Development of Black Ink for Calligraphy Purpose in the Production of Al-Quran Manuscript

Fatin Fatiha binti Abdul Rahim, Prof. Madya Dr. Junaidah Jai, Dr. Fazlena Hamzah and Dr. Noor Fitrah Abu Bakar

Faculty of Chemical Engineering, Universiti Teknologi MARA

40450 Shah Alam, Selangor Darul Ehsan Malaysia

***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. S9 however still need to have some improvement in terms of soft handling and storage whereby it formed flocculation after few days untouched.**

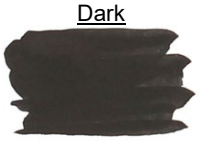
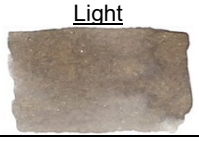
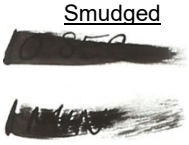
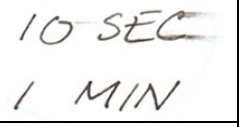
Keywords-component; *black ink, calligraphy, graphene, charcoal, lampblack, shellac, acrylic emulsion, ethanol, ink formulation.*

1.0 INTRODUCTION

The writings of Al-Quran requires 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 1.1 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.

Table 1.1 Ink Properties and Explanation

Ink Properties	Explanation	Example
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.	<u>Feathering</u>  <u>Non-feathering</u> 
Darkness	Darkness of black inks are not the same depending on the formula created.	<u>Dark</u>  <u>Light</u> 
Drying Time	An ink that dry fast means high resistance to smearing and smudging.	<u>Smudged</u>  <u>Not smudged</u> 
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.	<u>Lifted</u>  <u>Not lifted</u> 
Waterproof	Able to maintain the permanency of ink when water is test on it.	-

Soft Handling	The flow of ink when writing on paper.	–

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, screening, packaging, 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 and enzymes that are used to be raw materials as a processing aid or finished goods should originated from halal sources for instance halal plants and animals, non-intoxications and non-hazardous to human health [2].

Inks generally are made up of four basic components and those are pigments, binders, solvents and additives. Pigments are coloured, organic or inorganic solid powder, and usually are insoluble 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 [4].

Solvents on the other hand 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 [5]. The lower the boiling point of solvent, the faster the drying rate of an ink. Inks are typically consists of two or more solvents that can include a percentage of alcohol, acetates and glycols [6]. Finally, the additives are used to alter the final properties of an ink. Each additives represents specific role in order to alter the quality of an ink. The most common types of additives are rheology, wax, driers, chelating agents, surfactants and many more. 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.

The effectiveness of an ink will be determined from few properties; waterproofness, soft handling, drying time, feathering, lifting and darkness. Waterproofness of an ink is a requirement for this study as to produce a black ink. The binder will cause the ink to be waterproof, whereby the application of water onto the surface of paper with written ink shall not be interrupted. The concern for a calligrapher is that the sweat produced from palms while writing the manuscript has direct contact with the paper thus smudging the manuscript. Lifting occurs when there is suspended particles on the surface of paper is due to the particle size of the pigment. The smaller the particle size, the smoother it will be.

Drying time also plays an important role in calligraphy work. This factor is taken into account in order to prevent the ink from smudging off the line when it is accidentally disturbed. The lower the drying time, the preferable it would be. Feathering occur when the inks creating blurry and indistinct lines. This factor can be caused by the paper, nib, and the nature of the ink. For calligrapher, the obstacle when there is a feathering on manuscript is the extensive time taken to edit the faulty which is then to be printed on large scale. The lesser the feathering the preferable it will be. Pigment are the source of colourant of an ink. In this work, a dark and black ink is strongly preferred.

Soft handling refers to the smoothness of an ink when written on a paper and factors that affect the smoothness of an ink is the particle size of pigment. If large particle pigment is used thus the ink flow will not be very satisfying when written for the large pigment causes the nib of a pen having a high friction upon the surface of a paper, showing a bad criteria of ink produced. Smaller size of pigment is preferable usually in nano sized particles. The chosen of paper also affects the performance of an ink. In order to achieve a satisfactory practice, the paper should be smooth enough that the nib of 'batang resam' will not catch or bump along the surface of the paper but not so smooth that it will skid uncontrollably [7].

2.0 METHOD

2.1 Materials

Charcoal was obtained in a bulk of wood approximately about 3 kg and was rich black in colour. First of all, 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 of 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 as in Fig 2.1. The deposited soot (lampblack) on top of cracker container was removed by means of a feather with care to reject all oily particles Fig 2.2. 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 (Fig 2.3).

Fig 2.1: A form of flame carbon prepared by burning kerosene oils.

