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Full Length Research Paper

Physico-chemical properties of clayey soils used traditionally for cosmetics in Eastern Cape, South Africa

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Clayey soils used traditionally for cosmetic purposes in Oliver Reginald Tambo (OR) District in Eastern Cape Province, South Africa were studied and analysed for their physico-chemical properties. Forty clayey soil samples were collected from selected communities within the District and standard laboratory methods were used to determine their colour, particle size distribution, texture, pH, specific surface area (SSA) and cation exchange capacity (CEC). The study found that the colours of the samples varied from white to gray; and pH values ranged between 4.53 and 9.57. Majority of the samples were silt loam in texture. The SSA values were between 0.5 and 2.4 m^2/g and CEC values ranged from 0.5 to 54.5 meq/100 g. From the colours of the samples, they are inferred to contain hematite and goethite which are present in many skin sunscreen and beauty products. The percentage of clay size particles in the samples were similar to those generally used in Thermal Centres. Their high CEC values may ensure skin cleansing through ion exchange between the clay mixtures and the skin. The physico-chemical properties can thus influence cleansing, sunscreen and body beautification roles for which the clayey soils are used.

Key words: Colour, particle size, pH, cation exchange capacity, cleansing, sunscreen, beauty.

INTRODUCTION

The use of clays in cosmetic applications has been widely studied (Juch et al., 1994; Summa and Tateo, 1998; Viseras and Lopez-Galindo, 1999; Cara et al., 2000; Lopez-Galindo and Viseras, 2000; Allen, 2001; Carretero, 2002; Diffey, 2002; Lim et al., 2005; Carretero et al., 2006, 2010; Pelotherapy, 2006; Choy et al., 2007; Lopez-Galindo et al., 2007; Tateo and Summa, 2007; Veniale et al., 2007; Mpuchane et al., 2008, 2010; Carretero and Pozo, 2009; 2010; Hoang-Minh et al., 2010; Karakaya et al., 2010; Matike et al., 2010). According to these authors, such clays are widely used for cleansing the skin, emulsification, detoxification, adsorption, UV radiation protection, ion exchange with the skin, and trans-dermal nutrient supplementation of elements such as calcium, iron, magnesium and potassium. The ability of clays to perform these various functions is influenced by among others, their colour, particle size, specific surface area and cation exchange capacity (CEC) (Carretero et al., 2006; Lopez-Galindo et al., 2007; Veniale et al., 2007). The SSA of clay refers to the surface area per unit volume or unit mass of the particles; and the ability of clay colloids to attract and hold positively charged ions, is referred to as the CEC (Tan, 2011).

Many cosmetic clay products are in the form of ointments, pastes, creams and gels (Juch et al., 1994; Carretero, 2002; Lopez-Galindo et al., 2007), and are applied topically (Viseras et al., 2007). Suitable consistency and appropriate viscosity are required for products to remain in contact with the application area until the objective is achieved. Cosmetic products must therefore be smooth, adhesive and without grittiness (Viseras et al., 2007). In addition, they must be easy to

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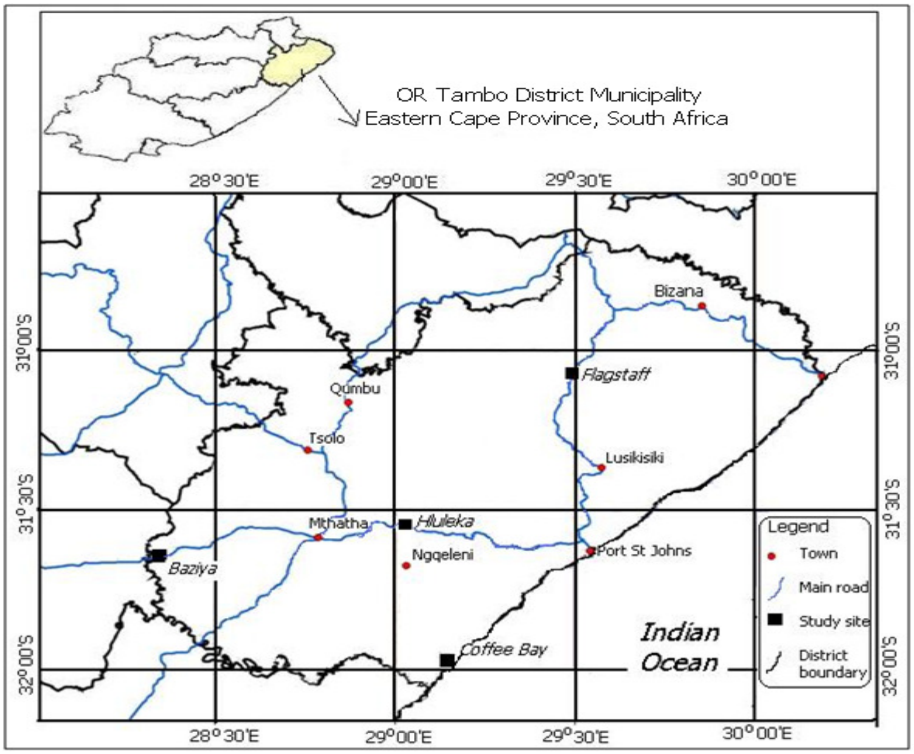

Figure 1. Map of OR Tambo District Eastern Cape, showing study areas.

handle and should have a pleasant sensation when applied to the skin (Veniale et al., 2007). These requirements are greatly influenced by particle size of the clays. According to Carretero (2002) Carretero et al. (2006) and Lopez-Galindo et al. (2007), the physico-chemistry of raw clays therefore plays a significant role in their cosmetic suitability.

