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POTENTIAL USE OF CHROME-TANNED LEATHER WASTE AS CERAMIC PIGMENT

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Abstract- Waste is can be defined as materials which no longer can be used for the intended purposes for originally. Hazardous waste from industries might be the source of pollution if there is no proper treatment. Many industries use chromium as a material in the production process. The existence of chromium waste will bring harmful effects to the environment. Forms of chromium in environment are trivalent and hexavalent forms. One of alternative methods to utilize waste is by using it as a pigment. Chromium waste can be utilized as a pigment in industries such as ceramics, tile, ornamental and household ceramic

Index Terms—Chromium, Waste, Pigments

INTRODUCTION

Waste is the residue of a business and / or activity. Based on the form, waste is classified into three form; solid waste, liquid waste and gas waste. Solid waste are generated by almost activity, and the amount varies by source, season, geography, and time [1]. Solid waste generation can be subdivided into residential and nonresidential, depending on its source. Liquid wastes include industrial wastes such as oil and natural gas refinery byproducts, municipal waste, chemical byproducts, agricultural wastes and radioactive water used as coolants in nuclear power plants. When improperly handled and disposed of, liquid wastes pose a serious threat to human health and the environment because of their ability to enter watersheds, pollute ground water and drinking [2]. The toxic gases produced during combustion and other chemical process may be removed by destructive disposal, dispersive dilution or as recoverable side products [3].

Hazardous waste is waste with the properties that make it potentially dangerous or harmful to human health or the environment. Controlling hazardous waste has become a serious problem to prevent environment pollution. In 1976, The U.S Congress imposes the Resource Conservation and Recovery Act (RCRA) to protect public health and environment.

The leather industry is still using two tanning methods – chrome and vegetable. For the last hundred years, chrome tanning has been the dominant method of making leather. Efforts are now being made to find alternatives, and there has been some increase in the use of vegetable tanning of leather for footwear and other products and non-chrome tanning methods have become quite popular with automobile manufacturers [4].

Chromium is material that widely used in tanning industry for the excellent properties attained by the leather. Advantages by using Chromium are simple operation, have good mechanical resistance of the hides, an extraordinary dyeing suitability and better hydrothermic resistance in comparison with hides treated with vegetable substances [5]. Reference [6] described that Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Chromium tanning will be used for years to come because of the characteristics it imparts to final productts and its ease of application [6]. Compared to vegetable tanning, Chrome tanning is faster and produces a stretchable leather. Reference [7] explained that conventional vegetable tanning cannot be conceived further environmentally congenial than Chromium tanning Due to the higher contamination load and low treatability.

Chromium is one of the most common pollutants in tannery industry and has several oxidation states ranging from -2 to +6. Chromium contained Cr_2O_3 which its content is at least 3.5% in solid leather waste. The properties of Cr are highly dependent on the molecular structure of the Cr compound, particularly on the oxidation state (or oxidation number) of the Cr. Cr is an element that exists primarily in two different oxidation states, hexavalent; Cr(VI) and trivalent; Cr(III) [8]. Cr(VI) is far more mobile than Cr(III) and more difficult to remove from water [4].The negative impact of the tanned leather waste upon environment is due to the chromium compounds toxicity, especially Cr(VI) compounds [9]. The oxidative of Chroium is mainly in three form; Cr(0), Cr(III), and Cr(VI), which are the most stable forms of Cr where Cr(0) is the metallic form, the forms of Cr(III) and Cr(VI) are the most preponderant in soils and water [10].

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the Cr^{3+} and Cr^{6+} form through natural processes and human activities. The main human activities that increase the concentrations of Cr^{3+} are steal, leather and textile manufacturing. The main human activities that increase Cr^{6+} concentrations are chemical, leather and textile manufacturing, electro painting and other Cr^{6+} applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils.

Cr(VI) negatively affects the environment due to its eminent solubility, mobility and responsiveness. Soils and groundwater surrounds are the most fictile to Cr(VI) pollution from spills, unlawful disposition and unguarded stock piles of new techniques chromium products. Though Cr(III) is an important nutrient for human beings, there is no uncertainty that Cr(VI) compounds are both acutely and inveterately poisonous [7].

There are several types of pigments. The main one is oxide dye which is a combination of oxygen and element. Chromium waste from tanning industry in terms of its composition and stability was studied that has potential use as a ceramic pigments for the glass and ceramic industries [5]. Reference [11] investigated the use of chromium from tannery waste for ceramic dye. Utilization of this chromium used a small-scale extraction tool of chromium. This extraction tool could be used to process the dry leather waste to produce chromium oxide. The chromium oxide could be used as a dye, both by colored glaze or decoration under glaze at 1250 °C. Chromium depending on synthesis conditions, it can be found in different states of oxidation (II–VI) and these generate different properties, stability and coloration. To produce a green coloring pigment, the Cr_2O_3 content needs to exceed Al_2O_3. Coloring ranges from green to red, depending on the chromium content [11].

