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Chemical Studies on the Composition of Natural Paint Pigment Materials from the Kassena-Nankana District of the Upper East region of Ghana

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Abstract

Three materials used in traditional paint making were analysed for their physical and chemical properties. Equipment employed were pH meter, AAS, Flame Photometer and X-ray diffractometer. The "kugsabla" has a density of 0.5, and is sparingly soluble in water. The "kugpela" has a density of 0.6, and is very sparingly soluble in water. The "zigmolgo" has a density of 0.46, and is sparingly soluble in water. Aqueous solutions of all the three materials were mild basic, having pH values of 7.98, 7.99 and 7.91 respectively. The X-ray diffraction results showed that the black pigment contained quartz, [SiO_2], Muscovite, [$KA_{l2}(Si_3Al)O_{10}(OH)_2$] and graphite, [C]; the white pigment contains Nimite, [$(Ni,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$], a nameless compound [$Ni_3Si_4O_{10}(OH)_2$], and Talc [$Mg_3Si_4O_{10}(OH)_2$], whilst the brown-red pigment contains hematite [Fe_2O_3] with 3 other peaks which could not be assigned – indicating also the presence of other substance(s). The "kugsabla" had an Iron content of 4440.754 mg/Kg. It also contains 211.939 mg/Kg of Lead, 233.214 mg/Kg of Magnesium and 39.428 mg/Kg of arsenic. The "kugpela" had 2802.065 mg/Kg Iron, 205.336 mg/Kg of Lead, 277.539 mg/Kg of Magnesium and the Arsenic content was 34.828 mg/Kg. The "zigmolgo" had 4886.976mg/Kg Iron content, 205.689mg/Kg of Lead, 15.569 mg/Kg of Magnesium and 36.244 mg/Kg Arsenic content. Zinc, Nickel, Calcium, and Potassium were also present in all the three pigments in amounts ranging from 55.988-107.057, 89.895-106.014, 50.150-342.011, and 25.473-871.275 mg/kg respectively.

Keywords: Paint, ochres, rocks, pigments, hematite

1. Introduction

All paints require particular finely ground solid colour called pigments, a solvent or liquid vehicle which keeps the paint in suspension until applied, and a binder or resin that has the ability to dry or otherwise harden and adhere the paint to the surface for an extended period of time (Bently and Turner, 1997).

The properties of paints depend on the relative amounts of the ingredients in the paint. A typical paint consists of 35% pigment and filler and about 21% fil-forming and other ingredients (Trurner, 1998). There are natural, synthetic as well as organic and inorganic pigments. Early pigments were simply ground earth or clay. However, modern pigments are often sophisticated masterpieces of chemical engineering.

Paint for application to brick masonry walls should be durable, easy to apply and have good adhesive characteristics. It should be porous if applied on exterior masonry, thereby permitting the wall to breathe and preventing the trapping of free moisture behind the paint film (Manual on the Selection and Use of Paints, 1950).

Some natural paints are made from rock materials that offer brown, black and white pigments. These materials have also been used as natural paints in the Catholic Minor Basilica in Navrongo (CRATerre-EAG, 1998) and in houses of the local community in Sirigu (Adwoa, 2006) both in the Upper East Region of Ghana. These paintings have lasted for so many years.

The Sirigu Women in Potry and Art (SWOPA) is a community women's group that has been doing traditional mud wall plastering, painting and decoration in their community and other places for several decades. They use materials dug from the ground around the Ghana-Burkina Faso border near Sirigu in the Upper East region of Ghana for their painting works. The colours produced are black, red and white (see appendix) and do not easily fade (Adwoa, 2006; Margaret, 2002). Analyses of the pigment materials used by SWOPA were therefore done to establish the suitability of the materials for paint making, and to check for some potential danger(s) emanating from the formulation or use of that paint which may affect humans and/or the environment.

2. Materials and methods

2.1 Materials

Three paint pigment materials from the Kassena-Nankana district were analysed. All reagents/chemicals used were of analytical reagent grade. Equipment used: Flame Photometer, Atomic Absorption Spectrometer, and X-ray diffractometer.