The cosmetic capabilities of clays are being exploited by many beauty spas around the world. In these spas, the colour of the clays greatly determines their use. Yellowish clay is used in some spas to prevent bacterial infection on the skin; reddish clays are used for cleansing the skin, and bluish clays against the development of acnes (Ma'or et al., 2006). Similarly, greenish coloured clays are applied to reduce the amount of oil on the skin; and black clays for general body nourishment (Ma'or et al., 2006). In many African communities, the traditional usage of clays for cosmetic purposes is a common practice (Ettagale, 1999; Mpuchane et al., 2008). The Wodaabe men of Niger use different clays to beautify their faces during their annual Gerewol festival (Wood, 2000; Jefkins-Elnekave, 2006). The Himba of Namibia smear clays from head to toe to protect their skin from ultraviolet radiation (Nelda, 2004; Baeke, 2009), and the Maasai of Kenya as well as the Xhosas of South Africa smear clays on their bodies for skin cleansing purposes (Ettagale, 1999). This practice, which is based on indigenous knowledge has been going on for several years, and has been handed from one generation to another (Ettagale, 1999).

In the Eastern Cape Province of South Africa, clayey soils are still widely used traditionally for cosmetic applications, specifically for cleansing, sunscreen and body beautification in many communities. Studies have been conducted on cosmetic clays in Southern Africa (Mpuchane et al., 2008, 2010) but cosmetic clayey soils used traditionally in the Eastern Cape Province have not been investigated and their physico-chemical properties are not known. This paper thus reports on the physico-chemical properties of clayey soils used traditionally for cosmetic purposes in the OR Tambo District of Eastern Cape Province, South Africa and their influences on cleansing, sunscreen and body beautification.

MATERIALS AND METHODS

Collection of clayey soil samples

A survey was conducted in OR Tambo District (28°20'E, 30°13'E; 30°40'S, 32°5'S) (Figure 1). Individuals who used clays for cosmetic applications in Baziya (30°36' S and 28°21' E), Coffee Bay (31°58'S and 29°90'E), Flagstaff (31°5'S and 29°29'E) and Hluleka (31°32'S and 29°1'E) (Figure 1), which are rural communities within the OR Tambo District, were contacted to identify clayey soils used for cosmetic purposes. Sixteen different clayey soils used either for cleansing, sunscreen or body beautification, were identified; and with the use of a shovel, forty samples were collected for physico-chemical characterisation. Nine of the samples were used for cleansing, nine for sunscreen and 22 for body beautification (Table 1). The samples were collected from hillsides, riverbeds, caves, ponds, roadsides and in the courtyard. All samples were packaged

Table 1. Sources of clayey soil samples used for cleansing, sunscreen and body beautification in study sites.

Reason for application	Sample no.	Source of clayey sample	Study site where used
Cleansing	B 1	Mountain	Baziya
	CB 1	Riverbed	Coffee Bay
	CB 2	Riverbed	Coffee Bay
	H 1	Cave	Hluleka
	H 2	Courtyard	Hluleka
	H 5	Courtyard	Hluleka
	H 8	Riverbed	Hluleka
	H 13	Cave	Hluleka
	H 14	Cave	Hluleka
Sunscreen	B 3	Mountain	Baziya
	CB 3	Riverbed	Coffee Bay
	CB 4	Mountain	Coffee Bay
	F 1	Courtyard	Flagstaff
	F 6	Courtyard	Flagstaff
	F 7	Courtyard	Flagstaff
	F 12	Courtyard	Flagstaff
	H 10	Pond	Hluleka
	H 11	Riverbed	Hluleka
Body beautification	B 2	Mountain	Baziya
	B 4	Mountain	Baziya
	CB 5	Roadside	Coffee Bay
	CB 6	Roadside	Coffee Bay
	CB 7	Roadside	Coffee Bay
	CB 8	Roadside	Coffee Bay
	CB 9	Roadside	Coffee Bay
	CB 10	Roadside	Coffee Bay
	F 2	Roadside	Flagstaff
	F 3	Roadside	Flagstaff
	F 4	Roadside	Flagstaff
	F 5	Roadside	Flagstaff
	F 8	Roadside	Flagstaff
	F 9	Roadside	Flagstaff
	F 10	Roadside	Flagstaff
	F 11	Roadside	Flagstaff
	H 3	Courtyard	Hluleka
	H 4	Courtyard	Hluleka
	H 6	Courtyard	Hluleka
	H 7	Courtyard	Hluleka
	H 9	Cave	Hluleka
	H 12	Cave	Hluleka

in airtight plastic bags, labelled and transported to the laboratory for physico-chemical analyses.

Physico-chemical analyses

The samples were air-dried after collection to reduce the rate of possible reactions in them (Tan, 1996; van Reeuwijk, 2002) and gently disaggregated using an agate mortar and pestle. Analyses for colour, particle size distribution, specific surface area, pH and CEC were carried out on all the samples. Colour determination was done by visually comparing the samples with soil colours in the Munsell Soil Colour Charts to obtain the hue, value, chroma and colour of the samples (Munsell Soil Colour Charts, 1992; Ekosse et al., 2007; Young et al., 2008). Particle size distribution and specific surface area of the samples were determined using a Malvern

Table 2. Colour of cosmetic clayey samples used for cleansing, sunscreen and body beautification in study sites.