There are several types pf pigments. The main is oxides pigments which is a combination of oxygen and elements. Chromium oxide (Cr_2O_3) is one of principal oxides of chromium and can be used as a pigment. Due to stability, chromium is commonly used pigment and was originally called glazes and is used in several industries: paints, inks, and glasses. (Cr_2O_3) can yield a variety of colors: red, yellow, pink, brown, and especially green.
This review article provides on the detailed information about the potential of chromium waste as ceramic pigments. The present paper proposes a solution to utilize the leather wastes to improve the environment quality

EXPERIMENTAL

Chromium waste source was from solid waste from dump site of a tanning industry in Yogyakarta, Indonesia and collected randomly from the dump site and collected using plastic bags. Figure 1 presents dump site of Chromium waste of a tanning industry.
For the treatments, Chromium waste were dried to constant weight at 110°C for 4.5 hours in an oven. Then dried waste were refined and sieved using a sieve with size 60. Fig. 2 presents Chromium waste before drying and Fig. 3 presents Chromium waste after firing at 110°C for 4.5 hours.

Figure 1. dump site of Chromium waste of a tanning industry

Figure 2. Chromium waste before drying

Figure 3. Chromium waste after firing at 110 °C for 4.5 hours.

Chromium wastes as much as 0%, 15%, 30% and 45% were added into the basic glaze composition to make samples. Materials of basic glaze were feldspar, kaolin, quarts sand and salt. Those samples were fired at 900 °C, 1000 °C and 1100 °C.

RESULT AND DISSCUSION

The waste identification was conducted to measure the concentration of heavy metal using AAS (Atomic

Adsorption Spectrophotometry). The result of chromium waste identification is shown in Table 1.

Table 1. Chromium Waste Characteristic

No	Parameter	Concentration (ppm)		
		I	II	III
1.	Fe	1331.643	1385.123	1345.013
2.	Cr	55808.741	55808.741	57324.597
3.	Ti	ND*	ND*	ND*

The basic glaze compositions were 55% of feldspar, 15% of kaolin, 15% of quartz sand and 15% of salt. Chromium waste as much as 0%, 15%, 30% and 45% was added to basic glaze mixture. Kaolin served as a source of alumina and silica in the glaze. It added the strength and hardness of glaze and made the glossy glaze. Quartz sand was a source of silica in the glaze. Silica was a glass forming element and provided the mechanical properties of the glaze. Silica prevented cracking, rupture or explodes during drying or firing. The feldspars were a class of minerals known as the aluminum silicates. Feldspar was a flux agent. When glaze was fired, feldspar is melting and forming molten glass which causes another particle of glaze mixture adheres. Feldspar added strength, hardness, glossy of glaze [13]. Three samples were made in each glaze composition and fired at 900 °C, 1000 °C, and 1100 °C during 8 hours. The different temperature gave the different characteristic of glaze. The result of each temperature firing and Chromium waste composition is shown in Fig. 4-7.

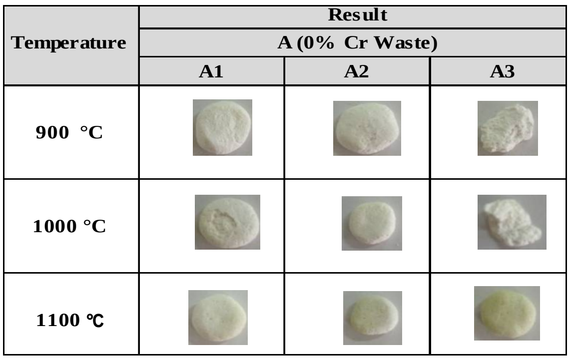

Figure 3. 0% Chromium waste after firing for 8 hours.

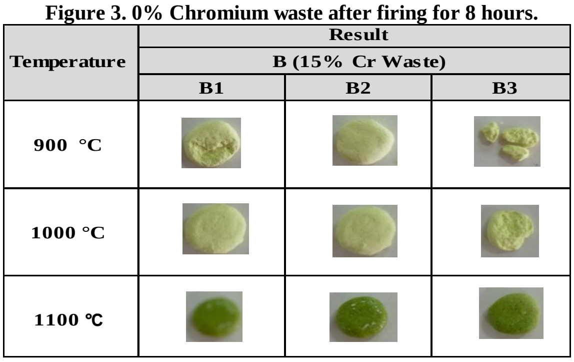

Figure 3. 15% Chromium waste after firing for 8 hours.

