The physical properties, color direction and color difference of stamp ink from gambier (*Uncaria gambir roxb*) with complexing Al\(_2\)(SO\(_4\))\(_3\) compound

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Abstract. The raw materials of stamp ink are usually made from synthetic materials and are toxic that can damage human health. This research uses gambier which is material from the local natural resource. The purpose of this study was to see the influence of Al\(_2\)(SO\(_4\))\(_3\) on the direction and difference of color, pH, and density of the stamp ink. The study was conducted in several stages, namely the making of gambier extract, the dissolving process of raw gambier with water, drying, reducing the particle size of 100 mesh, and extracting the gambier powder with an alcohol solvent. The complexing compound Al\(_2\)(SO\(_4\))\(_3\) and other supporting materials were added into the gambier extract to produce stamp ink. The stamp ink was examined the direction and difference of color, pH, and density. The optimum treatment was obtained at a concentration of 30% Al\(_2\)(SO\(_4\))\(_3\) with the results of test pH 4.053; density 1.16 g/cm\(^3\); and color direction L* 41.579; a* 13.023, b* 21.132. The result of the stamp test on white paper showed that the color of the ink is visible, compact, unified and does not expand.

1. Introduction

Stamp ink is the liquid used to stamp a document and become an identity of the existence of an institution or organization. This identity is very useful for data validation such as diplomas, decrees, and several other important documents. The stamp ink that is on the market today is made from synthetic chemicals, some of which are poisonous and not eco-friendly. Gambier stamp ink is a product made from the local natural resources. It’s a non-toxic nature, hypoallergenic, and more eco-friendly. Gambier stamp ink development will provide several benefits, namely increasing the added value of raw materials, increasing the income of gambier farmers, substituting imported products, and developing eco-friendly products.

The main ingredients of gambier are tannins (20%-50%) and catechins (7%-33%) [1]. Research about the use of gambier tannins has been carried out by earlier researchers, gambier tannins for textile dyes [2]–[5] and for leather tanner [6]. The use of gambier tannin as a raw material for ink products is due to tannin complex compounds that react with metal salts to form colors. Gambier tannins with saturated alcoholic FeCl\(_3\) and saturated NaOH will produce a blue to black color. The complex compound of gambier tannin in alkaline conditions will produce a blood-red color. The reaction of tannins with FeCl\(_3\) will form a complex compound as in Figure 1 [7], [8].

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Figure 1. The reaction of tannin with FeCl₃ (Source: [9]).

The color obtained on stamp ink with saturated alcoholic complexing FeCl₃ and FeSO₄ was similar namely blue to black color. However, the ink obtained was still sticky with physical and chemical properties, namely pH (3.27), total solids (41.33%), tannins (2.58%) [1], [10]. Based on the physical properties and stamp ink deposits [11], the Al₂(SO₄)₃ complexing compounds are used because they have ionic bonds larger than the central atom Al (+3). The complex bonds that are formed are expected to be more stable and the stamp ink will not coagulate. The purpose of this research was to see at the effect of Al₂(SO₄)₃ on the stamp ink products and to determine the optimum process by varying the concentration of Al₂(SO₄)₃.

2. Experimental
2.1 Materials and tools
The materials used were raw gambier (*Uncaria gambier* Roxb), ethanol for extracting fine gambier, Al₂(SO₄)₃ as complexing of tannin, glycerin, and distilled water. The gambier was in the dry form taken from gambier processing farmers in Harau Subdistrict, Lima Puluh Kota Regency, West Sumatra Province – Indonesia. The Al₂(SO₄)₃ used was in the form of white crystalline solid. It is soluble in water, non-combustible, and nontoxic. All chemicals used were technical grade which purchased from *brataco* chemical company. The equipment for analysis includes colorscan SS 6200 spectrophotometer, pH meter (HACH), and pycnometer. The research was carried out in the laboratory of the Institute for Research and Standardization of Industry - Padang, the laboratory of the Padang State University, the Laboratory of Institute of Textile Technology - Bandung.

2.2 Research implementation
The process of making stamp ink was done through two stages. The first step was to make gambier extract by grinding the raw gambier and dissolve it in water with a ratio of gambier and water 1:4. The solution was heated at 60°C and then filtered to remove impurities in the raw gambier. The gambier solution is allowed to stand for 1 night and the residue was taken. The gambier residue was dried at room temperature, then ground and sieved with a 100 mesh sieve. The fine Gambier was dissolved in alcohol with ratio gambier and alcohol 1:4. It was stirred with 250 rpm and temperature 60°C for 5 hours, then precipitated for 1 night and then filtered. The filtrate was taken and the residue was removed.

In the second step, stamp ink formulations were made by varying the concentration of complexing Al₂(SO₄)₃, namely 15, 20, 25, 30, and 35% (v/v). Al₂(SO₄)₃ with the concentration according to the treatment was added to 35% (v/v) gambier extract solution and stirred at speed of 250 rpm for 2 hours. 20% glycerin (v/v) and water were then added to the ink solution while continuing to stir. The stamp ink was analyzed for its physical and chemical properties and tested for the quality of the stamp on white paper.
2.3 Analysis
Analysis and observations made on the stamp ink were density, pH, direction and difference of color, and testing the stamp ink produced on the white paper to see the stamp quality.