Application	Sample no.	Hue/value/chroma	Colour
Cleansing	B 1	5Y / 8 / 1	White
	CB 1	5Y / 5 / 4	Olive
	CB 2	5Y / 5 / 4	Olive
	H 1	5Y / 8 / 3	Pale yellow
	H 2	5Y / 6 / 2	Light olive gray
	H 5	5Y / 6 / 4	Pale olive
	H 8	5Y / 6 / 4	Pale olive
	H 13	2.5Y / 7 / 4	Pale yellow
	H 14	2.5Y / 8 / 2	White
Sunscreen	B 3	2.5YR /4 / 8	Red
	CB 3	2.5Y / N6 / 0	Gray
	CB 4	2.5YR / 5 / 8	Red
	F 1	5YR / 5 / 8	Yellowish red
	F 6	2.5YR / 5 / 8	Red
	F 7	5YR / 5 / 4	Reddish brown
	F 12	2.5YR / 5 / 8	Red
	H 10	2.5Y / 8 / 4	Pale yellow
	H 11	2.5Y / 8 / 2	White
Body beautification	B 2	10YR / 7 / 8	Yellow
	B 4	5Y / 8 / 1	White
	CB 5	2.5Y / 6 / 4	Light yellowish brown
	CB 6	5Y / 7 / 2	Light gray
	CB 7	7.5YR / N6 /	Gray
	CB 8	5Y / 6 / 3	Pale olive
	CB 9	2.5 Y / 6 / 2	Light brownish gray
	CB 10	10YR / 5 / 6	Yellowish brown
	F 2	10YR / 6 / 8	Brownish yellow
	F 3	10YR / 6 / 8	Brownish yellow
	F 4	7.5YR / 6 / 4	Light brown
	F 5	5YR / 6 / 8	Reddish yellow
	F 8	2.5Y / 7 / 4	Pale yellow
	F 9	7.5YR / 5 / 8	Strong brown
	F 10	7.5YR / 6 / 4	Light brown
	F 11	2.5Y / 7 / 4	Pale yellow
	H 3	2.5Y / 8 / 4	Pale yellow
	H 4	2.5Y / 8 / 4	Pale yellow
	H 6	5Y / 6 / 4	Pale olive
	H 7	5Y / 6 / 4	Pale olive
	H 9	5Y / 7 / 1	Gray
	H 12	10YR /7 / 4	Very pale brown

YR, Yellow-red; Y, yellow.

Mastersizer 2000 Particle Size Analyzer (Xu, 2000). With the aid of a Texture Auto Lookup Software Package (TAL Version 4.2), the results obtained from particle size analysis were used to determine the texture of each sample. The pH of each samples was determined in a 1:2.5 clayey soil:water suspension according to the procedure advanced by van Reeuwijk (2002). The ammonium acetate method advanced by Tan (1996) was used to identify exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and H^{+}) in each sample; and their concentrations were obtained by use of a 5300 DV PerkinElmer Inductively Coupled Plasma Optical Emission Spectroscope (ICPOES). The concentration of each cation in meq/100 g was calculated from the formula:

$$Y = \left(\frac{20 \times a \times b}{1000 \times \frac{c}{d}}\right) \text{ meq/100g} \quad (1)$$

where Y = exchangeable cation; a = mass of analysed sample; b = reported concentration of cation obtained from ICPOES; c = atomic mass of element, and d = valence of cation.

The CEC of each sample was obtained from the summation of the concentration of exchangeable cations identified using the formula:

$$\text{CEC (meq/100 g)} = \sum \text{exchangeable } Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} \text{ and } H^{+}. \quad (2)$$

RESULTS

Colour of analysed cosmetic clayey soils

Colour of the analysed samples ranged from white to yellow, red and gray (Table 2). Whereas majority of the

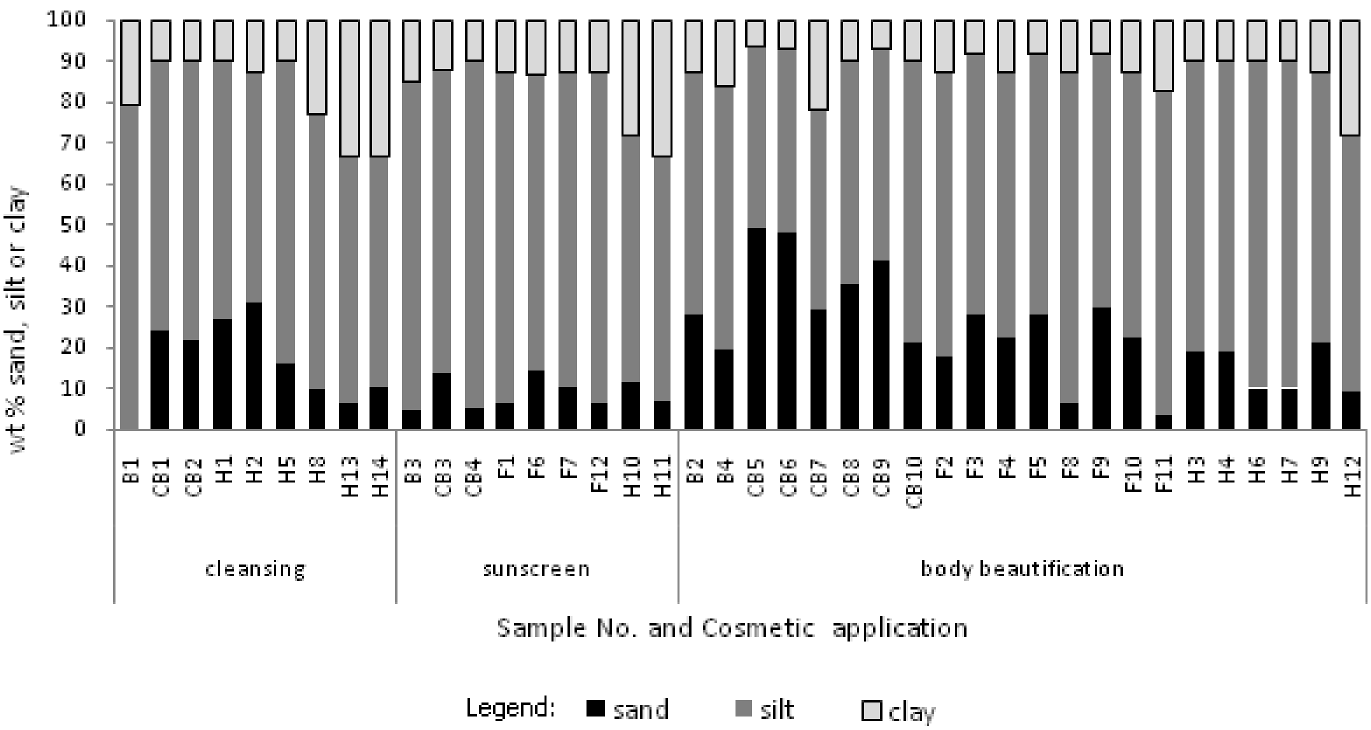

Figure 2. Particle size distribution of clayey soil samples used for cleansing, sunscreen and body beautification in study sites.

samples used for cleansing recorded hue of 5Y, those used for sunscreen had hue of 2.5YR and 2.5Y; and the samples used for body beautification showed variety of hue values (Table 2). The values observed were from five (5) to eight (8), and the chroma ranged from zero (0) to eight (8). The colours varied from whitish to greyish. The most frequently occurring colours were the yellowish and brownish colours; followed by the greyish, reddish and whitish colours as indicated on Table 2.