2.2 Methods

2.2.1 Sample collection and identification

Dry samples of the three materials were purchased in the Yelwongo market near the Ghana-Burkina Faso border. The materials collected were confirmed by Madam Magarette Adongo and Milani Kassise, leaders of the Sirigu Women in Pottery and Art (SWOPA). The pigment materials were identified with local names as "Kugsabla" a dark looking solid material from which comes the black pigment, “Kugpela" a whitish material which is produced the white pigment and "Zigmolgo" which is a reddish rocky material from which the red pigment is formulated.

Further identification of the samples was done by Mr. Emmanuel Arhin, an Earth Scientist and lecturer at the Department of Earth and Environmental Sciences of the University for Development Studies, Ghana. "Kugsabla" was suggested to be made of carbonaceous phyllites; “Kugpela" suggested to be a tuffaceous rock" and Zigmolgo" was suggested to be a tuff hematite rock that has undergone secondary overprint.

The chemicals and reagents were obtained at Asafo market in Kumasi, from Revelation Products Ltd., agents of BDH laboratory supplies Ghana, chemical stores of the Chemistry Departments of both Kwame Nkrumah University of Science and Technology and University for Development Studies. Doubly distilled water was used for the preparation of all solutions.

2.2.2 Sample preparation

The samples were air-dried for three days in the laboratory, crushed using a porcelain mortar and pestle, and sieved using a 76 micron diameter pore-space sieve to remove lumps. The powdered samples were stored in labelled polyethene bags.

2.3 Analytical procedures

Density, solubility, pH, and the mineralogy of the pigments were determined on the stored powdered samples.

1.5g of each sample was weighed separately for determination of density. The measured sample was placed in 40.0ml of distilled water in a graduated cylinder and the new volume was recorded. The volume of the sample was calculated as the difference between the initial volume and the final volume. The density was then calculated using the equation:

$$\text{Density} = \text{Mass}/\text{Volume}$$

To determine the solubility in water, 1.50g portion of each pigment sample was added to 5.0ml water in a test tube and shaken vigorously for 5 minutes. The contents were saved under laboratory conditions for 24 hours and shaken briefly again before making a conclusion/recording of soluble, sparingly soluble or insoluble.

The pH was determined at 29.7 ^{o}C. Aqueous solution of each sample was made in a small beaker enough to submerge the sensitive electrodes of the pH meter. The meter was then calibrated using buffers of pH 4 and pH 7. The electrode was then rinsed with distilled water and placed in a beaker containing a sample. The pH reading was noted and recorded. The electrode was rinsed after each measurement.

The Powder X-ray diffraction technique was also used for characterizing the samples using a model of PANalytical X-ray diffractometer. X-ray analysis was conducted on portions of the sieved, mortar-ground samples. Glancing angles ranging from 0 – 100 degrees were used. The angle of diffraction, theta (θ), the d-spacing, d, and the wavelength, λ were all measured. θ was then used to calculate for 2θ.

A UNICAM model 929 Atomic Absorption Spectrometer (AAS) or the Spectronic 21, Multon Roy model Flame Photometer were further used for AAS and Flame analyses. 1.0g portions each of the dry powdered samples was weighed into a digestion flask and moistened with 1ml of distilled water. 2ml of 1:1 proportions of HNO_3: $HClO_4$ mixture and 5ml of H_2SO_4 were then added and the flask was covered with a watch glass. The mixture was heated for about 30 minutes on a hot plate under the hood to 200 $^oC \pm 5$ ^oC. Heating was continuous until the production of brown fumes had ceased. The hot digested sample was taken from the hot plate and allowed to cool to room temperature. More distilled water was added and the solution filtered through a funnel using a Whatman No. 41 filter paper into a 50ml volumetric flask. More distilled water was added with occasional swirling to make up to the 50ml mark of sample solution. Sample standards of the elements to be analysed were prepared and used to calibrate the AAS. Each sample solution was subsequently analysed in triplicates.

A blank was also analysed. Iron, zinc, lead, nickel and arsenic were analysed using the AAS, whilst calcium, magnesium and potassium were analysed by Flame Photometry.

