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Application of copper(II) oxide of electrocoagulation products of electroplating waste water as ceramic glaze dyes

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Application of copper(II) oxide of electrocoagulation products of electroplating waste water as ceramic glaze dyes

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Abstract. This study aims to determine the effect of combustion temperatures and copper(II) oxide concentrations on ceramic glaze color. Electrocoagulation process was carried out using optimum conditions: pH 8, electrocoagulation time of 120 minutes, Al-Fe electrodes, and current density of 1.25 mA/cm^2. Experiment variables include combustion temperatures (999, 1060, 1101 ^{o}C) and copper(II) oxide concentrations (0.88; 1.76, 2.64, 3.53%). The results of the coagulant characterization with XRF showed copper(II) content of (22.04 ± 0.73)%. Besides that it also contains of other metals such as Cr, Cd, and Pb however below the detection limit. Coagulant is a metal hydroxide which is dried and calcined formed the oxide. Then, it was applied as a glaze ceramic dye. Based on the analysis of homogeneity using chromameter, the brightness value (L*) increased at the combustion temperature of 999 and 1060 ^{o}C, but at a temperature of 1101 ^{o}C it decreased. The green color value (a*) decreases when the combustion temperature is raised but the yellow value (b*) increased. When the metal oxide concentration was increased, L* and a* values decreased. While the b* value increased at a concentration of 0.88 to 1.76%, but at a concentration of 2.64 to 3.53% decreased.

1. Introduction

Electroplating waste water of the silver handicraft industry contains heavy metals such as Ag^{+}, Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Bi^{3+}, Cu^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} [1]. Electroplating waste water that is discharged directly into the sewer without being treated first will cause environmental pollution. Water contaminated with electroplating liquid waste will endanger health if it used for daily needs [2]. The impact of the metal pollution varies, for example if someone is exposed to copper(II) exceeds the threshold, the excess of copper(II) in the body can cause stomach upset, nausea, and within a certain period of time causing the liver and kidney disease [3]. Therefore, this electroplating wastewater treatment needs to be done so as not to pollute the environment.

Electroplating wastewater treatment in Kotagede has been carried out by neutralization method with lime and precipitation with alum [1]. Another method is precipitation with hydroxides, sulfides, and carbonates from several precipitation agents [4-5]. In addition, electroplating liquid waste can be used as a metal coating material by recovery method or electrolysis technique [6-7]. Waste processing has advantages and disadvantages in each process and condition. In this study, we chosen the electrocoagulation method it is an easy, cheap, and without the addition of reagent. The method produced coagulants (floc) so that electroplating waste water could be utilized. The coagulant is expected to contain a maximum amount of heavy metal ions so that it can be used for purposes that are more useful and of economic value.

Electrocoagulation is a coagulation process using electric current in the direction of electrodes into the waste. Electrocoagulation is a combination of electrolysis and flocculation [1]. In this method there are no additional reagents so that new species that cause pollution will not form [8]. In addition, floc of coagulation contain heavy metal ions can be used as a mixture of oxides. Then, the oxide mixture from the electrocoagulation process can be used as a ceramic glaze material by calcination process [7].

Optimum conditions of electrocoagulation process encompass: pH 8, current density 1.25 mA/cm^2, combination of Al-electrode Fe (cathode-anodes), and electrocoagulation time for 120 minutes [9]. The electrocoagulation process using the optimum conditions of copper(II) ions allows maximum floc or coagulant deposition. Coagulant is expected that in the form of $Cu(OH)_2$ mixed with other metal hydoxides including $Pb(OH)_2$, $Zn(OH)_2$, $Cr(OH)_3$, $Cr(OH)_6$, $Cd(OH)_2$, dan $Fe(OH)_2$. The coagulant will pass through the drying and calcination process so that the oxide form will be applied as a glaze ceramic dye. The color of a ceramic glaze is influenced by several factors including the combustion temperature, dye concentration, combustion conditions, the composition of the glassy material, and the type of metal oxide as coloring [10]. In this study, the effect of dye concentration and combustion temperature on the final color of ceramic glaze will be studied. Other factors that influence the color of ceramic glassware have been controlled.