Particle size distribution and texture of analysed cosmetic clayey soils

The particles ranged in sizes from 0.3 – 2000 µm in diameter, and was indication that the samples contained fractions of sand (> 50 µm), silt (> 2 < 50 µm) and clay (< 2 µm) as specified by the United States Department of Agriculture (USDA) Soil Taxonomy System. The samples used for body beautification contained considerably higher vol % sand size particles (mean sand = 23.25 vol %) than those used for cleansing and sunscreen (Figure 2). Silt size particles were higher in samples used for sunscreen (mean silt = 74.54 vol %) than cleansing and body beautification; and clay was highest in samples used for cleansing (Figure 2), with mean vol% clay of 17.9 than those used for sunscreen and body beautification which recorded mean clay of 16.64 vol% and 11.89 vol% respectively. The samples were classified into five textural classes namely: silt loam, silty clay loam, silt, loam and sandy loam; with the majority of the samples identified as silt loam in texture (Figure 3).

Specific surface area of analysed cosmetic clayey soils

Specific surface area of the samples ranged from 0.55 m^2/g for sample CB5 to 2.4 m^2/g for sample H12 (Figure 4). The samples used for sunscreen recorded the highest mean SSA of 1.42 m^2/g, than those used for cleansing and body beautification which recorded mean SSA of 1.31 m^2/g and 0.96 m^2/g respectively.

pH of analysed cosmetic clayey soils

The pH of the analysed samples ranged from 4.53 (sample B2) to 9.57 (sample H8). Majority of the samples were acidic (Figure 5). Whereas samples used for cleansing had mean pH values of 7.45, those used for sunscreen had mean pH of 6.31. The samples used for body beautification had mean pH values of 6.43.

Cation exchange capacity (CEC) of analysed cosmetic clayey soils

The CEC values of the samples were between 0.5

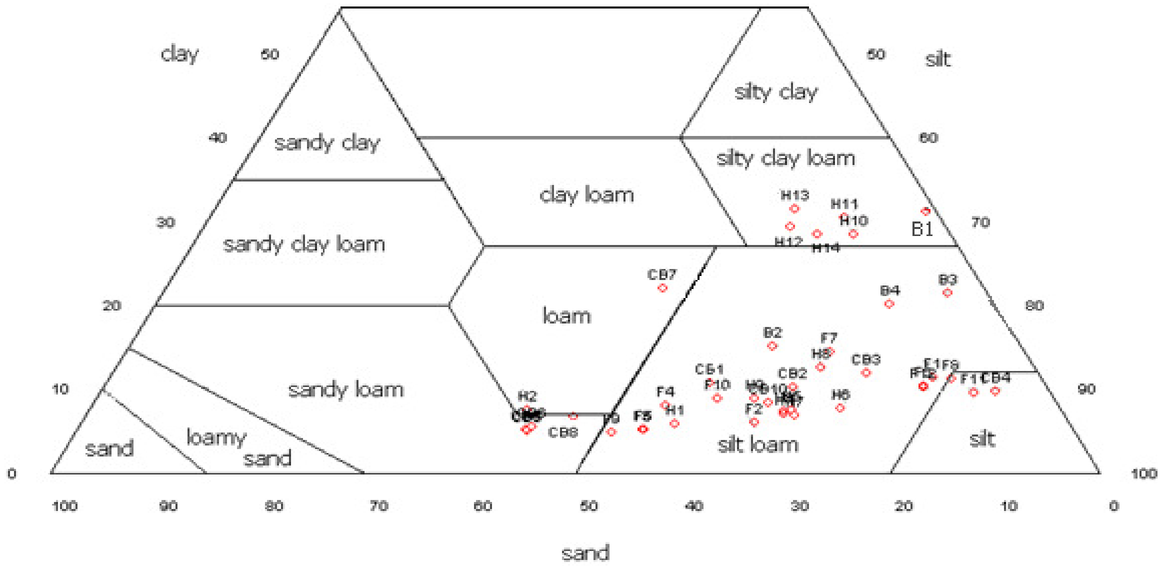

Figure 3. Textural triangle showing texture of cosmetic clayey soil samples from study sites.

