The Evaluation of Dyeing Leather Using Batik Method

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Abstract
Tanned leather dyeing with Batik Method has been observed with the use of chrome tanned goat leather material. Tanned dyeing generally produces less variable homogenous color without motives. The dyeing with Batik Method has produced various and patterned tanned leathers. Changes in the use of media from textiles to leather on dyeing batik method will cause a lot of problems that must be resolved is the solution. Especially on the stages of the process are: sticking batik wax and dyeing. Two stages are involved. We find that the best wax composition for tanner leather as color barrier for the balance between resina colophonium and animal fat is 2.5 : 10. The use of acid color substance provides the better quality of leather batik than indigozol, napthol and remazol such that it is useful for the dyeing of tanned leather with Batik Method.

Keywords: dyeing, tanned, leather and Batik

1. Introduction
Batik, or wax resist dyeing, is a method to dye the cloth using wax as color barrier [1]. Research about Batik Method dyeing used in tanned leather media is rarely conducted. The change of the use of media from cloth to tanned leather in the Batik Method dyeing has caused many troubles which require the solution. Especially, the process involves stages such as wax adherence, dyeing, and wax release [2].

Tanned leather dyeing technique, according to Burkinshaw and Paraskevas [3], is using tanning drum, spray and brush. The dyeing with this technique only produces one color without motive, and then, the motive depends on the original leather. The advantage of Batik Method dyeing compared to general tanned leather dying is that it produces various motives on the surface of tanned leather and with various colors. Tanned color dyeing with Batik Method is applied to cow leather with vegetable tanning [4], to goat leather with combination tanning [5], and to rabbit leather with chrome tanning [6].
To produce the satisfied Batik Method dyeing, it depends on the composition of Batik wax and the selection of dyeing agent [7]. The adherence rate of Batik wax agent to the tanning leather is influenced by some factors. Heated Batik wax temperature, Batik wax composition, and leather surface texture [4]. Wax temperature has very dominant influence on the incoming wax into leather tissue. The more Batik waxes are absorbed into chorium layer of leather, the more difficult it is to detach [8].

Batik wax detaching process is successful if all waxes are solved without the influence of color and leather strength [7]. The detachment of wax from leather may be using hot alkali solution [4] and may be natrium silica [9] for silk media. The physical characteristics of Batik wax, including melting point, adherence rate, penetrating rate, and freezing speed, are influenced by the comparison of the composition of Batik wax mixing materials such as paraffin wax, beeswax, resina colophonium and animal fat [7].

In other side, leather thickness differs from cloth, and the leather is consisting of three layers such that the penetration of dyeing material into leather is very determining the success of leather dyeing [10]. The selection of dyeing type for Batik Method dyeing on leather is relying on chemical structure between dyeing and leather, tanning type and the presence of chemical active substance on leather surface [11].

The objective of research is to find the appropriate ratio between resina colophonium and animal fat as dyeing barrier and to determine the appropriate dyeing type in the Batik Method dyeing of tanned leather.

2. Materials

Chrome tanned leather with thickness of 1.2-1.5 mm and 3.6 % chromium oxide are supplied by a Tannery located in Yogyakarta, Indonesia. 

Auxiliary chemicals such as Leathernol SPU (fat liquor), Tanigan TAK (retaining agent) and chrome tanning agents are obtained from commercial sources.

Batik Wax made by a mixture of materials such as paraffin wax, beeswax, resina colophonium and animal fat are supplied by Research and Development House of Leather, Rubber and Plastic Goods Industries, Yogyakarta, Indonesia.

The four following commercial dyes were supplied by LIK Magetan, Indonesia with different chemical structures:
- Acid black 210 (anionic dye)

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\text{Acid black 210 (anionic dye)}
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- Indigozol blue IBC

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\text{Indigozol blue IBC}
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- Remazol back 5

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\text{Remazol back 5}
\]

- Napthol AS

\[
\text{Napthol AS}
\]
3. Methods

3.1. Mixing Batik Wax
The mixture of Batik Wax includes paraffin wax, beeswax, resina colophonium and animal fat. Mixing Batik Wax is by melting resina colophonium because it has the highest melting point (700°C). It is followed in order by melting paraffin max, beeswax, and animal fat which has the lowest melting point. The variable of research is the difference of ratio between resina colophonium and animal fat (A = 2.5 : 10 ; B = 5 : 7.5 ; C = 7.5 : 5 ; D = 10 : 2.5).

3.2. The Tanning and Dyeing of Batik Method
The tanning and dyeing of Batik Method are completely explained in Enclosure 1.

3.3. Testing and Measurements
Batik wax test has adherence rate, freezing speed, melting speed and melting point measured based on AOAC Procedure [12]. Batik Wax Penetration is assisted by Hitachi TM 3000 Table Top and examined Scanning Electron Microscope. Degree of penetration wax is calculated along cross-section of Batik Wax sample with 300 x magnification [11].

