Development of black ink for calligraphy purpose in the production of Al-quran

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Abstract. Commercialised calligraphy inks are currently formulated for general purposes and is not to be practiced solely for the writings of Al-Quran. Thus the usage on Al-Quran is uncertain due to the unknown ingredients used. The virtue of this work is to develop halal and genuine formulations of black inks for calligraphy purpose in the production of Al-Quran manuscript. The black ink produced is required to have few properties; rich solid black, soft handling, fast drying time, non-lifting, non-feathering and waterproof. Pigment used include graphene, charcoal and lampblack. The binders are shellac and acrylic emulsion while solvent used are glycerol and ethanol. From the chosen pigments, binders and solvent, 19 formulation of inks were developed by manipulating the type and amount of each element. Evaluation of all 19 inks produced were done by an expert calligrapher using a professional scale. From the evaluation, one ink was chosen to have the best characteristics of an ink (ink code S9) with formulation of 0.3 g lampblack and 13 mL shellac. The produced black ink has fulfilled the requirement by the calligraphy expert.

1. Introduction

The writings of Al-Quran require the best quality of black inks which has the properties of; rich solid black, waterproof base, non-feathering, soft handling when written, drying time and non-lifting as accordance to an expert calligrapher. Table 1 explains the properties of inks to be produced. At present, commercialized inks are primarily utilized with the purpose of general writings but not specialized for the writings of Al-Quran. Therefore, the ingredients used are uncertain to be applied on it. In order to preserve the purity of Al-Quran, few researches has been developed by using natural resources for instance lampblack, mangosteen charcoal and salt [1]. However, the establishment from local researches are yet still in development. The purpose of this paper is to develop formulations of black inks for calligraphy purpose which is halal and pure suitable to be used on Al-Quran manuscript.

Halal prescription often related to foods and drinks. In terms of inks, standard practical guidelines emphasize on the source of raw material used, preparation, handling, storage, processing aids and manufacturing process based on Islamic law. In terms of raw material, Islam has clarify few important guidelines; it must be clean and safe without anything dirty that is considered to be lawful according to Islamic law.
Raw materials from plant origin and plant products that are poisonous or hazardous to health are considered ‘haram’ unless it has been removed completely [2]. Arabic calligraphy is a form of artwork which is closely associated with the Quran. The Quranic calligraphy came to be recognized as highly regarded form of art in the nineteenth century. There are six types of Arabic calligraphy scripts which are well known to be as the kufic, thuluth, nasakh, taqi, muhaqqaq and riqa [3]. Black ink is extensively used in the writings of Al-Quran manuscript by using the stated styles of script.

Inks generally are made up of four basic components; pigments, binders, solvents and additives. Pigments are colored, organic or inorganic solid powder acting as the source of coloristic properties of an ink. Hiding power and coloring power of an ink will depend on the particle size of a pigment; the smaller the particle size, the darker the pigment will become [3].Binders has a specific role to bind all ingredients of the ink together ink onto the paper. Manipulating the type and amount of binder used will influence the penetration of ink towards paper surface. Therefore, the amount of binder should be sufficient enough so that the pigment has an adequate adhesion to the paper surface [5].

Solvents are used to keep the ink liquid flow from when it is applied to papers. Factors affecting good solvents are the evaporation rate of the solvents [6]. The lower the boiling point of solvent, the faster the drying rate of an ink [7]. Finally, the additives are used to alter the final properties of an ink. The most common types of additives are rheology, wax, driers, chelating agents and surfactants. However, the additives element will not be included yet in this work so as to ensure the effectiveness when using pigment, binder and solvent into formulations.

| Ink Properties | Explanation |
|----------------|-------------|
| Feathering     | Feathering is when the ink spreads out, creating blurry indistinct lines. It can be caused by the paper, nib, and the nature of the ink. |
| Darkness       | Darkness of black inks are not the same depending on the formula created. |
| Drying Time    | An ink that dry fast means high resistance to smearing and smudging. |
| Lifting        | Lifting is when an ink becomes visibly lighter due to erasing. When half of the ink has come off, this shows a bad ink produced. |
| Waterproof     | Able to maintain the permanency of ink when water is test on it. |
| Soft Handling  | The flow of ink when writing on paper. |

2. Experimental procedure and methodology

2.1. Materials

Charcoal was obtained in a bulk of wood approximately about 3 kg and was rich black in colour. First, the material was crushed using a hammer before grinding it by using a dry blender. Then, the course powdered charcoal was further grinded using mortar and pestle. In order to form the smallest particles, the material was sieved using a sieve shaker to obtain 45µm particle size. The fine powdered of charcoal was then stored in plastic bottles for further used. Graphene is obtained in the finest particle size about 0.142 nm and is black in colour. It can be directly used after received.

