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Hydroquinone and Heavy Metals Levels in Cosmetics Marketed in Nigeria

F.O. Oyedeji, G.O. Hassan and B.B. Adeleke
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

Corresponding Author: F.O. Oyedeji, Department of Chemistry, University of Ibadan, Ibadan, Nigeria

ABSTRACT

Eighty cosmetic emulsions were purchased from a whole sale supermarket in Ibadan, Nigeria with the aim of finding out if the creams contained hydroquinone and heavy metals at levels which were harmful to the populace. The 41.25% of these emulsions were manufactured in Africa, 30.00 in Europe, 1.25 in Asia and 27.50% in USA. Their physico-chemical properties were determined. The results obtained indicate that the color of the samples ranged from white through blue to light brown. The emulsions were mostly oil-in-water. pH was from 4.91-7.32; moisture content, 0.45-88.93%; total volatile matter 2.43-89.67% and total non volatile matter from 10.33-97.57%. The neutral fatty matter of the emulsions, were in the range 10.17-83.24%; total fatty acids 1.32-15.86%. The acid values of the emulsions from 1.30-51.80 mg KOH g⁻¹. Their ester values were in the range 9.95-61.40 mg KOH g⁻¹, their saponification values 13.30-101.80 mg KOH g⁻¹ and the unsaponifiable matter content 1.32-75.75%. The glycerol content ranged from 1.15-2.56% and sorbitol from 1.39-1.45. About 51.25% of the emulsions contained hydroquinone having concentration ranging from 9.50-50.35 mg g⁻¹ showing that hydroquinone present are within, usual limit in most cases. Iron levels of the emulsions were in the range 0.05-1.830 mg L⁻¹ and lead from 0.01-0.9 mg L⁻¹. Chromium level from 0.002-0.097 mg L⁻¹ and aluminum 0.320-1.002 mg L⁻¹. In conclusion most of the emulsions do not contain hydroquinone or heavy metals at levels that are detrimental to human health and the manufacturers are likely to have used utility water during production.

Key words: Cosmetics, physicochemical analysis, hydroquinone, heavy metals

INTRODUCTION

Cosmetics can be defined as any preparation intended to be applied to the human body for purpose of cleansing, beautifying, promoting attractiveness or altering the appearance without affecting the body's structure and function (Reed, 2004). Cosmetics are generally used to improve the appearance by the removal or correction of blemishes or deformities and to prevent diseases of the skin and hair. It can also be used to repair or hide skin imperfections, to cleanse, adorn, protect and treat the human body.

Majority of cosmetic creams and lotions contain lipid (oil) and water as their major components and other minor ingredients like surface active agents, moisturizers, emollients, waxes, thickeners, active ingredients, sunscreens, antioxidants, colors, preservative and so on. All of these substances usually have distinctive effects on the resulting emulsion (Andrade *et al.*, 2007).

Cosmetics can either be emulsions or single phase products. The majority of cosmetic creams, lotions and milks are emulsions. The emulsion droplet usually varies in diameter from about 0.2 to

0.5 μm (Harry, 2002). In order to stabilize the emulsion formed and prevent creaming, the free surface energy of the system is reduced by the addition of surfactants such as soaps.

Cosmetic creams are emulsified products whose physical form can vary from a liquid to a spreadable solid. If an emulsion is of sufficiently low viscosity to be pourable then it may no longer be referred to as a cream but a lotion. A successful cream must not only be dermatological acceptable, technically well-balanced and stable in character, it must be attractive in appearance, delicately perfumed and fulfill a definite cosmetic purpose. A properly formulated cream should possess the following properties; good consistency and ease of application, good and reasonable persistent adherence to the skin, ability to form coherent, impervious, flexible and non-cracking film, freedom from any tendency to irritate the skin, ease of removal when desired and it must be stable and have good appearance (CTPA, 1987).

All cosmetic creams, lotions and milks can be categorized into four major groups; cleansing, moisturizing, all-purpose and protective products based on their functional properties (Latuen, 1958). These products usually leave behind a thin emollient layer of oil giving a healthy, supple feel, to the skin surface. Depending on the skin type, oily, dry, normal, or combination and according to the activity of the oil producing sebaceous glands, water can easily be lost from the skin surface. Occlusion, humectancy and restoration of deficient materials can be used to restore water to dry skin. Moisturizing emulsions contain many occlusive water impermeable substances like mineral, vegetable and silicone oils and lanolin. Humectants like glycerol, propylene glycol and sorbitol could be used alone or mixed together. Ammonium complexes film that seems to be able to influence the rate of trans-epidermal water loss has also been used (Schwartz *et al.*, 2010). Majority of these effective moisturizing ingredients cannot be applied without some modifications because they are difficult to apply and can leave the skin feeling tacky. Hence, they are formulated into cosmetic emulsions and micro emulsions which can be stabilized with an appropriate emulsifier system.