% penetration from grain side = VZ / VX x 100 %

Fastness testing for leather batik samples was tested according to ISO standard methods. The specific tests were: ISO 105-X12 (1987), color fastness to rubbing; ISO 105-CO2 (1989), color fastness to washing; and ISO 105-E04 (1989), color fastness to perspiration.

The test of the quality of tanned leather Batik is measured based on SNI Standard which involves stitching strength of SNI 06-1117-1989, pulling strength of SNI 06-1795-1990, stretching strength of SNI 06-1795-1990 and leather fainting of SNI 06-4085-1996.

4. Results and Discussions

4.1. The influence of the ratio of resina colophonium to animal fat on batik wax quality
Table 1 indicates that the different ratio of resina colophonium to animal fat will influence adherence rate, melting point, melting speed and freezing speed of batik wax. The highest adherence rate of the wax is found at ratio of resina colophonium to animal fat of 10 : 2.5, while the lowest adherence rate is obtained at ratio of 2.5 : 10. The adherence rate of batik wax is greatly influenced by the rate of resina colophonium material. The more resina colophonium is used as the mixture of batik wax, the stronger adherence rate of tanned leather is given by resina colophonium containing the monomer of resin acids. These resin acids are the derivate of diterpenoid-monocarboxylate from hodrypoenantren alkyl, which has molecule formulation C_{20}H_{30}O_2 [13].

Figure 1 explains SEM of grain leather surface penetrated by batik wax. Indeed, batik wax containing monomers of resin acids will lift some epidermis layer and open collagen fibril such that the monomer of resin acids penetrates into tanned leather. The depth of penetration during the adherence of batik wax into tanned leather depends on ratio of acid monomer to other material mixture. At high ratio of resina colophonium to animal fat, the penetration rate reaches 21 % of leather grain thickness.
Figure 1: The photo based on Scanning Electron Microscope of cross-section of batik wax on leather

Figure 2 explains the ionic bonding between batik wax and tanned leather. Resina colophonium contains monomer of resin acids, with the highest proportion contributed by abietate at 63.4-70.3 %, while the remaining includes sandarakopimarat acid, dehydroabietat acid, and isopimarat acid [14].

Figure 2: The bonding of batik wax with chrome tanned leather

In figure 2, there are compound bonding and carboxylate cluster from abietate ester methyl which is the functional cluster of resin monomer, which binds chrome on tanned leather with ionic bonding. Carboxyl cluster in the abietate ester methyl hydrophobic monomer is functioned to release H+ ion such that there is ionic bonding with chrome. Next, it forms a very stable bonding with chrome tanned leather and polymerizes with monomers contained within resin composite such that it produces stronger adherence rate.

Table 1: Effect of ratio of resina colophonium to animal fat on batik wax

<table>
<thead>
<tr>
<th>Variable</th>
<th>The treatment of ratio of resina colophonium to animal fat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 : 10</td>
</tr>
<tr>
<td>Wax batik properties</td>
<td></td>
</tr>
<tr>
<td>Adherence rate (gram)</td>
<td>135a</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>41.88a</td>
</tr>
<tr>
<td>Melting speed (second)</td>
<td>57.88a</td>
</tr>
<tr>
<td>Freezing speed (second)</td>
<td>87.77a</td>
</tr>
<tr>
<td>Penetration rate (%)</td>
<td>10.6</td>
</tr>
</tbody>
</table>
At high ratio of resina colophonium and animal fat in the preparation of batik wax mixture in Table 1, the increase of melting point needs longer time to melt and to freeze. It is caused by the influence of intermolecular styles between batik wax mixture agents. The use of resina colophonium at batik wax tends to increase the melting point because the melting point is influenced by melting point of raw material. The melting point of resina colophonium at 700C – 800C is higher than melting point of animal fat at 400C-500C, and the mixing of batik wax agents which have different melting point will produce the mixture with melting point between agents’ melting points. The addition of resina colophonium into batik wax elongates the time needed to melt and to freeze. It is caused by Van Der Waals Style between molecules of batik wax crystal which is greater with the growth of resina colophonium. It may need longer time to increase the distance between atoms or between molecules in batik wax to increase the possibility of melting.

4.2. The influence of dyeing paint on the quality of leather batik

Table 2, clearly shows that the adherence rate of paint and leather in the batik method dyeing depends on dyeing paint type. The adherence rate of acid paint into leather is higher than the adherence rate of paints such as indigosol, napthol and remazol. It is related to the binding between chrome tanning material and acid paint type. Essentially, leather affinity is the result of collagen affinity. Chrome salt will bind with leather protein cluster which will improve the content of cation in the tanned leather. Therefore, tanned leather will acidified and very cationic such that the surface of chrome tanned leather will be bound fast with anionic acid dyeing agent. The binding of dyeing paint and tanned leather is relying on chemical structure of dyeing paint and tanned leather. Tanned leather depends on tanning type and active agent on the surface of leather, while dyeing paint relies on dyeing paint structure.