2. Experimental Section

2.1 Materials
Electroplating liquid waste from Kotagede, Yogyakarta, taken on August 22, 2017, at 11.00 WIB, the buffer solution was pH 4 and 7, Fe and Al Electrodes were 15 x 3 x 0.03 cm, acetone, 5 M NH_4OH solution, transparent soft glaze (TSG), zircon oxide (ZrO_2), ceramic biscuits, plastic wrap, distilled water, whatman filter paper no. 42. All of the materials were purchased from various commercial sources. The grade of them is pure analysis (pa) and used without further purification.

2.2 Instruments
XRF (X-Ray Fluorecense), AAS (Atomic Absorption Spectroscopy) AA-7000, Pyrometer dan Thermocouple, Pyrometric Cone, Chromameter, DC Power Supply (Cimarec dan Faithful), furnace, oven, pH meter (Gemmy), digital scales, Hot plate-magnetic stirrer, and laboratory glassware.

2.3 Characterization of the physical-chemical properties of the sample
As many as 1.5 liters of homogenized samples were analyzed at the Yogyakarta Health Laboratory Center (BLK). The parameters tested were physical properties such as odor, turbidity, color, temperature and chemical properties such as anion content, heavy metals, DO, and pH. In this study, electroplating wastewater samples are estimated to contain dangerous heavy metal ions.

2.4 Precipitation of metal ions by electrocoagulation method
As many as 500 mL of electroplating liquid waste samples were put into a 1 liter beaker and a 4 cm magnetic bar was also included. Then the electrocoagulation process was carried out using optimum conditions for copper(II) metal deposition including pH 8, electrocoagulation time of 120 minutes, combination of Al-Fe electrodes, current density of 1.25 mA/cm^2.

2.5 Characterization of sample coagulants with XRF
5 grams of coagulant were analyzed using X-Ray Fluoresence at BATAN.

2.6 Application of copper(II) oxides as ceramic glaze coloring with combustion temperature variations and copper(II) oxide concentrations
As many as 21.74 grams of TSG glassware, 3.26 grams of ZrO_2, and 2 grams of copper(II) oxide were mixed with water little by little. Then the mixture is mashed using pestle and mortar to form a slurry-like mixture. The mixture of the glassy formula is filtered using a filter mesh measuring 120 mesh and

accommodated in a small bowl. Ceramic coating is then carried out by dipping for 5 seconds into a glassy formula mixture. Furthermore, the ceramic is burned using a furnace to reach temperatures of 999, 1060 and 1101^{o}C.

The effect of variations concentration of copper(II) oxide was studied by repeating all treatments and changing the concentration of Cu(II) oxide to 0.88; 2.64; and 3.53% or equivalent to 1, 3 and 4 grams of coagulant. Furthermore, the ceramic is burned using a furnace at a temperature of 1060^{o}C.

2.7 Analysis of ceramic glaze color homogeneity using a chromameter

As many as 2 pieces of ceramic glaze from each combustion temperature variation and variation of copper(II) oxide concentration were analyzed by using chromameter konica minolta CR-400 at the UGM Faculty of Agricultural Engineering.

3. Discussion

Electroplating liquid waste sample characterization aims to determine the content of heavy metals. Characterization results of electroplating liquid waste showed samples containing several dangerous metal ions such as Cu^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, and Zn^{2+}. The highest level of metal ions in waste, namely copper(II) is 178.4510 ppm.

Metal ions in the sample are then precipitated using electrocoagulation method at optimum conditions. The sample electrocoagulation process was carried out 31 times. The results of sedimentation in the form of colored coagulants obtained as much as 19.266 grams. The coagulants obtained are still in the form of wet hydroxide. In this study, the coagulant applied and acts as a dye for ceramic glaze is a form of metal oxide. Wet metal hydroxide coagulant will be dried using an oven until it turns into dry hydroxide. The calcination process in the process of burning ceramic glaze will convert hydroxide to oxide. Coagulant drying was carried out at 110^{o}C for 6 hours. Before the coagulant is applied as a dye, it needs to be characterized to determine the composition of the elements in the coagulant qualitatively and quantitatively. The color of the glaze is determined by the largest metal content. So, the characterization to determine the composition of the metal content in the coagulant needs to be done. Based on the results of the characterization, it is known that the largest metal content in the coagulant is copper(II) of 22.04±0.73%, while other metals such as Cr, Cd, and Pb are below the detection limit of the XRF device. Then the copper(II) coagulant was used as a coloring material in a glassy formula. The application of copper(II) oxides as dyes in combustion temperature variations and concentrations results in green ceramic glaze, as in figures 1, 2 and 3.