2.3.1 Analysis of pH
A sample of 20 ml was measured by using a pH meter (HACH) at room temperature with constant agitation. pH shows the negative logarithm of the hydrogen ion concentration in the sample.

2.3.2 Density
Density is the ratio between the weight compared to the volume of a substance at a temperature of 25°C [12]. The density analysis was used to determine the specific gravity of a solution.

2.3.3 Analysis of direction and difference of color
Testing the color direction using the CIELAB 1976 method, namely color measurement based on three-dimensional color coordinate spaces in three axes, namely L* (brightness), a* (green - red direction), and b* (blue-yellow direction). The reading of the value L* (brightness) is 0 = black and 100 = white. Readings of a* + = red and - = green. Readings of b* + = yellow and - = blue [13], [14]. Testing the color direction of the gambier extract solution was done as a control of the stamp ink obtained by treating the percentage difference of Al₂(SO₄)₃.

3. Results and Discussion
3.1 Analysis results of gambier and gambier extract
The analysis results of gambier and gambier extract are shown in Table 1. The tannin and catechin content of raw gambier used in this study was 33.25% and 51.75% respectively. Gambier with high tannin content is usually blackish brown, while gambier with high catechins content is usually yellowish brown. In the production of stamp ink, it is expected to use gambier with high tannin content. The levels of tannin in stamp ink from gambier at several concentrations of gambier extract ranged from 1.86% - 2.78% [10].

The gambier extract had tannin content 4.05% with a pH of 3.35. Tannins are compounds that play a role in textile coloring (Sofyan & Failisnur, 2016) and tanners (Ardinal et al., 2014). It is used in industry for drugs and ink as well (Muchtar, 2013). The tannin content of gambier extract is crucial in the complexes formed with Al₂(SO₄)₃ and produces ink dyes.

| No. | Parameter | Sample Gambier (%) | Sample Gambier Extract (%) |
|-----|-----------|--------------------|---------------------------|
| 1.  | Tannin    | 33.25              | 4.05                      |
| 2.  | Catechin  | 51.75              | -                         |
| 3.  | pH        | -                  | 3.35                      |

3.2 Density
The analysis results of the stamp ink density give fluctuating results (Figure 2). However, the difference in each treatment is not significant. The difference between the smallest and the largest density is 0.072. The density will affect the ink quality produced. The high density can cause the ink not to adhere properly on the paper. The density can be influenced by the particle size of gambier and supporting materials, as well as the conditions of the ink production process such as stirring speed and temperature.

The largest density was the treatment with adding 30% Al₂(SO₄)₃ which is 1.155 gr/cm3. This treatment was the best result with pH 3 having a more stable ink condition than other treatments. When compared to the stamp ink density values according to SNI 06-1567-1999 (minimum 1 gr/cm3),
the density of the stamp ink produced has met this standard. The results of another study of ink from gambier were carried out by [15] who reported that the marker ink from gambier had a density 1.0254 g/cm³. The stamp ink in the market has a density of 1.0010 g/cm³.

![Figure 2](image2.png)

**Figure 2.** The density of stamp ink with varying concentration of Al₂(SO₄)₃.

### 3.3 pH

pH is the degree of acidity used to express the level of acidity or base owned by a substance, solution or object. pH value of the stamp ink produced is shown in Figure 3. The pH value of stamp ink for all treatments is acidic (3.739-4.069). The acidic pH conditions are caused by the gambier extract and the use of complexing Al₂(SO₄)₃ which is also acidic. Gambir contains katechu tannic acid compounds as its biggest component (20-55%) which are acidic [16]. The pH conditions will affect the color direction and color difference of stamp ink produced and can make the ink more stable and reduce clotting.

![Figure 3](image3.png)

**Figure 3.** pH of stamp ink with varying concentration of Al₂(SO₄)₃.

One of the supporting material used in the stamp ink from gambier is glycerin. According to [10], glycerin has a neutral pH. The more glycerin added, the more easily oxidized the stamp ink formula so that the pH of the stamp ink is higher. The pH of stamp ink from gambier on the glycerin addition with several concentrations ranged from 3.39 to 3.98 [10].
3.4 Analysis of color direction and color difference

The analysis results of the color direction of the stamp ink show a positive value of L*, a*, and b* (Table 2). The L* value of gambier extract was 63.811 while the stamp ink ranged from 41.579-68.050. The value of a* is between 13.023-14.625. Gambier extract had b* value 34.583 and the stamp ink ranges from 21.132-40.234.