3.0 Results and Discussion

3.1 Solubility, pH and density

Table 1 Results of solubility, pH and density determinations

Sample	Solubility in water	pH	Density (g/cm^3)
Kugsabla	sparingly soluble	7.98	0.50
Kugpela	insoluble	7.99	0.60
Zigmolgo	sparingly soluble	7.91	0.46

The kugsabla (carbonaceous phyllite) would produce a paint of density of about 0.5 g/cm^3, which would be sparingly soluble in water and basic. The paint would not be corrosive to human skin. With a density of 0.6, the kugpella (white tuffaceous pigment) would produce medium density paint, quite insoluble in water and having a pH value of about 7.99 which makes it mild basic, not be harmful to the skin with respect to acidity. The zigmolgo (red ochre tuffacceous pigment) sample has medium density and is sparingly soluble in water. It would produce medium density paint that would be mild basic and would not corrode the skin of users.

3.2 Mineralogy

3.2.1 X-ray diffraction

Data collected from the diffractions and deductions from the diffraction patterns are presented in **tables 2-5**

Table 2 X-ray diffraction results of analysis of Kugsabla

2 Theta (2θ)	Intensity (I)	Relative intensity (I/I_o)	d-spacing
9.00	12000	17.14	9.8268
17.96	5000	7.143	4.9395
20.99	16000	22.86	4.2328
26.78	70000	100	3.3293
28.05	5000	7.143	3.1814
30.02	2000	2.857	2.977
36.67	6000	8.571	2.4509
42.59	3000	4.286	2.123
45.93	2500	3.571	1.9761
50.24	6000	8.571	1.8162
55.46	1500	2.143	1.657
60.10	3500	5.0	1.5397
68.66	2500	3.571	1.3671

The X-ray diffraction results showed the presence of Quartz [SiO_2], Muscovit [$KA_{l2}(Si_3Al)O_{10}(OH)_2$] and Graphite [C] in the black pigment.

Table 3 X-ray diffraction results of analysis of Kugpela

2 Theta (2θ)	Intensity (I)	Relative intensity (I/I_o)	d-spacing
6.43	20000	10.87	13.7475
9.67	184000	100	9.14737
12.68	38000	20.652	6.98191
19.16	35000	19.022	4.63273
25.75	31000	16.848	3.46012
28.82	118000	64.13	3.09814
32.09	6000	3.2609	2.78951
49.01	4500	2.4457	1.85885
59.87	1000	0.5435	1.54504

The X-ray diffraction results showed the presence of Nimite [$(Ni,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$], a nameless compound [$Ni_3Si_4O_{10}(OH)_2$] and Talc $Mg_3Si_4O_{10}(OH)_2$ in the white pigment.

Table 4 X-ray diffraction results of analysis of Zigmolgo

2 Theta (2θ)	Intensity (I)	Relative intensity (I/I_o)	d-spacing
12.58	1400	60.87	7.0372
24.54	750	32.609	3.6279
25.58	1000	43.478	3.4827
27.32	600	26.087	3.2647
33.90	2300	100	2.6446
36.37	1700	73.913	2.4705
39.11	200	8.6957	2.3035
41.55	500	21.739	2.1737
50.11	650	28.261	1.8206
54.82	900	39.13	1.6748
58.23	200	8.6957	1.5846
63.14	500	21.739	1.4727
64.72	450	19.5654	1.4405
72.70	250	10.87	1.3008

The X-ray diffraction results of the zigmolgo showed the presence of hematite [Fe_2O_3] with 3 other peaks which could not be assigned – indicating also the presence of other substance in the red pigment.