![Image of Table 2: Effect of type of dye on the dye properties and fastness properties of dyed leather using batik dyeing method](image-url)

Table 2, explains the result of the resistance of leather batik dye against washing, water and sweat, and the best rubbing resistance of leather batik dyed with acid > napthol > indigosol > remazol. It is caused by the fixating of the stronger binding between chrome salt and acid paint compared to other dyeing paint. The binding styles between dyed paint and chrome salt are bigger than the styles working between dyed molecule and water, which causes acid dyeing paint more resistant to washing, water and sweat.

The color resistance of dyeing agent is determined by molecule weight or molecule size, and molecule form of dyeing agent [15]. The binding forms chrome3+ with leather protein through hydroxyl clustering bridge (OH). Chrome salts, principally, bind carboxylate acid cluster from leather protein such that leather is tanned with chrome, and cationic content tends to increase (+). Chrome salts are hydrolyzed by releasing acid to increase the acidity rate from the tanned leather. The higher acidity rate in the surface of leather is the stronger the binding of acid dyeing paints. It gives acid dyeing paint with resistance.

5. Conclusion

The tanned leather dyeing is using batik dyeing method. Result indicates that the appropriate ratio of resina colophonium to animal fat as dyeing barrier is 2.5 : 10 because it gives the lowest melting point which needs fast timing to freeze and to melt.
However, adherence rate of wax to leather is low such that wax removing process is easier. The recommended dyeing paint for batik method dyeing is using acid dyeing paint because it gives better adherence rate of paint and dyeing resistance compared to indigozol and napthol dyeing paints.

6. Acknowledgements


References

### Appendix 1. The Stage of Batik Method Tanning and Dyeing

<table>
<thead>
<tr>
<th>Steps process tanning</th>
<th>Used Chemicals</th>
<th>Concentration (%)</th>
<th>Time (Min)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing</td>
<td>Water</td>
<td>--</td>
<td>30'</td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>300</td>
<td></td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>Soda ash/ Na2O3</td>
<td>0.3</td>
<td>30'</td>
<td>Neutral</td>
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<tr>
<td></td>
<td>Tepol</td>
<td>0.5</td>
<td></td>
<td>Neutral</td>
</tr>
<tr>
<td>Soaking</td>
<td>Water</td>
<td>--</td>
<td>30'</td>
<td>Neutral</td>
</tr>
<tr>
<td>Liming</td>
<td>Na2S (± 10Be)</td>
<td>3-4</td>
<td></td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>Ca(OH)2</td>
<td>5</td>
<td>30’, Stop 30’ (3X)</td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>50</td>
<td></td>
<td>Neutral</td>
</tr>
<tr>
<td>Unhairing</td>
<td>Washing</td>
<td>Water</td>
<td>30’</td>
<td>Neutral</td>
</tr>
<tr>
<td></td>
<td>Unliming</td>
<td>Water</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>NH4Cl</td>
<td>2</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Bating</td>
<td>Palkobet/bating agent</td>
<td>1</td>
<td>60’</td>
</tr>
<tr>
<td>Washing</td>
<td>Water</td>
<td>--</td>
<td>30’</td>
<td>Neutral</td>
</tr>
<tr>
<td>Degreasing</td>
<td>Sandopan DTC</td>
<td>0.5 – 1</td>
<td>60’</td>
<td>Neutral</td>
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<td>Pickling</td>
<td>Water</td>
<td>100</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>11-12</td>
<td>5’</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>HCOOH</td>
<td>0.5</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>H2SO4</td>
<td>1</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>--</td>
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<tr>
<td>Tanning</td>
<td>Chrome tanning</td>
<td>6</td>
<td>90’</td>
<td>3.8-4.2</td>
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<tr>
<td></td>
<td>NaCO3</td>
<td>2.5</td>
<td>20’ (3x)</td>
<td>5-5.5</td>
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<tr>
<td>Neutralization</td>
<td>Water</td>
<td>200</td>
<td></td>
<td>5-5.5</td>
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<tr>
<td></td>
<td>Sodium Formate</td>
<td>0.5</td>
<td>20’</td>
<td>5-5.5</td>
</tr>
<tr>
<td></td>
<td>Sodium bicarbonate</td>
<td>0.5</td>
<td>30’</td>
<td>5.5</td>
</tr>
<tr>
<td>Retanning</td>
<td>Water</td>
<td>100</td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Tanigan TAK</td>
<td>2</td>
<td>15’</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Retingan R7</td>
<td>3</td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Tanigan XO</td>
<td>3</td>
<td>120’</td>
<td>5.5</td>
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<tr>
<td>Drying</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a The adherence of batik wax on tanned leather
* Ratio of resina colophonium to animal fat
  2.5:10  5:7.5  7.5:5  10:2.5

*b The adherence of batik wax

Dyeing type | Acid Black 210 | Indigozol IBC | Blue | Remazol Back 5 | Napthol AS

*a The Research Stage I. The treatment of wax adherence on tanned leather with different ratio of Colophonium sp and animal fat.

*b The Research Stage II. The treatment of various dyeing agent for batik method dyeing to tanned leather.