Fig 2.2: The soot produced in the cracker container gradually became thick.

Fig 2.3: Lampblack soot obtained

2.2 Preparation of the Inks

For shellac base binder, the pigment powder; either single pigment or combined pigment, were measured by using a weighing balance. While shellac binder was measured by using a measuring cylinder. The two elements were then mixed in a beaker and stirred for 2 hours with magnetic stirring bar on a hot plate at 450 rpm. No specified temperature were set because the usage of hot plate were only to keep the sample inks stirred constantly for 2 hours. The finished inks was bring into a glass bottle for storage and is 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].

For acrylic base binder, the procedure were the same as for shellac base binder but with the addition of ethanol and glycerol solvents. The pigment powder; either single pigment or combined pigment, as well as the acrylic binder were measured by using a weighing balance. The two elements were mixed together in a beaker with a stirring rod until the pigment had fully dispersed in the acrylic binder. It became like a sticky emulsion. Then, the glycerol solvent was measured in measuring cylinder and poured into the mixture. The solution were then mixed in a beaker and stirred for 2 hours with magnetic stirring bar on a hot plate at 450 rpm. No specified temperature were set because the usage of hot plate were only to keep the sample inks stirred constantly for 2 hours. All steps were repeated by using ethanol as the solvent. The finished inks was bring into a glass bottle for storage and is kept away from direct contact with any form of lights.

Inks produce will be varies 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 in order to obtain a smooth texture of an ink since larger particles of pigment had been remove. 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 2.1.

Table 2.1: Formulation of Inks Produced

Ink Code / Formulation			
S1	0.5 Graphene 5 mL Shellac	A1	0.5 g Graphene 5 g Acrylic-based binder 7 mL Distilled water
S2	0.8 g Graphene 7 mL Shellac	A2	0.3 g Graphene 3 g Acrylic-based binder 6 mL Glycerol
S3	0.3 g Graphene 1 g Charcoal 7 mL Shellac	A3	0.5 g Graphene 3 g Acrylic-based binder 6 mL Ethanol
S4	3 g Charcoal 5 mL Shellac	A4	3 g Charcoal 3 g Acrylic-based binder 8 mL Ethanol
S5	3 g Charcoal 0.3 g Lampblack 12 mL Shellac	A5	0.3 g Lampblack 2 g Acrylic-based binder 9 mL Ethanol
S6	0.3 g Graphene 0.3 g Lampblack 9 mL Shellac	A6	0.3 g Graphene 2 g Charcoal 2 g Acrylic-based binder 8 mL Ethanol
S7	3 g Charcoal 0.3 g Lampblack 12 mL Shellac (After filtration from S5)	A7	0.3 g Graphene 0.3 g Lampblack 3 Acrylic-based binder 10 mL Ethanol
S8	0.3 g Graphene 0.3 g Lampblack 9 mL Shellac (After filtration from S6)	A8	0.3 g Lampblack 3 g Charcoal 4 g Acrylic-based binder 16 mL Ethanol
S9	0.3 g lampblack 13 mL shellac	A9	0.3 g Graphene 0.3 g Lampblack 3 Acrylic-based binder 10 mL Ethanol (After filtration from A7)
		A10	0.3 g Lampblack 3 g Charcoal 4 g Acrylic-based binder 16 mL Ethanol (After filtration from A8)

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 were explained as in Table 2.2. This guideline had been approved by a calligraphy expert hence to be used as a guideline to evaluate the prepared inks.

Table 2.2: Benchmark and standard while conducting performance test

Subjects to Measure	Scale	Explanation on Scale
Waterproofness	Yes No	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 1 minute	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.
Darkness	1 - 5	1 represent least resulting colour black while 5 shows the best result of black. Least dark (Scale 1)  Most dark (Scale5) 
Soft Handling	1 - 5	1 represent the 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. Feathering (Scale 1)  Non-Feathering (Scale 5) 
Suspended Particles	1 - 5	1 represent the least suspended particles (pigment) on a paper while 5 has the most suspended particles on a paper. 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. Lifted (Scale 1)  Not Lifted (Scale 5) 

3.0 RESULT AND DISCUSSIONS

3.1 Performance of Waterproofness on Prepared Ink

From the performance test, all showed an excellent result on waterproofness because 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].

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.

3.2 Comparison on Different Formulated Ink Based on Drying Time

From the performance test, an acrylic-based ink, the solvent used were distilled water (A1), glycerol (A2) and ethanol (A3 until A10). Distilled water has a boiling point of 100℃, glycerol is 290℃ and ethanol is 78℃. All three solvents showed a discouraging result on drying time; dried in more than 5 minutes, especially glycerol it dried more than 1 hour.

