the prepared metal or metal oxides.



Com.	Crystallographic parameters				
	Crystal system	*Space group*	*A(nm)*	*b(nm)*	*C(nm)*
Co_3O_4	Cubic	Fd3m	0.78	0.78	0.78

Figure (5) Shows XRD pattern of CO_3O_4 crystallographic parameters of the prepared nanoparticles or metal oxides.

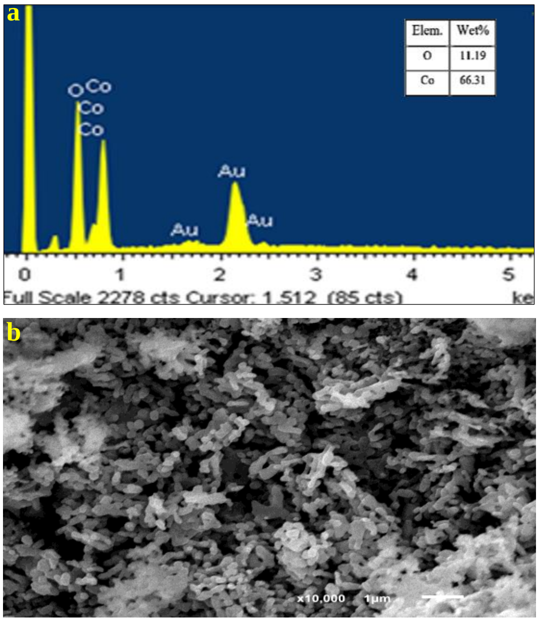


Figure (6) Shows **a.** EDX pattern of CO_3O_4 nanoparticles; **b.** SEM image of CO_3O_4 nanoparticles

3.3. *Examination of the blue color samples after heat installation*

3.3.1. Stereo microscope

Through the microscopic examination, fig_s. (7), we observe in the sample (B1) a color cluster on the surface, which did not merge and colored oxides as a stuck material tends to black with enlargement. In sample (B2), incomplete melting of the color and a porous surface full of pits appeared. A network of fine cracks appeared in sample (B3), which increased in peeling and began to separate after exposure to the normal atmosphere at the rate of 24 hours. Sample (A1) showed the merging of color on the surface with some air bubbles. Sample (B4) gave good results for the merging of color on the surface. Sample (A3) gave a distinctive color and a perfect merging of the color with the surface of the glass.

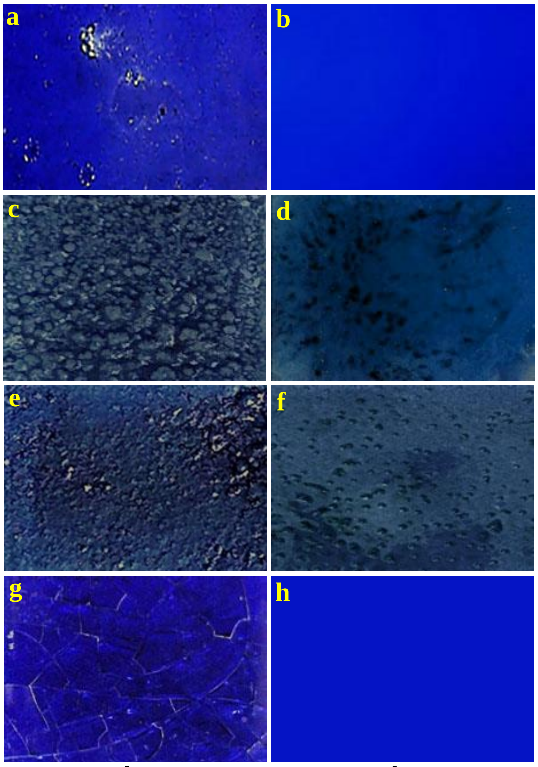


Figure (7) Shows stereo microscope photos; **a.** sample (A1) shows air bubbles 50x, **b.** sample (B1) color cluster on the surface 70x, **c.** sample (A3) shows good merging of blue color from Co_3O_4 10x, **d.** sample (B1) the appearance of colored oxides as a stuck material 60x, **f.** sample (B2) incomplete melting of color on surface 70x, **g.** sample (B2) porous surface full of pits 70x, **e.** sample (B3) shows a network of fine cracks 50x, **h.** sample (B4) shows good merging of blue color from CoO 10x.

3.3.2. SEM

The results of SEM, fig_s. (8) showed clumping and non-melting of color on the surface in sample (B1), incomplete melting of color in sample (B2), and micro-cracks in sample (B3). They gave good results and perfect merging of blue color grains with the surface of the glass in sample (A3).

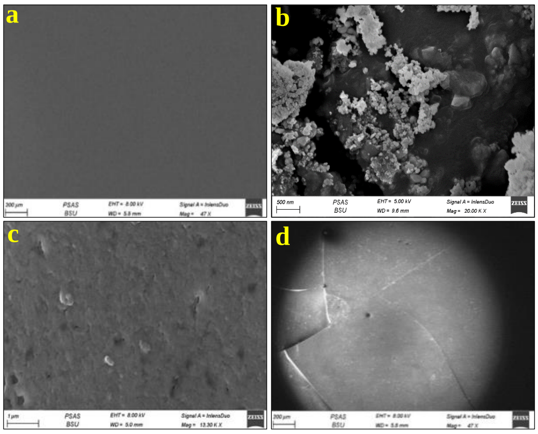


Figure (8) Shows SEM photo-microphotograph, **a.** sample (A3) good merging of blue color from Co_3O_4, **b.** sample (B1) clumping, and non-melting of color on the surface, **c.** sample (B2) incompletely melting of color, **d.** sample (B3) micro cracks,