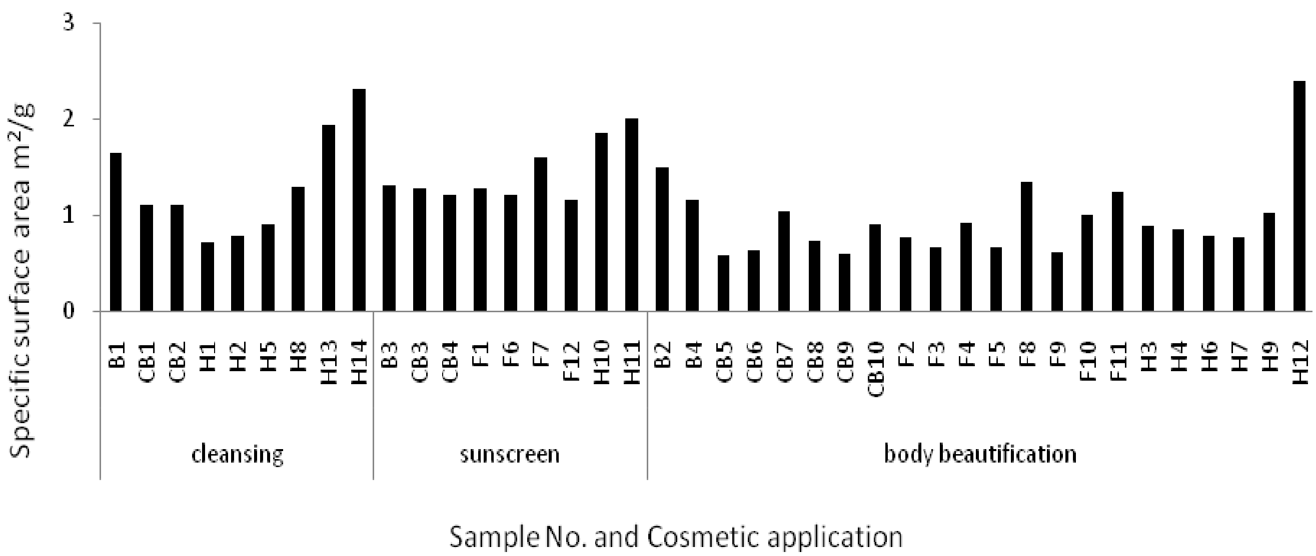

Figure 4. Specific surface area of clayey soil samples used for cleansing, sunscreen and body beautification in study sites.

meq/100 g in sample B1 and 54.5 meq/100 g in sample F5 (Figure 6). Samples used for cleansing recorded the highest mean CEC (22.9 meq/100 g), than those used for body beautification and sunscreen which recorded mean CEC of 19.2 and 14.9 meq/100 g, respectively.

DISCUSSION

Influence of physico-chemical properties of the analysed clayey soils on cleansing

Particle size distribution and texture of the clayey soils may influence their cleansing ability. More than 20 % of clay size particles were identified in B1, H8, H13 and H14; and majority (that is, 95% of B1, 66.5% of H13 and 78.4% of H14) of their particle sizes were < 20 *µm* in diameter. Their particle sizes were similar to those of clay mixtures used for cleansing in Thermal Centres, where 57 to 70% of the clay mixtures have particle sizes within the 2 to 20 *µm* diameter size range (Viseras and Lopez-Galindo, 1999).

Clays with high CEC have been reported to ensure cleansing through absorption of toxins, bacteria and unwanted substances from the skin during topical application (Szántó and Papp, 1998; Lopez-Galindo et

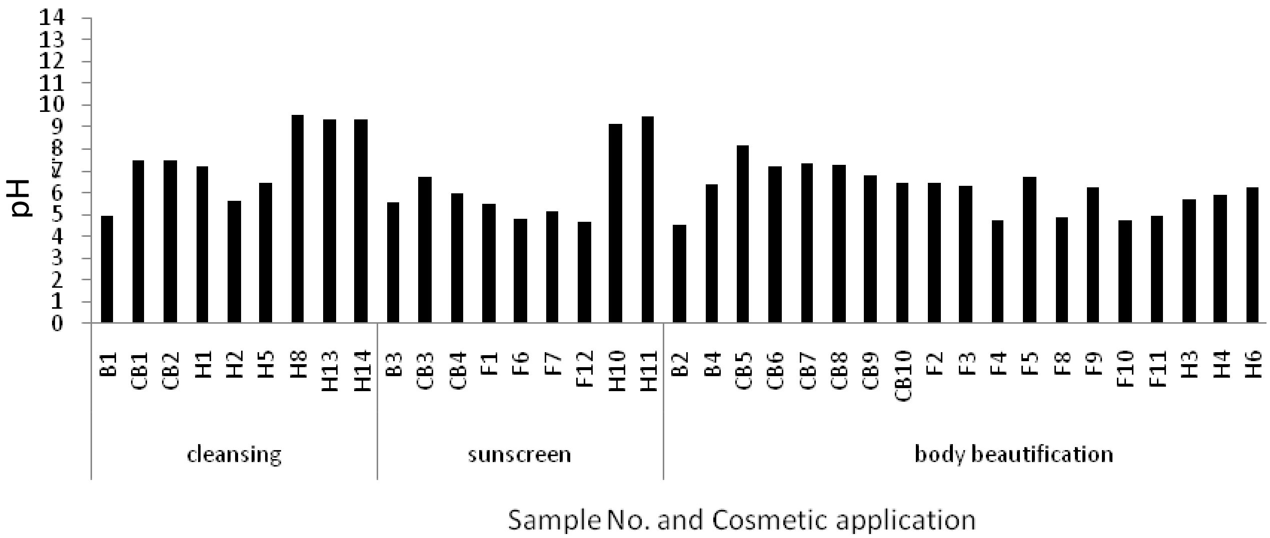

Figure 5. The pH of clayey soils samples used for cleansing, sunscreen and body beautification in study sites.