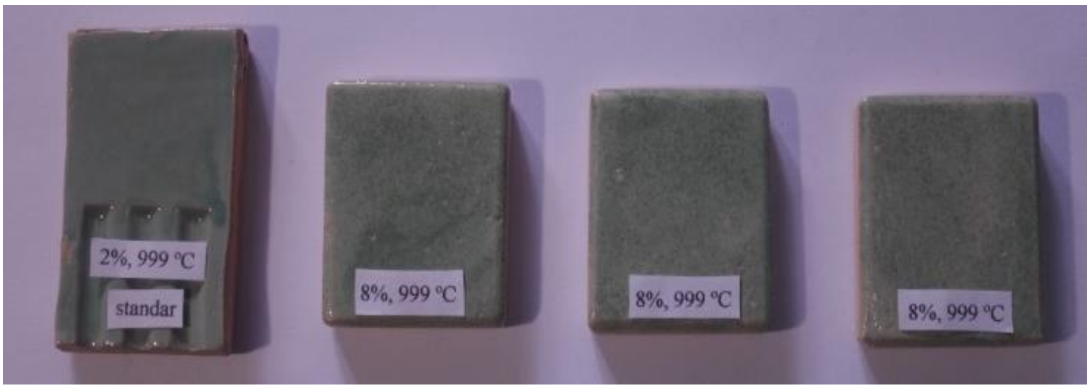

Figure 1. Ceramic tiles produced by combustion at a temperature of 999^{o}C.

Figure 2. Ceramic tiles produced by combustion at a temperature of 1060°C.

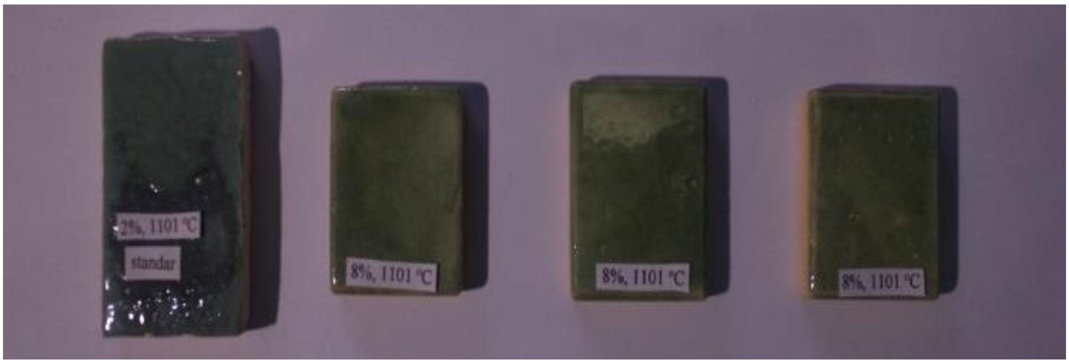

Figure 3. Ceramic tiles produced by combustion at a temperature of 1101°C.

Based on a visual analysis of the color of the emerging ceramic glaze, it has a typical copper metal oxide color at all temperature variations. In general, the typical color of copper metal oxide in all ceramic glazes is almost the same, namely green. A striking difference is the 999°C ceramic glaze, which is less visible green color. The green color that appears in the form of bluish green and uneven on the surface. This is due to the fact that there are still many coagulants that have not melted, which is marked by the appearance of many black dots on the surface of the ceramic.

Furthermore, the ceramic glaze with a heating temperature of 1060°C, the color is light green and more evenly distributed on the surface of ceramic glaze. That is, copper(II) oxides on ceramic glaze with this combustion temperature have fused more, so that the black dots begin to fade compared to the previous temperature. One of the reasons is that the combustion temperature of 1060°C is the temperature that is closest to the melting point of the copper metal which is around 1038°C [11]. At a temperature of 1101°C, the color of the ceramic glaze is dark green. This dark green color appears more evenly on the surface of the ceramic glaze. Metal oxide that has not melted on the surface of the glaze looks less than ceramic with the previous combustion temperature. That means the coagulant has fused more maximally. According to the theory, the sparkling color that appears for copper(II) oxide is light green or Turkish [10]. So visually, ceramics with a combustion temperature variation that has been carried out successfully produces ceramic colors that are close to the color of the theory. The higher the temperature of combustion of ceramic glaze, the lower the brightness and green color of Cu(II) oxide.