3.3.3. STEM

STEM results, fig. (9-a) showed that the color did not merge with the surface of the glass and grains appeared in sample (B2) but color completely merged in sample (A3), fig. (9-b)

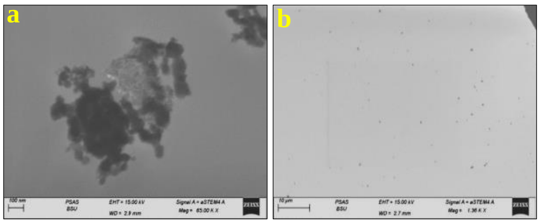
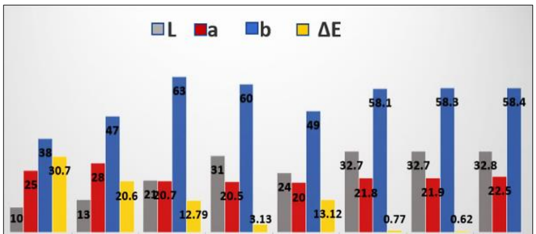


Figure (9) Shows TEM photo-microphotograph, **a.** sample (A3) color completely merges, **b.** sample (B2) color does not merge and grains appear,

3.3.3. Colorimetry-CIE L*a*b*

A comparison was made for the produced blue samples with a standard sample for cobalt blue using the CIELab colorimetric method, recommended by the Commission Internationale de l'Eclairage. Two mutual orthogonal axes, **a*** and **b***, represented the hue or color dimensions. The third axis, lightness **L***, was perpendicular to a* and b* plane and had a value of 0 for black and 100 for white. Positive a* value corresponded to the red color, while negative value corresponded to the green color. At the meantime, positive b* value corresponded to the yellow color, while negative values corresponded to the blue color [25]. Figure (10) shows the colorimetric data of the results, indicating that L* values are less than 10 in sample (B1), a* value converged in all samples, and b* value increase in the negative direction. The deep blue color appeared in all samples, with the lowest registration in sample (B1).



B1	B2	B3	B4	A1	A2	A3	STANDR
10	13	21	31	24	32.7	32.7	32.8
25	28	20.7	20.5	20	21.8	21.9	22.5
38	47	63	60	49	58.1	58.3	58.4
30.7	20.6	12.79	3.13	13.12	0.77	0.62	

Figure (10) Shows a comparison between the data of colorimetric samples.

4. Discussion

Results of the examination and analysis of the prepared nano-cobalt oxide using TEM, XRD, and FTIR emphasized that the prepared Co_3O_4 have particle size of 0.78 nm. SEM attached to EDX analysis of Co_3O_4 indicated the presence of Co and O composition without impurities to obtain pure cobalt oxide Co_3O_4 [11]. The results of the STM and TEM examination showed that the samples to which the blue color was applied with nano cobalt oxide showed good results in sample (A1) in terms of color merging on the surface with the presence of some air bubbles, which is one of the defects in the application of the color, that appeared to be darker than the standard sample, so (A2) mixture was prepared by reducing the percentage of colored oxide to 2% which gave very good results and a distinctive blue color. Sample (A3) gave excellent results for the degree of the blue color and perfect merging with the surface of the glass. Substrate ΔE gave the lowest reading. It is worth mentioning that the percentage of glass powder was increased, and the percentage of smelter was reduced to improve the properties of the produced color and its resistance to various weathering deterioration factors, especially moisture. [26]. Furthermore, the samples of blue color for CoO had some defects, the most important of which was the color clumping on the surface of the glass, causing the appearance of the colored oxide as a suspended substance tending to black [27] in sample (B1) due to the low firing temperature of 600 °C. At 620 °C, a rough layer on the surface filled with blisters and pits [28] appeared in sample (B2); thus, L* value decreased in colorimetric results in B 1 and B2. A network of fine cracks appeared on the surface of sample (B3), which developed into the beginning of peeling and separation from the surface of the glass due to the increase in the proportion of the smelter in the mixture [27], causing instability of the produced color, especially in humid atmosphere, which increases the rate of color melting, cracking, and separation [1]. Sample (B4) gave excellent color results in terms of the merging of the grains with the surface of the glass, but this mixture requires raising the installation temperature to 700 °C with installation for 30 m, which explains the appearance of the highest reading of the colorimetric results of b* value. The increase in temperature and firing duration produce a darker color of glass [12], as it weakens the resistance of the glass to weather factors and mechanical resistance and makes it subject to rapid fracture with any pressure on it [24].

5. Conclusion

A vitreous paint blue color was prepared from nano-cobalt oxide Co_3O_4 by the Sonochemical method and Calcination, which gave excellent results in the cobalt blue color properties in terms of merging and depth of the color on the surface of the glass compared to the standard sample. It improved thermal properties, where the color was installed at a temperature *of 620 °C; 80 °C lower than the color obtained from CoO, which allowed reducing the percentage of smelt in the color mixture. These properties help in facilitating the color completion of stained glass panels, which is an important problem facing the restorer during the restoration of archaeological glass panels. They also enhance the resistance of glass panels to weather deterioration factors, especially humidity. Therefore, this study can contribute and pave the way in reserving stained glass panels considered a great part of the history of art.*

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