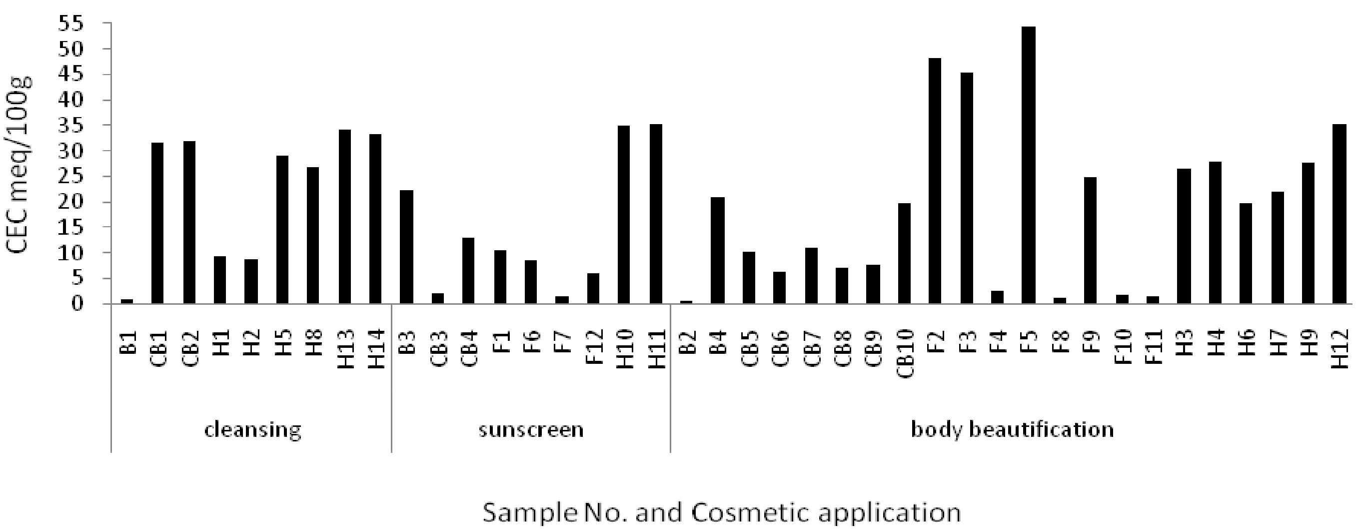

Figure 6. Cation exchange capacity of cosmetic clayey samples used for cleansing, sunscreen and body beautification in the study sites.

al., 2007; Tateo and Summa, 2007; Tateo et al., 2009; Carretero et al., 2010). The high vol % of clay size particles in the analysed clayey soils can justify the high CEC of H8, H13 and H14, whose absorption capacity could be high. High CEC of the clayey soils can influence exchange of ions from the clayey mixture to the skin and vice versa (Tateo and Summa, 2007; Tateo et al., 2009; Sparks, 1995). The exchange of ions between the clay mixture and the skin can enable absorption of unwanted substances from the skin by the clay; hence ensuring skin cleansing action. In addition, the smearing of clay on the skin can influence perspiration, which forms a medium through which ions are exchanged from the skin (Carretero et al., 2010), and the result is a refreshing effect on the skin. Samples B1, H1 and H2 which had CEC values < 15 meq/100 g, could have low absorption capacity and may not absorb ions from the skin, but may be able to supply ions to the skin depending on the concentration of the ions in the clayey soils.

The pH of the clayey soils used for cleansing can also influence their cleansing activity. According to Baranda et al. (2002), Korting et al. (1991, 1992), Schmid and Korting (1995), Gfatter et al. (1997), Ananthapadmanabhan et al. (2004) and Nash et al. (2007), suitable skin cleansers must have pH similar to that of the skin or near neutral. Considering that the pH of healthy skin ranges between 4.5 to 5.5 (Korting et al., 1992; Gfatter et al., 1997) samples B1, H2 and H5 which recorded acidic and near neutral pH can be considered suitable for cleansing application as little chemical reaction is expected to occur when they are applied on the skin. However, H8, H13 and H14 which recorded pH values > 9 can pose problems to the skin when used as cleansers. This is because highly alkaline cosmetic cleansers have high skin irritation potential (Nash et al., 2007) and can cause damage to the lipid bilayer of the skin's stratum corneum, leading to dryness of the skin, itching and after wash tightness (Ananthapadmanabhan et al., 2003). Frequent application of alkaline clayey soils for cleansing purposes is thus discouraged and moisturisation of the skin after the cleanser is washed off is advised.

Influence of physico-chemical properties of the analysed clayey soils on sun screening

The colour of the clayey soils may play a role in their sun screening abilities. Most of the clayey soils used for sunscreen had a hue of 2.5 YR corresponding to the colour of hematite (Fe_2O_3). This hue value may infer to the occurrence of hematite and goethite in the clayey soils. Both hematite and goethite are oxides of Fe, which are colour causing minerals in soils and are responsible for the reddish and yellowish colour (Carretero and Pozo, 2010) reflected in the analysed soils used for sunscreen. According to Ngole et al. (2010), the presence of one of the minerals could depend on the reduction or oxidation of the other (Equations 3 and 4).

$$Fe^{2+} + O_2 + 4H^{3+} \rightleftharpoons 4Fe^{3+} + 2H_2O \quad (3)$$

$$4Fe^{3+} + O_2 + 6H_2O \rightleftharpoons 4FeOOH + 8H^{+} \quad (4)$$

The ability of yellowish and reddish coloured clays to perform sun screening activity has been reported by Hoang-Minh et al. (2010) to be influenced by hematite and goethite which have low UV radiation transmission values due to their high refractive indices (n_w=3.15 and n_α=2.39, respectively) (mindat.org/min-1719.html). Knowledge of the sun screening ability of the use of reddish and yellowish clayey soils is not only known to people of OR Tambo District of Eastern Cape Province, but is also common knowledge to other African tribes such as the Himba of Namibia (Namibia Direct, 2006).

Sun screening by clays is also influenced by their small particle sizes (Juch et al., 1994). Most of the clayey soils used for sunscreen had majority of their particle sizes in the 2 to 50 *µm* range. Given their small particle sizes, their specific surface area may provide a platform for the absorption or scattering of radiant energy (Juch et al., 1994) and thereby reduce the intensity of UV radiation that reaches the skin. The clay size contents of H10 and H11 used for sunscreen also compare well with the clay content of sunscreen products studied by Hoang-Minh et al. (2010), which recorded low UV transmission values.

Influence of physico-chemical properties of the analysed clayey soils on body beautification

The beautifying effect of the clayey soils could be influenced by their colour. White, red, yellow, gray and brown are common colours of several modern body beautifying cosmetic products such as face powders, lip glosses, nail polishes, blushers and eye shadows (Mpuchane et al., 2008). These colours, which occur as a result of the presence of colour causing clay and non clay minerals in soils, can cause radiance during application of the derived cosmetic mixture. The clayey soils had values ranging from 5 to 8, which are light shades that facilitate the painting of bright and colourful decorative patterns on the body.