Based on figure 4, it can be seen that the L* value increases at the combustion temperature of 999 and 1060°C, ie from 60.79 to 61.52, while at the combustion temperature of 1101°C it shows a decrease to 56.67. The increase and decrease in the L* value indicate the brightness level on the surface of the ceramic glaze. Meanwhile, the higher the combustion temperature, the a* value decreases to -7.45; -6.35; and -5.64. Decreasing the value of a* indicates a reduction in green on the surface of ceramic glaze. The value of b * is directly proportional to the increase in the temperature of burning ceramic glaze. Increased b * value is 3.95; 7.59; and 9.28 indicates increased yellow color, although visually less visible.

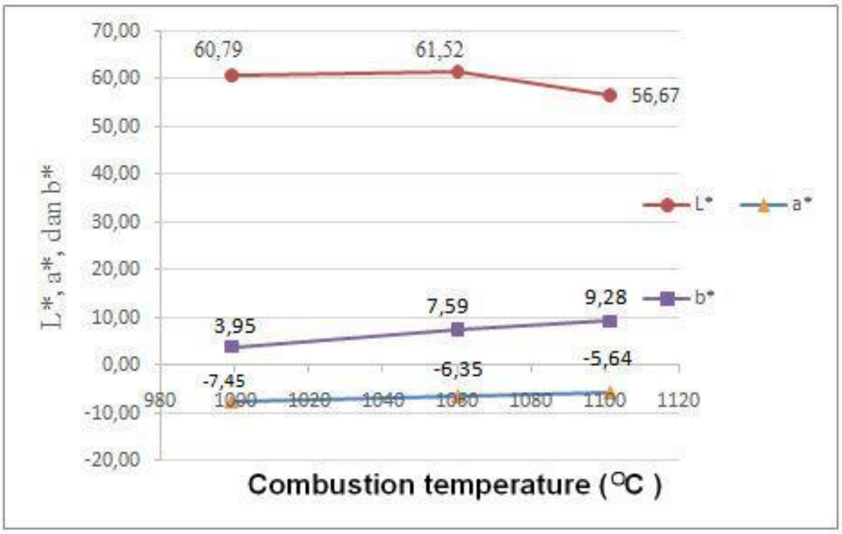

Figure 4. Graph of the relationships of L*, a*, and b* to the combustion temperature.

Based on a visual analysis of the color of glassy ceramics, all variations of copper(II) oxide (impure) concentration produce typical colors of copper(II) oxide. Smoothness in each color of ceramic glaze has similarities, but brightness decreases with increasing concentration. The typical color of copper(II) oxide seen in all ceramics is green. However, the green color of the ceramic glaze that appears has a difference in each variation of concentration. The difference is seen in the ceramic glaze with 0.88% copper(II) oxide concentration in the form of bluish green with dark green dots scattered on the glassy surface. Ceramic glaze with 1.76% copper(II) oxide concentration, light green color spread evenly on the surface of ceramic glaze. That is, the coagulant on glaze ceramic has fused more at this combustion temperature, so that black dots begin to fade compared to previous concentrations. Ceramic glaze with a concentration of copper(II) oxide 2.64%, the resulting color is a rather dark green. Ceramic glaze with 3.53% copper(II) oxide concentration, the color is darker green than before with black dots covering evenly on the surface of ceramic glaze.

The results of the glassy ceramic variation of copper(II) oxide concentration can be seen in figures 5, 6, 7, and 8.