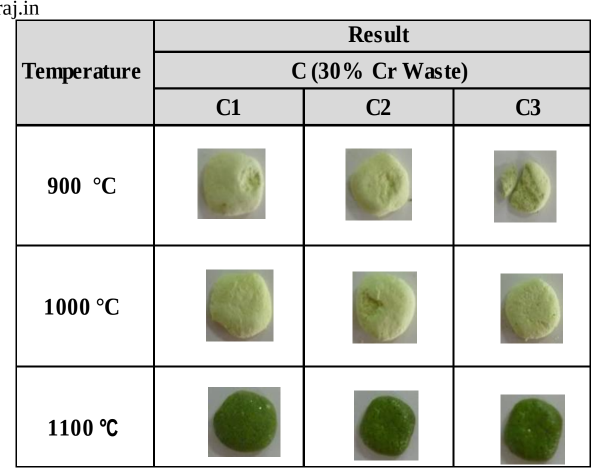

Figure 6. 30% Chromium waste after firing for 8 hours.

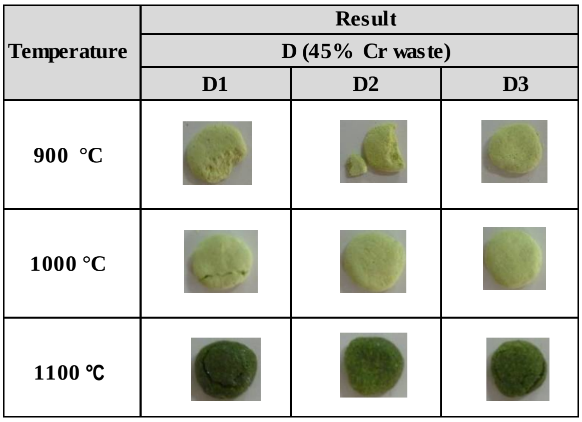

Figure 7. 45% Chromium waste after firing for 8 hours.

Every composition and firing temperature gave the diffrent properties. The physical properties of glaze were brittle and fragile after firing at 900°C and 1000 C. The addition of chromium as much as 0%, 15%, 30% and 45% produced a variation of green color after firing at 900 °C, 1000 °C and 1100 °C for 8 hours. The increase of chromium waste content does lead to insentification of color.

Chromium, especially chromium oxide, Cr_2O_3, is well known for resulting in strong green coloration in ceramic glazes for the ceramic. It can be used as a igment in tile industry and may also be used in the container glass industry. The exsitence of soluble salts and organic matter of the tannery sludge as undesirable material can leave superficial imperfections such as pores or cracks, resultant from their volatilization or decomposition in the case of glazes [5].

Reference [14] conducted research on colored glaze from sludge of electroplating manufacture which has a chromium content of 20-30%. After processing of chemical and physical properties, the sludge could be used as ceramic colorant. The method of colored glaze making was performed by varying the composition. The sludge was calcined at 900 °C to obtain green color. The brown color was made by adding the other metal oxide as an additive and calcinations was performed at 1280 °C.

Based on resaerch that was conducted by Reference [15], pigments used in the production of traditional colored glazed and unglazed tile must show thermal and chemical stability at high temperatures (1200-1250 °C). For initial step in the production of pigments, the selection of raw materials and purity is a important step to get good result due to the mostly metal oxides or salts of the desired. After drying, the powders were tested as pigments for ceramic body coloring. The pigments, added to the composition at 3%, were dry mixed for 30 min. The mixtures were pressed at 400 kg/m2 and then fired at 1250 °C for 40 min following an industrial cycle.The colors of pigment range from dark black to light grey depending on chromite or manganese content.

Compostional study that conducted by Munoz (2004) showed that a green pigment was obtained with a lower starting chromium content, using Cr_2O_3 and not Cr(VI) compounds as precursors,which has improved chromatic co-ordinates compared with the STD pigment and segregates less Cr(VI) in the washing water

A new red ceramic pigment based on the solid solution of chromium (IV) in calcium $(Cr_xCa_{1-x})TiO_3$ has been obtained and characterized by 5%w addition to a CaO-ZnO-SiO_2 transparent glaze used for ceramic tiles [16].

Reference [9] explained that the minimum temperature to achieve pure pink colour is 1200 °C and bluish-green color is 1100 °C for 2 h. The color of the samples does not change between 1200 °C and 1300 °C. Testing pigments obtained by using leather waste as a source of chromium in coloring some ceramic glazes has proven that they behave similarly to similar pigments obtained by the classical method.

CONCLUSION

This study indicated solution to reduce the polluting effect of chroium waste from tanning industry. Through several stages of treatment, chromium waste can be utilized as pigment in the ceramic industry, glass, paints, etc. Colours that obtained from chromium waste are red, yellow, pink, brown, and especially green depending the condition and content of chromium waste. These pigments can reduce the consumtion of commercial pigments in order to get cost savings.

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