The pH of the clayey soils could also influence their abilities to beautify the skin. Majority of the clayey soils used for body beautification were acidic and within the pH range of the skin, as well as near neutral. The acidic nature of the skin enables it to act as the body's first defence mechanism against bacteria by creating an unfavourable environment for bacterial growth (Gfatter et al., 1997). However samples H9 and H12 recorded alkaline pH values which were much higher than the pH of the skin. Studies conducted on the skin's pH by Korting et al. (1992) revealed that optimum growth for the bacteria *Propionibacterium acnes (P. acnes),* which causes acnes was found at pH 6.0 and 6.5; but the growth rate was found to be much lower at a pH of 5.5. This led to the conclusion that minor shifts in skin surface pH from its normal acid range towards alkaline values may be detrimental to the skin (Korting et al., 1992). Thus, application of H9 and H12 clayey soils may instead cause damage to the skin rather than beautifying it, even though this may depend on the frequency of application. Beneficiation of the alkaline clayey soils through treatment with acetic acid (Ekosse et al., 2007) is however advised before application of the derived cosmetic mixture on the skin.

Although majority of the particle sizes in the clayey soils were < 50 *µm* in diameter; there was a considerable amount of sand present in them, especially in the clayey soils used for body beautification. Sand particles could cause problems when the derived cosmetic mixture is smeared on the skin, as sand particles are dominated by quartz (SiO_2), which is a very hard mineral measuring 7 on the Mohr hardness scale (Ngole et al., 2010). The outermost layer of the skin is relatively softer than quartz, and sand particles in the cosmetic clayey soils could damage the skin through bruising during application. Sand particles can therefore prevent the clayey soils from performing the body beautifying role for which they are used. Studies conducted by Veniale et al. (2007) indicate that cosmetic mixtures must be smooth, less gritty and non abrasive. Therefore, beneficiation of the cosmetic clayey soils through elimination of sand size particles prior to application on the skin is advised.

Conclusion

This paper has examined the physico-chemical properties of cosmetic clayey soils from selected communities within the OR Tambo District of Eastern Cape Province, South Africa. Based on the results obtained, the colours of the analysed clayey soils infer the presence of hematite which is present in several modern sunscreen products. Due to high CEC values of some of the samples, ion exchange from the skin to the clayey mixture, as well as release of ions unto the skin can occur during application, and thereby facilitate skin cleansing and refreshing. The acidic and near neutral nature of majority of the clayey soil samples may limit the chemical reactions that could occur between the skin and the clayey mixture during application; and the acid balance of the skin may remain intact. The cosmetic ability of clays however, is not only influenced by their physicochemical properties. Other specific mineralogical and chemical properties also play vital roles in the cosmetic capabilities of clays. It is therefore recommended that furthers studies be conducted on the identified samples to obtain in-depth understanding of cosmetic properties and capabilities of the identified clayey samples.

ACKNOWLEDGEMENTS

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REFERENCES

Allen J (2001). Ultraviolet radiation: how it affects life on earth. Available on NASA's Earth Observatory website http://earthobservatory.nasa.gov/Library/UVB/printall.php.Accessed April 4 2011.

Ananthapadmanabhan KP, Lips A, Vincent C (2003). pH induced alterations in stratum corneum properties. Internat. J. Cosmet. Sc. 25: 103-112.

Ananthapadmanabhan KP, Moore DJ, Subramanyan MM, Meyer F (2004). Cleansing without compromise: the impact of cleansers on the skin barrier and the technology of mild cleansing. Dermat. Thera. 17: 16-25.

Baeke V (2009). Cosmetics and Culture: The cultural significance of body painting. UNESCO Courier: Available at<http://findarticle.com/p/articles/mim1310/is1996Dec/ai19090929 Accessed 13 January 2010>.

Cara S, Carcangui G, Padalino G, Palomba M, Tamanini M (2000). The bentonites in pelotherapy: chemical mineralogy and technological properties of materials from Sadina deposits (Italy). Appl. Clay Sc. 16 (1): 117-128.

Carretero MI (2002). Clay minerals and their beneficial effects upon human health: a review. App. Clay Sc. 21: 155-163.

Carretero MI, Pozo M (2009). Clays and non clay minerals in the pharmaceutical industry, Part 1: Excipients and Medical Applications. Appl. Clay Sc. (1): 73-80.

Carretero MI, Pozo M (2010). Clay and non-clay minerals in the pharmaceutical and cosmetic industries Part II active ingredients. Appl. Clay Sc. 47(3-4): 171-181.

Carretero MI, Gomes CS, Tateo F (2006). Clays and human health: handbook of clay science. Develop. Clay Sc. 1: 717-741.

Carretero MI, Pozo M, Martin-Rubi JA, Pozo E, Maraver F (2010). Mobility of elements in interaction between artificial sweat and peloids used in Spanish spas. Appl. Clay Sc. 48: 506-515.

Choy JH, Choi SJ, Oh JM, Park T (2007). Clay minerals and layered double hydroxides for novel biological applications. Appl. Clay Sc. 36: 122-132.

Diffey BL (2002). Sources and measurement of ultraviolet radiation. Methods 28: 4-13.

Ekosse G, Mulaba-Bafubiandi A, Nkoma J (2007). Physico-chemistry of continental bentonites and kaolin for ceramic applications. Afr. J. Sci. Technol. Eng. Series 8(1): 107115.

Ettagale B (1999). African Elegance. Rizzoli, New York.

Gfatter R, Hackl P, Braun F (1997). Effects of soap and detergents on skin surface pH, stratum corneum hydration and fat contents in infants. Dermatology 195: 258-262.

Hoang-Minh T, Le LT, Kasbohm J, Gieré R (2010). UV -protection characteristics of some clays. Appl. Clay Sc. 48(3): 349-357.

Jefkins-Elnekave (2006). Tribal identity through body art: extraordinary people living in the remnants of time. PSA J. Available at http://finarticles.com/p/articles/mi/m1306/is772/ain16619437/ Accessed January 2010.