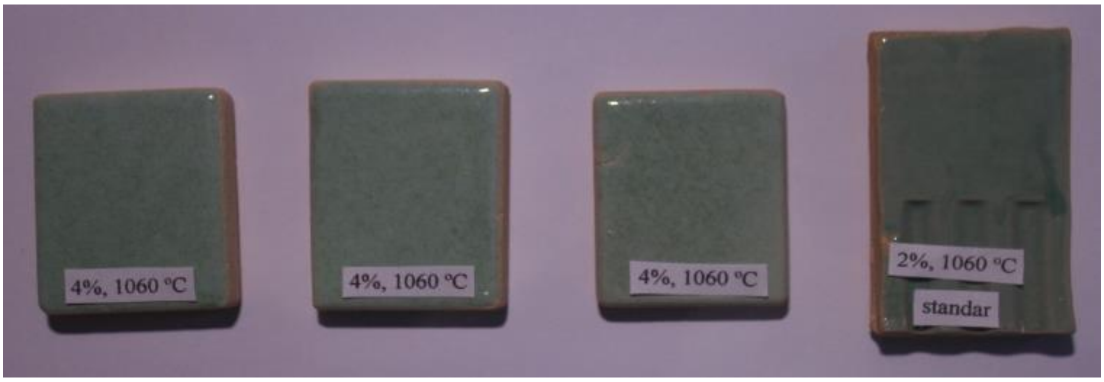

Figure 5. Ceramic glaze with a concentration of Cu(II) oxide 0.88%.

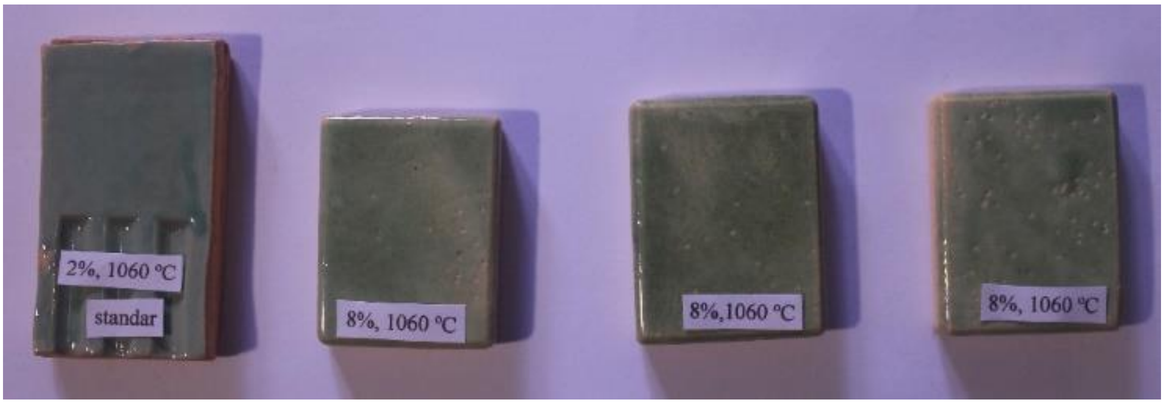

Figure 6. Ceramic glaze with a concentration of Cu(II) oxide 1.76%.

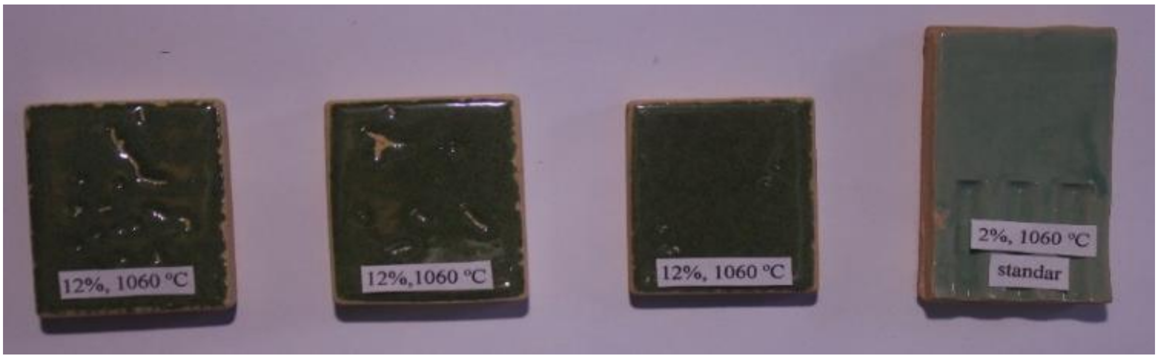

Figure 7. Ceramic glaze with a concentration of Cu(II) oxide 2.64%.