Lampblack was obtained homemade from the combustion of kerosene oil, burnt with insufficient supply of oxygen in a cracker container. The particle size of lampblack ranging from 9 nm to 25 nm. The fine powdered of lampblack was then kept in glass bottles for further used.

2.2. Preparation of the Inks

The pigment powder; either single pigment or combined pigment, were measured by using a weighing balance. Shellac binder was measured by using a measuring cylinder while acrylic binder used a weighing balance and the solvent were used a measuring cylinder. Firstly, the binder and the pigment were brought into a beaker and stirred with stirring rod until it has fully dispersed. Then the solvent was added and stirred for 2 hours with magnetic stirring bar on a hot plate at 450 rpm. No specified temperature was set because the usage of hot plate was only to keep the sample inks stirred constantly.
for 2 hours. The finished inks were stored into a glass bottle for storage and kept away from direct contact with any form of lights. This is because the exposure to lights will cause the inks to fade and cause damages to physical and chemical structure of an ink [8].

Inks produce will be varied in terms of the formulation and amount of materials used however the procedure to produce one shall remain the same. There were also few inks set to be filtered. This method was hypothesized to improve soft handling and darkness.

2.3. Ink Formulation

Nineteen trials of producing black ink varies in the amount of pigment, solvent and binder. As one of the subjects was manipulated, the remaining two were controlled. The formulation of the 19 inks were tabulated in Table 2.

Table 2. Formulation of Inks Produced.

| Ink Code / Formulation | Shellac-Based Binder | Acrylic-Based Binder |
|------------------------|----------------------|----------------------|
| S1 0.5 g Graphene      | 5 mL Shellac         | A1 0.5 g Graphene    |
| S2 0.8 g Graphene      | 7 mL Shellac         | A2 0.3 g Graphene    |
| S3 0.3 g Graphene      | 1 g Charcoal         | A3 0.5 g Graphene    |
| S4 3 g Charcoal        | 5 mL Shellac         | A4 3 g Charcoal      |
| S5 3 g Charcoal        | 0.5 g Lamplblack     | A5 0.3 g Lamplblack  |
| S6 0.3 g Graphene      | 9 mL Shellac         | A6 0.3 g Graphene    |
| S7 3 g Charcoal        | 12 mL Shellac        | A7 0.3 g Graphene    |
| S8 0.3 g Graphene      | 9 mL Shellac         | A8 0.3 g Lampblack   |
| S9 0.3 g Lampblack     | 13 mL Shellac        | A9 0.3 g Graphene    |
| S10 0.3 g Lampblack    | 2 g Acrylic binder   | A10 0.3 g Lampblack  |
| S11 0.3 g Lampblack    | 9 mL Ethanol         | (Filtered)           |
| S12 0.3 g Lampblack    | 16 mL Ethanol        | (Filtered)           |
| S13 0.3 g Lampblack    | 3 g Charcoal         | (Filtered)           |
| S14 0.3 g Lampblack    | 4 g Charcoal         | (Filtered)           |
| S15 0.3 g Lampblack    | 5 mL Shellac         | (Filtered)           |
| S16 0.3 g Lampblack    | 2 g Acrylic binder   | (Filtered)           |
| S17 0.3 g Lampblack    | 9 mL Ethanol         | (Filtered)           |
| S18 0.3 g Lampblack    | 16 mL Ethanol        | (Filtered)           |
| S19 0.3 g Lampblack    | 3 g Charcoal         | (Filtered)           |
| S20 0.3 g Lampblack    | 4 g Charcoal         | (Filtered)           |

2.4. Guideline for Performance Test

As the inks has been produced, performance test were conducted as based on few characteristics; waterproofness, drying time, feathering, darkness, soft handling, suspended particles. The benchmark and standard had been approved by a calligraphy expert which is explained as in Table 3.