Table 2. Analysis results of L*, a*, b* the stamp ink with varying concentration of Al₂(SO₄)₃.

| Treatment      | Wavelength (nm) | Absorbance | L*    | a*    | b*    |
|----------------|-----------------|------------|-------|-------|-------|
| Gambier extract| 400             | 1.422      | 63.811| 12.104| 34.583|
| 15% Al₂(SO₄)₃ | 400             | 1.305      | 50.356| 13.971| 30.254|
| 20% Al₂(SO₄)₃ | 420             | 1.157      | 62.354| 13.237| 39.987|
| 25% Al₂(SO₄)₃ | 420             | 1.074      | 65.644| 14.266| 40.234|
| 30% Al₂(SO₄)₃ | 400             | 1.323      | 41.579| 13.023| 21.132|
| 35% Al₂(SO₄)₃ | 400             | 0.879      | 68.05 | 13.665| 28.661|

The results of color direction measurements of stamp ink and gambier extract had a reddish-yellow color. Gambier extract solution had a maximum wavelength or maximum light absorption at a wavelength of 400 nm with an absorbance value of 1.422 (Table 3). Stamp ink with treatment Al₂(SO₄)₃ concentration results in varying color intensity. The Color intensity can be seen from the value of absorbance at the same maximum wavelength. The stamp ink with the treatment of 15, 30, and 35% Al₂(SO₄)₃ have the same maximum wavelength in the visible light area which is 400 nm. However, the stamp ink with treatment 20 and 25% Al₂(SO₄)₃ have different maximum wavelengths that are 420 nm. This shows that in the treatment 20 and 25% Al₂(SO₄)₃, the batochromic effect occurs, which means a shift in wavelength from 400 nm to 420 nm.

The wavelength area 400 nm (gambier extract, 15, 30, and 35% Al₂(SO₄)₃), the color intensity decreases. The biggest color intensity reduction is at 35% Al₂(SO₄)₃ with absorbance value 0.879. The 15 and 30% Al₂(SO₄)₃ treatments are darker than gambier extract and other treatments, especially with treatments that have the same wavelength. This can be seen from the value of L* (brightness) which is lower than gambier extract. The measurement results of stamp ink color lead to reddish-yellow. this is in accordance by the results of the study [17] with the reaction shown in Figure 4.

Figure 4. The reaction of tannin and Al₂SO₄ [17]
Table 3. Color direction and color difference of the stamp ink with varying the concentration of $\text{Al}_2(\text{SO}_4)_3$.

| Treatment  | Color difference |
|------------|------------------|
| 15% $\text{Al}_2(\text{SO}_4)_3$ | 14.257 |
| 20% $\text{Al}_2(\text{SO}_4)_3$ | 5.710 |
| 25% $\text{Al}_2(\text{SO}_4)_3$ | 6.322 |
| 30% $\text{Al}_2(\text{SO}_4)_3$ | 26.001 |
| 35% $\text{Al}_2(\text{SO}_4)_3$ | 7.448 |
Figure 5. Test results of stamp ink on white paper

The reaction of tannin and $\text{Al}_2(\text{SO}_4)_3$ will form a complex compound as shown in Figure 4. The stamp ink color with $\text{Al}_2(\text{SO}_4)_3$ treatment is brownish. Visually, this is in accordance with the results of the color direction testing. The color character can be seen from the value of the color difference and color direction. The color difference in the treatment $\text{Al}_2(\text{SO}_4)_3$ addition from the smallest value to the largest value is $20\% \text{Al}_2(\text{SO}_4)_3 > 25\% \text{Al}_2(\text{SO}_4)_3 > 35\% \text{Al}_2(\text{SO}_4)_3 > 15\% \text{Al}_2(\text{SO}_4)_3 > 30\% \text{Al}_2(\text{SO}_4)_3$. The colors of resulting stamp ink are shown in Table 3. The biggest color difference is 26.001 in the treatment of $30\% \text{Al}_2(\text{SO}_4)_3$. Variations in the treatment $\text{Al}_2(\text{SO}_4)_3$ concentration affected the color difference (light-dark).

Test results of stamp ink on white paper are shown in Figure 5. The results of the stamp on the treatment of $30\% \text{Al}_2(\text{SO}_4)_3$ appear to be more stable from the beginning to the third stamp compared to other treatments. The stamp is clearly visible, the ink is more compact, unified and does not expand. The stamp results of the other treatment are seen not compact, widen and not clear from the beginning of the stamp.

Stamp ink that is on the market today is made from synthetic chemicals and some of them are toxic so we need to find substitutes that are more eco-friendly. The use of gambier for stamp ink as a substitute for synthetic chemicals is an alternative with excellent prospects. Gambier is a natural organic material that is eco-friendly, renewable, and produces good stamp ink products technically. This plant has been cultivated and is available throughout the year so it is very feasible when used as raw material for the stamp ink industry. Its use as an industrial raw material will increase the added value of gambier in the market.

4. Conclusion
The results showed that the treatment variation of $\text{Al}_2(\text{SO}_4)_3$ concentration did not significantly influence the physical and chemical properties of the ink, but it did affect the color difference. Ink test results on white paper obtained the best results on the treatment of $30\% \text{Al}_2(\text{SO}_4)_3$ with the
characteristic of pH 4.053; density 1.166 g/cm³; color difference 26.001, and color direction with values L* 41.579, a* 13.023, and b* 21.132.

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