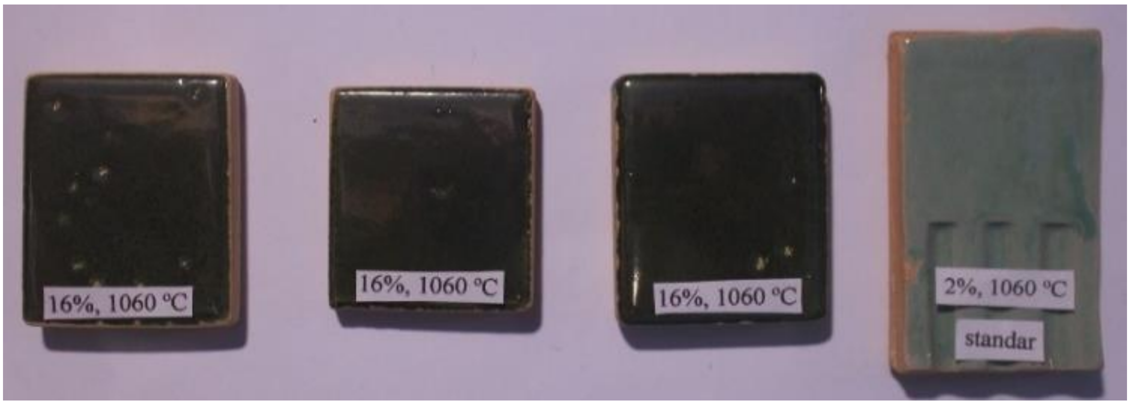

Figure 8. Ceramic glaze with a concentration of Cu(II) oxide 3.53%.

Figure 9 shows that the higher the copper(II) oxide concentration, the lower the L* and a* values. The decrease in L* value is 70.36; 61.52; 47.96; and 43.03. This shows the brightness on the surface of the ceramic glaze is decreasing. Meanwhile, a decrease in the value of a* is -9.09; -6.35; -3.71; and -0.03. Decreasing the value of a* shows a reduction in green on the surface of ceramic glaze. The value of b* is increasing at a concentration of 0.88 and 1.76%, which is from 0.34 to 7.59. However, at concentrations of 2.64 and 3.53%, the value of b* decreased to 6.65 and 2.67. The increase and decrease in b* value shows an indication of increasing or decreasing yellow color although visually less visible.

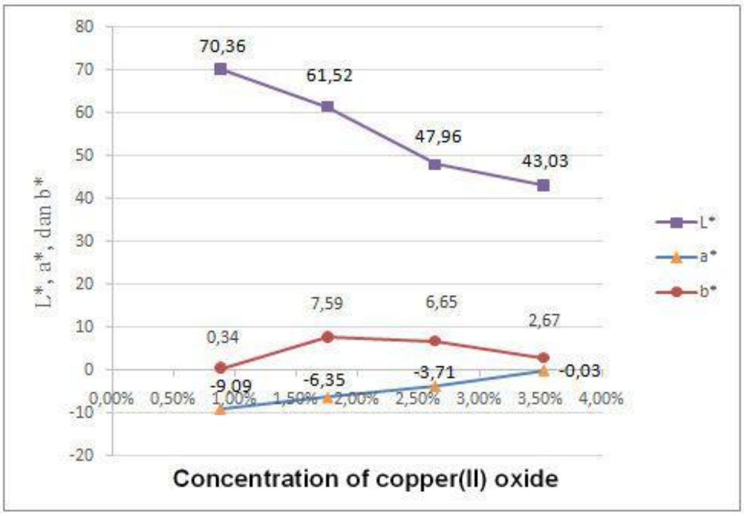

Figure 9. Graph of the relationship of L*, a*, and b* to the concentration of copper(II) oxide.

4. Conclusions

Based on the research that has been done, it can be concluded that the higher the temperature of combustion of ceramic glaze, the brightness of the ceramic color will increase, the green color of copper(II) oxide will decrease, but the resulting yellow color increases. Meanwhile, the greater the concentration of copper(II) oxide causes the less brightness and green color to be produced, while the yellow color increases.

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