Table 3. Benchmark and standard while conducting performance test.

| Subjects to Measure | Scale | Explanation on Scale |
|--------------------|-------|----------------------|
| Waterprooofness     | Yes   | The sample inks will be tested with water to determine whether the ink will be taken out from the surface of the paper. The sample inks are not preferable if there is any elements taken out from the surface of the paper. |
| Drying Time         | 10 seconds | The sample inks will be written on a paper. At 10 seconds and 1 minute respectively, the written inks on paper will be stroke gently with a ply of tissue. The sample inks are not preferable if the inks do |
not dry within those period of time.

|         | Smudged (Scale 1) | Not smudged (Scale 5) |
|---------|-------------------|-----------------------|
| Darkness| 1 - 5             | 10 SEC                |
| Light (Scale 1) |                     | Dark (Scale 5)         |
| Soft Handling | 1 - 5          | 1 represent least smooth of an ink as it is being written on a paper while 5 shows the smoothest result of an ink on a paper. For scale 1, the pen might get stuck in the middle of writing due to large particle size of pigment or having clumps of the ink on the nib or whether insufficient amount of solvent used. For scale 5, the pen goes smoothly when writing without having any obstacles as stated in scale 1. |
| Feathering | 1 – 5           | 1 represent the most feather of an ink while 5 shows the least feather of an ink. The least feathering of an ink is the most desired. |
| Lifting | 1 - 5             | Lifted (Scale 1)      |
| Not lifted (Scale 5) |                     |

All nineteen produced inks were tested and evaluated by the calligraphy expert as according to the guideline mentioned in Table 3. The method of writing as well as the paper used were as same as usual calligraphy work.

3. Result and discussions
3.1. Performance of Waterproof on Prepared Ink
From the performance test, all ink showed an excellent result on waterproofness from both shellac-based and acrylic emulsion-based binder. Waterproofness of an ink depends largely on solubility of binder used [9]. If the ink is not waterproof, this means that the ink will not be able to bind the pigment on the surface of a paper. An ink is said to be waterproof because it is not soluble in water.

Shellac and acrylic emulsion base binder were not soluble in water. Shellac is soluble in alcohol solvent as well as acetone solution [10] while acrylic emulsion is soluble in ammonia solution, isopropyl alcohol, denatured alcohol, acetone an lacquer thinner [11].

3.2. Comparison on Different Formulated Ink Based on Drying Time
From the performance test for an acrylic-based ink, the solvent used were distilled water (A1), glycerol (A2) and ethanol (A3 until A10). All three solvents showed a discouraging result on drying time; dried in more than 5 minutes, especially glycerol which took more than 1 hour to dry.
Drying time of an ink depends on the boiling point of solvent used whereby a fast drying rate has low boiling point. This proved that solvent with high boiling point takes time to dry. While for a shellac-based ink, there were none of formulations that use element of solvent because the binder itself acts as the binder and solvent at the same time. Shellac binds on the paper easily with pigment and since it already being used in liquid form thus it flowed well on paper. Shellac is approved to have an excellent outcome in quick drying and is reported in many articles [12], [13] and [14].

### 3.3. Comparison of Ink in terms of Darkness Based on Binder Type

Based on Figure 1, charcoal-based and lampblack-based pigment showed a promising result in terms of darkness as compared to graphene. The difference was because of the nature of pigment colour. Charcoal has the colour of black with the shades of dark grey, lampblack is a fine black pigment with a bluish tint and slightly greys while graphene has a plain dark grey solid colour.

Darkness of an ink is contributed by the source of pigment as well as its particle size. The smaller the particle size of a pigment, the blacker it would be. For example, a mars black pigment of 50 μm particle size is blacker than a 100μm.

However, colour black may change when it is blended with different binders; taking the example of S9 and A5. Lampblack and shellac scored 5 scale while lampblack with acrylic scored only 1. During preparation, when lampblack was mixed with shellac, the black did not change its colour. The case was not the same when it mixed with acrylic emulsion binder. As lampblack came into contact with the white emulsion of acrylic, it changed colour from black into slightly grey. This may due to the chromophore that is reactive to a change in energy; either heat or light. The energy causes a physical change in the chromophore, which changes the way it absorbs light. Ink may also change due to pigment that has chromophore groups which sensitive to the polarity of the solvents [15]. Ink code S4, S5 and S9 appeared to have the most promising result scaled of 5 in terms of darkness.

![Figure 1. Comparison on Darkness Based on Ink Formulation Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder.](image-url)

### 3.4. Comparison of Prepared Ink on Soft Handling when Written on Paper

By referring to Figure 2, shellac-based binder showed better result as compared to acrylic-based binder. Ink code S9 scored the highest mark which is 4 while A3, S4, S3, S5 and S6 scored 3 on scale. This shows that binders play an important role in the flow of an ink on paper. The acrylic-based binder inks appeared to have unsatisfactory result because the binder provided a sticky-like texture during preparation thus making the ink to be viscous and thickened that it did not flow well during writing.