3.2.2 AAS and Flame photometry

Table 6 Average levels of metals in the powdered samples

Metal	Average Amount (mg/Kg)		
	Kugsabla	**Kugpela**	**Zigmolgo**
K	871.275	25.473	84.805
Ca	342.011	110.155	50.150
Mg	233.214	277.539	15.569
Fe	4440.754	2802.065	4886.976
Ni	106.014	90.103	89.895
Pb	211.939	205.336	205.689
Zn	79.713	107.057	55.988
As	39.428	34.828	36.244

The red ochre tuffacceous pigment (zigmolgo) sample has a high concentration of Iron which could be dangerous to its users overtime. It could also be dangerous due to high levels of Lead which becomes legally hazardous to humans when at levels above 1000mg/Kg. The Arsenic content was high and could also contribute to increasing levels in humans beyond the provisional guideline value of 0.010mg/Kg accepted by WHO in humans. Hence the red pigment material may be dangerous to living tissue when ingested due to the high level of Iron, Lead and Arsenic (Green Facts Scientific Board, 2003). Apart from the potential dangers, zigmolgo paint may not effectively prevent corrosion and provide good tensile properties to a painted surface due to the small amount of magnesium present. But since the iron content is very high, paint made from this pigment would be extremely strong and long lasting, and would not easily fade (Paint Chemistry and Principles of Paint Technology, 1998).

The carbonaceous phyllite (kugsabla) would also produce paint that would be strong and long lasting due to the good Iron content. Also the high Lead content will contribute well to stabilization of the formulation, reduced drying time, and anti-mould properties. This pigment also contains a good amount of magnesium and can contribute largely to prevent corrosion to a surface. However, the high Arsenic content could make the paint potentially dangerous to living tissue when ingested.

The white tuffaceous pigment (kugpella) has a reduced Fe content and could make long lasting paints, having relatively less potential danger compared to paints made from the red ochre pigment. The level of lead and Mg also offer advantages of anti-corrosiveness. However, the Arsenic content is high such that the paint could be dangerous to living tissue when ingested.

Generally, the Lead content which is in large amounts, and Zinc could contribute to excellent anti corrosiveness of the paints if they exist in the form of their chromates. This is also provided for by the moderate levels of Magnesium. It could further increase the service lifespan of the paints against peeling, chalking, fading and fungus attack (Houwink and Salomon, 1965).

The contribution of Arsenic by these pigments to the environment could be phenomenal as the metal can be picked up and moved by the wind and water. This could be dangerous to underground drinking water sources near places where the paints have been applied. Also some food crops grown in such areas may accumulate excessive Arsenic from the paint waste. Also, dust produced during milling of the raw material may contain Arsenic and Arsenic compounds thus may cause cancer in humans when it is inhaled (Green Facts Scientific Board, 2003).

Zinc, Nickel, Calcium, and potassium were present in all the three samples in amounts ranging from 55.988 - 107.057 mg/kg, 89.895 - 106.014 mg/kg, 50.150 - 342.011 mg/kg, and 25.473 - 871.275 mg/kg respectively. In the red pigment the relative amount of these metals was Ni>K>Zn>Ca; in the black pigment the relative amounts was K>Ca>Ni>Zn; and in the white pigment it was Ca>Zn>Ni>K.

4. Conclusion

The level of Iron was highest in relation to any of the other elements that were probed. Iron ranged from 4886.976 to 2802.065 mg/kg sample. Generally, paints from these materials may not easily fade due to the presence of Iron oxides. These natural paints would also have a high covering power and short drying time, and would be long lasting on painted surfaces due to the iron present.

The paints would have excellent anti corrosiveness due to presence of Zinc and Magnesium. The paints would not easily be eroded by rain, thus would have a longer service lifespan against peeling, chalking, fading and fungus attack.

However, the large amounts of Iron may contribute to cause eye defects when the pigments contact and remain in tissues of the eye. Also, chronic inhalation of Iron oxide fumes or dust from the materials, especially during the powdering of the materials, may also pose health dangers.

In addition, the disposal of waste from paints of these pigments would also have some environmental concerns due to Lead and Arsenic.

Recommendations

Further research should be carried out to investigate the presence of chromium and other relevant metals.

The area around the Ghana-Burkina Fasso border near Sirigu should be prospected to know if quantities of the various pigment samples in the area have potential for commercialization.

SWOPA should be supported to procure a suitable mill for crushing/powdering the materials. This would be a big support of livelihood empowerment to women in this impoverished community. They should also be educated on the dangers of the art especially due to dust, lead and arsenic.

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Appendix

Fig. 1 The wall of a house in Kandiga (near Sirigu) decorated with the red, black and white natural paints (source: Margaret, 2002)