Drying time of an ink will depend on the boiling point of solvent used whereby a fast drying rate will have a solvent of low boiling point. This proved that solvent with high boiling point will 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 Fig 3.1, charcoal and lampblack pigment showed a promising result in terms of darkness as compared to graphene. The difference were because of the nature of pigment colour itself. 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.

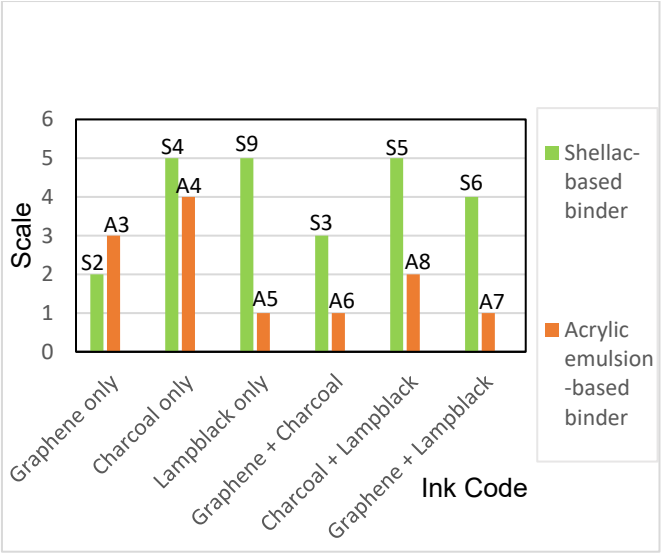


Fig 3.1: Comparison on Darkness Based on Ink Formulation Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder.

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

By referring to Fig 3.2, 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 itself had a sticky-like texture during preparation thus making the ink to be viscous and thickened enough 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.

Also, most inks from both type of binder had a rough texture due to large pigment particles. However graphene-based pigment for it had a smooth texture due to small particle size. 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].

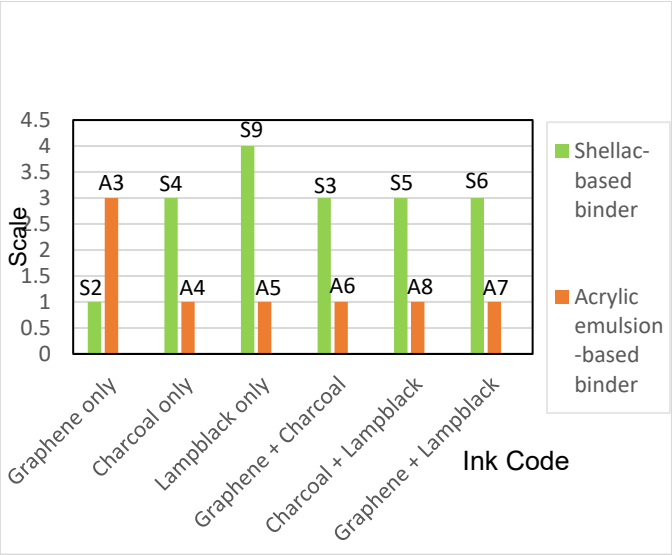


Fig 3.2: Comparison on Soft Handling Based on Ink Formulation Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder

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 Fig 3.3, the darkness of all four inks remains the same as before filtration.

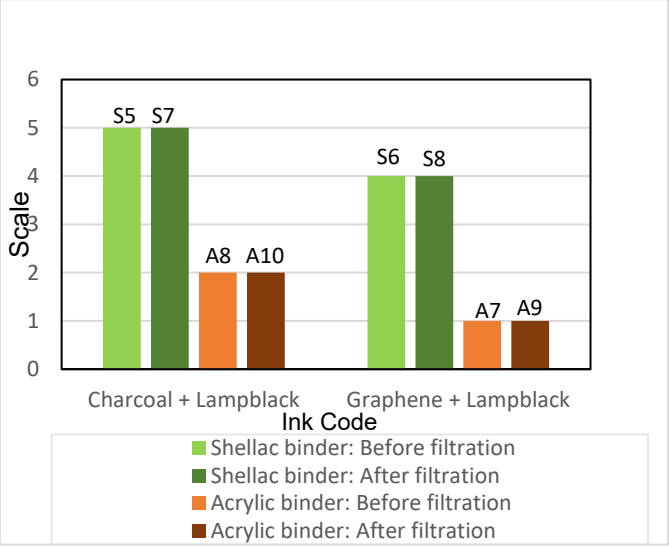


Fig 3.3: Comparison on Selected Ink (S5, A8, S6 and A7), Before and After Filtration (S7, A10, S8 and A9) by Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder in the Determination on Darkness.

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 Fig 3.4, 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.