According to an expert, inks with acrylic-based binder cannot be stroke more than one letter when written and had a sticky-like texture upon using it which showed a poor ink produced. This refers to the wetting ability of an ink which is the spreading of the liquid ink onto a surface.

Particle size of pigment will affect the flow of an ink on paper. In an article states that flocculation of pigment particles surrounded by the binder can cause the accessibility of ink flow. It is because the attraction between the pigment particles are greater than the adhesive force of the binder [13]. Most...
Inks from both type of binder had a rough texture due to large pigment particles. However, graphene-based pigment had a smooth texture due to small particle size.

![Figure 2](image)

Figure 2. Comparison on Soft Handling Based on Ink Formulation Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder.

3.5. Comparison on Selected Inks Before and After Filtration in terms of Darkness

Filtration was made for ink code S5, S6, A7 and A8 to observe the improvement on darkness after large pigment had been filtrate. By referring to Figure 3, the darkness of all four inks remains the same as before filtration.

![Figure 3](image)

Figure 3. Comparison on Selected Ink (S5, A8, S6 and A7), Before and After Filtration (S7, A10, S8 and A9) by Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder in the Determination on Darkness.

The graph shows that by removing larger particles of pigment will not improve the blackness of an ink. This is because there were no actions of force taken on the ink in order for the pigment to enhance its colour capability. Instead, dispersion of pigment should be done which can be achieved by grinding, whereby it is normally done in a mill; e.g. ball mill or pearl mill [16].

3.6. Comparison on Selected Inks Before and After Filtration in terms of Soft Handling

Filtration was also made for ink code S5, S6, A7 and A8 to observe the improvement on soft handling after large pigment had been filtrate. By referring to Figure 4, the soft handling criteria of all four inks remains the same as before filtration.

It is important that the ink is to be free from large pigment agglomerates in order to provide a smooth and clear surface [16], hence the purpose of filtration. This may due to the undue methods of filtration made. During preparations of filtration, material used was just a cloth of gauze. On the other hand in industry, a multiple stage filtration is typically used for pigmented inks [17]. Therefore, the filtration approach made in this work did not show any improvement because it did not fulfill the specification of filtration criteria for pigmented inks.
3.7. **Comparison on Ink Lifting Based on Different Binder Used**

As based on Figure 5, shellac-based ink showed better performance in ink lifting as compared to acrylic-based binder, whereby scale 5 represent a non-lifting criteria. When half of the ink has come off, this shows a bad ink produced. This was due to the shellac-based binder binds well with pigment but not with acrylic-based binder. The combination of pigment and binder plays an important role in determining ink rheology [18]. Amount of binder must meet the amount of pigment so as to avoid rub-off of pigment substance [19]. Since shellac-based ink showed an excellent performance on ink lifting, thus only ink with shellac-based will be chosen for further selection.

3.8. **Comparison on Feathering from Selected Inks**

From few tests above, ink code S4, S5 and S9 were selected for further selection for it had achieve the highest score for each tests; darkness, soft handling, waterproofness, fast drying time and lifting. Figure 6 shows the performance test on feathering.
Feathering can be caused by the paper, pen nib, and the nature of the ink. For the case of ink nature, the solvent plays an important role. If the amount of solvent is excessive, blurry lines appear and can be seen on the surface of paper. Since all three inks scored 4 scale, it shows that the inks could be considered to have a good response on feathering.

3.9. Selection of Best Ink Prepared
As according to the result of all inks, tested and evaluated by calligraphy expert, the best ink showing a promising result was S9 with formulation of 0.3 g lampblack and 13 mL shellac. The scores of each properties for ink code S9 is tabulated in Table 4.

Table 4. Performance test of S9.

| Waterproof | Drying Time          | Darkness | Soft Handling | Feathering | Lifting |
|------------|----------------------|----------|---------------|------------|---------|
| Yes        | 10 seconds: Yes ; 1 minute: Yes | 5        | 4             | 4          | 5       |

4. Conclusion
In conclusion, ink code S9 are able to fulfill the requirement of non-lifting, rich solid black ink, soft handling when written, non-feathering, fast drying time and waterproof. The formulation of S9 of using lampblack and shellac are considered as natural resources thus can be used to write on Al-Quran purposes.

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