Juch RD, Rufli T, Surbec C (1994). Pastes: What do they contain? How do they work? Dermatology 189(4): 373-377.

Karakaya MC, Karakaya N, Sarioglan S, Koral M (2010). Some properties of thermal muds of some spas in Turkey. Appl. Clay Sc. 48: 531-537.

Korting HC, Greiner K, Hubner K, Hamm G (1991). Changes in skin pH and resident flora by washing with synthetic detergent preparations at pH 5.5 and 8.5. J. Sci. Cosmet. Chemis. 42: 142-158.

Korting HC, Lukacs A, Vogt N, Urban J, Ehret W, Ruckdeschel G (1992). Influence of the pH value on the growh of *Staphylococcus epidermidis*, *Staphylococcus aureus* and *Propionibacterium acnes* in continous culture. Zbl. Hyg. 193: 78-90.

Lim HW, Cilchrest BA, Cooper KD, Bishoff-Ferrari HA, Rigel DS, Cyr WH, Miller S, de Leo VA, Lee TK, Demko CA, Weinstock MA, Young A, Edwards LS, Johnson TM, Stone SP (2005). Sunlight, tanning booths, and vitamin D. J. Amer. Acad. Derma., 52: 868-876.

Lopéz-Galindo A, Viseras C (2000). Pharmaceutical applications of fibrous clays (sepiolite and palygorskite) from some circum-Mediterranean deposits. Proceed. 1st Latin Amer. Clay Confer., **1**: 258-270.

Lopez-Galindo A, Viseras C, Cerezo P (2007). Compositional, technical and safety specifications of clays to be used as pharmaceutical and cosmetic products. Appl. Clay Sc. 36(1-3): 51-63.

Ma'or Z, Henis Y, Alon Y, Orlov E, Sorensen KB, Oren A (2006). Antimicrobial properties of Dead Sea black mineral mud. Int. J. Derma., 45(5): 504-511.

Matike DME, Ekosse GE, Ngole VM (2010). Indigenous knowledge applied to the use of clays for cosmetic purposes in Africa: a review. Indilinga: Afr. J. Indigen. Know. Syst., 9 (2): 138-150.

Mpuchane S, Ekosse G, Gashe B, Morobe I, Coetzee S (2008). Mineralogy of Southern African medicinal and cosmetic clays and their effects on the growth of selected test microorganisms. Fresen. Environ. Bull. 15: 547-557.

Mpuchane S, Ekosse G, Gashe B, Morobe G, Coetzee S (2010).

Microbiological characterization of Southern African medicinal and cosmetic clays. Int. J. Environ. Health. Res., 20(1): 27-51.

Munsell Soil Colour Charts (1992). The Munsell Soil Colour Book. Colour charts. Munsell Colour Company Inc., MD 2128 USA.

Nash F, Matta P, Ertel K (2007). Maintenance of healthy skin: cleansing, moisturisation and ultraviolet protection. J. Cosmet. Dermato., 6: 7-11.

Nelda P (2004). Beauty worlds: cosmetics and body decoration. Available at http://www.b.painting.com/about.htm. Accessed 25 February 2010.

Ngole VM, Ekosse GE, de Jager L, Songca SP (2010). Physicochemical characteristics of geophagic clayey soils from South Africa and Swaziland. Afr. J. Biotechnol., 9(36): 5929-5937.

Pelotherapy (2006). Pelotherapy. Available at www.phybiosis.com. Accessed 15 March, 2011.

Schmid JM, Korting HC (1995). The concept of the acid mantle of the skin: its relevance for the choice of skin cleansers. Dermatology 191: 276-280.

Sparks LD (1995). Ion exchange processes: Environmental soil chemistry. Academic Press London.

Summa V, Tateo F (1998). The use of pelitic raw materials in thermal centres: mineralogy, geochemistry, grain size and leaching tests. Examples from Lucania area (Southern Italy). Appl. Clay Sc. 12: 403-417.

Szántó Z, Papp L (1998). Effects of the different factors on the ionophoretic delivery of calcium ions from bentonite. J. Control. Rel. 56: 239-247.

Tan KH (1996). Sample Preparation. Soil Sampling Preparation and Analysis. New York, Marcel Dekker Inc p. 408.

Tan KH (2011). Principles of Soil Chemistry Fourth Edition. CRC Press, Taylor and Francis Group p. 362.

Tateo F, Summa V (2007). Element mobility in clays for healing use. Appl. Clay Sci., 36: 67-76.

Tateo F, Ravaglioli A, Andreoli C, Bonin F, Coiro V, Degetto S, Giaretta A, Menconi Orsini A, Puglia C, Summa V (2009). The *in-vitro* percutaneous migration of chemical elements from a thermal mud for healing use. Appl. Clay Sci., 44: 83-94.

Van Reeuwijk LP (2002). Procedures for Soil Analysis, International Soil Reference and Information Centre (ISRIC) Technical Paper, No. 9, ISRIC, p. 19.

Veniale F, Better A, Jobstraibizer P, Setti M (2007). Thermal muds: perspective of innovations. Appl. Clay Sc. 36: 141-147.

Viseras C, López-Galindo A (1999). Pharmaceutical applications of some Spanish clays (sepiolite, palygorskite, bentonite): some preformulation studies. Appl. Clay Sci. 14: 69-82.

Viseras C, Aguzzi C, Cerez, P, Lopez-Galindo A (2007). Use of clay minerals in semi-solid health care and therapeutic products. Appl. Clay Sci., 36: 37-50.

Wood D (2000). Gerewol Festival. Available at http://www.worldreviewer.com/travel-guides/festival/gerewol-festival/56706/. Accessed 25 February 2010.

XU R (2000). Particle Characterization: Light Scattering Methods, Kluwer Academic Publishers, Dordrecht.

Young SL, Wilson MJ, Miller D, Hillier S (2008). Toward a comprehensive approach to the collection and analysis of pica substances, with emphasis on geophagic materials. Plos One 3(9): 3147.