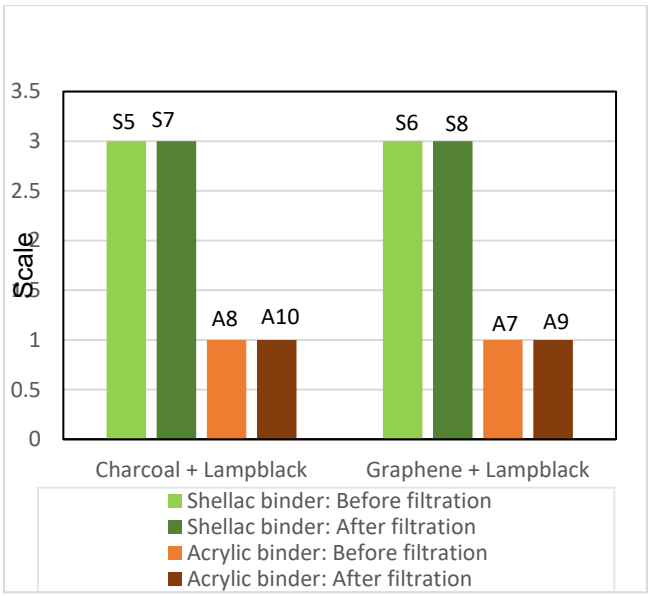


Fig 3.4: Comparison on Selected Ink (S5, A8, S6 and A7), Before and After Filtration (S7, A10, S8 and A9) by Using Graphene, Charcoal and Lampblack as Pigment while Shellac and Acrylic Emulsion as the Binder, in the Determination on Soft handling When Written

3.7 Comparison on Ink Lifting Based on Different Binder Used

As based on Fig 3.5, shellac-based ink showed better performance in ink lifting as compared to acrylic-based binder, whereby scale 5 represent a non-lifting criteria. 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. 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.

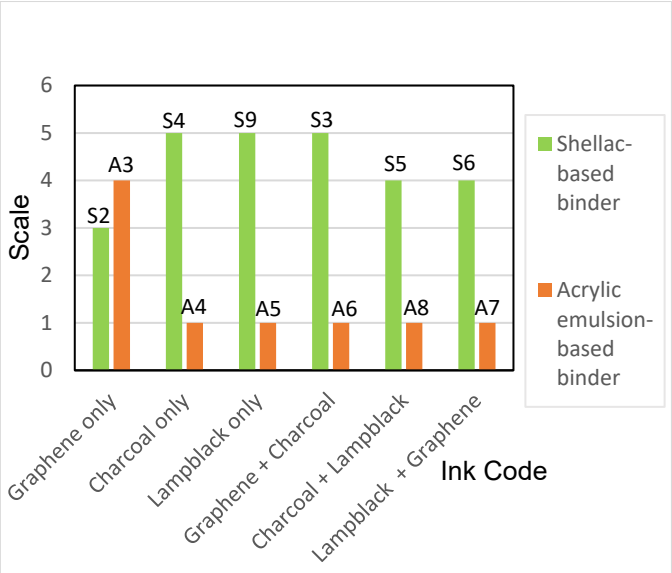


Figure 3.5: Comparison on Ink Lifting when Erased, Using Shellac and Acrylic Emulsion as the Binder.

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. Fig 3.6 shows the performance test on feathering.

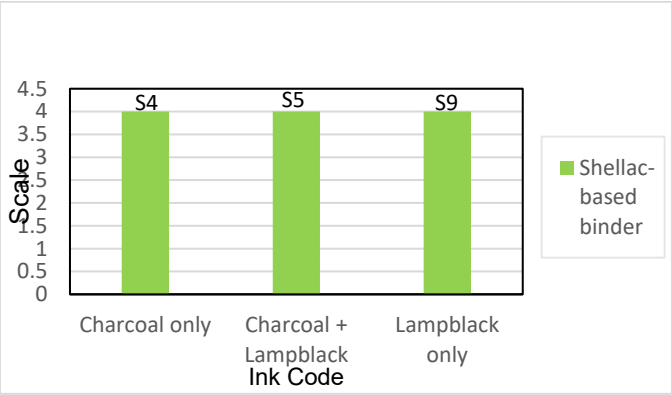


Fig 3.6: Performance on Feathering when Charcoal and Lampblack were Used as the Pigment with the Assess of Binder Shellac (Selected Inks; S4, S5, S9).

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 will spread 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 the 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 and13 mL shellac. The scores of each properties for ink code S9 is tabulated in Table 3.1

Table 3.1 Performance Test of S9

Properties	Scale
Waterproofness	Yes
Drying Time	10 seconds: Yes 1 minute: Yes
Darkness	5
Soft Handling	4
Feathering	4
Lifting	5

4.0 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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