Melanin is the main factor that determines skin colour (Walters and Roberts, 2008). Its major function is providing protection against UV irradiation. A local increase in melanin synthesis or uneven distribution can cause local hyper pigmentation or spots. Irregular pigmentation patterns are caused by various factors, including inflammation imbalance of hormones and genetic disorders. Ultra violet irradiation further aggravates these skin conditions.

Skin lighteners are defined as cosmetic preparations that can suppress or inhibit melanogenesis. Examples of skin lighteners include hydroquinone, arbutin, kojic acid, placental extract and L-ascorbic acid and its derivatives (Policarpio and Lui, 2009). Hydroquinone (HQ) is a tyrosinase inhibitor of the non suppressive type with a marked skin de-pigmenting property (Briganti, 2003). Tyrosinase catalyzed oxidation of hydroquinone leads to the formation of 2-hydroquinone (THQ) which is the active de-pigmenting agent. Hydroquinone when applied at levels higher than the recommended can result in the thinning of the skin, irreversible white patches where the melanin producing cells have been destroyed, hyper pigmentation and can act as an eye, nose, skin and mucous membrane, gastro-intestinal and respiratory irritant.

Baumann (2007) reported that hydroquinone (HQ) has been used for decades in creams, gel and lotion for the treatment of hyperpigmentation disorders. It is the most frequently used compound in skin-toning preparations. According to Norlund (2006) the effects of hydroquinone are transitory and concentrations belows 3.0% do not cause skin injuries, however concentrations above 5.0% could provoke local irritation.

Kooyers and Westerhof (2005) in their own work discussed the adverse effects of hydroquinone. They stated that dermatitis may occur in small number of patients and responds

promptly to topical steroids. According to them, an uncommon, yet important, adverse effect of hydroquinone is exogenous ochronosis. This disorder is characterized by progressive sooty darkening of the skin area exposed to hydroquinone.

The skin acts as a barrier between the body and its environment maintaining a controlled dynamic equilibrium. Various stresses imposed by the environment can cause changes in the skin. One major purpose of cosmetic emulsion for skin use is to help to reverse these changes and maintain a normal healthy skin. The constituents of a cosmetic emulsion can give insight into whether these changes will be reversed by its use (Oyededeji and Oderinde, 2005).

In view of the above situation, the objective of this research work is to determine from the physicochemical parameters and level of hydroquinone and heavy metals certain skin creams and lotions available in Nigeria, if manufacturers are complying with the regulations put in place concerning cosmetics.

MATERIALS AND METHODS

Sampling and determination of continent of manufacture: Different skin creams and lotions were obtained by random purchase from a whole sale cosmetic shop in Ibadan, Nigeria in July 2008. The various cosmetic emulsions are listed in Table 1-5. The continent of manufacture was determined by the inspection of the labels on the cosmetic packaging. The country of manufacture was ascertained as most of the cosmetic emulsions contained the serial number for the registration of the cosmetic product by National Agency for Food and Drug Administration and Control.

Physicochemical analysis: Determination of emulsion type, pH, percentage volatile and non volatile component (TVM and TNVM), percentage Neutral Fatty Matter (NFM), percentage Total Fatty Acid (TFA), percentage Free Acid and acid combined with Weak Base (FAWB), percentage Free Base combined with Weak Acid (FBWA), Acid Value (AV), Ester Value (EV), Saponification Value (SV), percentage unsaponifiable matter(USM), percentage glycerol and percentage sorbitol were carried out using standard analytical methods (Pouchers, 1993).

Table 1: Physical characteristics of the cosmetic emulsions from Nigeria

Code	Type	Colour	Emulsion type	pH	MC (%)	TVM (%)	PM (%)	TNVM (%)
001	Cream	Off-white	O/W	6.85	79.25	79.96	0.71	20.04
002	Lotion	Pale pink	O/W	6.6	72.69	73.35	0.66	26.65
003	Lotion	Off-white	O/W	6.54	81.67	82.36	0.69	17.64
004	Cream	Cream	O/W	6.89	77.64	78.35	0.71	21.65
005	Cream	White	O/W	6.89	73.78	74.26	0.48	25.74
006	Cream	Pale-pink	O/W	6.99	80.83	81.98	1.07	18.02
007	Lotion	White	O/W	6.25	80.23	80.8	0.57	19.2
008	Lotion	Off-white	O/W	6.7	71.98	72.22	0.24	27.78
009	Cream	Yellow	O/W	6.81	77.96	78.69	0.73	21.31
010	Lotion	Cream	O/W	6.82	80.04	81.57	1.53	18.43
011	Cream	Off-white	O/W	6.8	74.08	74.61	0.53	25.39
012	Cream	Off-white	O/W	7.01	77.42	77.86	0.44	22.14
013	Lotion	Off-white	O/W	6.43	77.26	77.68	0.42	22.32
014	Cream	White	O/W	6.98	75.54	76.37	0.83	23.63
015	Jelly	Cream	W/O	7.21	0.49	2.62	2.13	97.38
016	Jelly	White	W/O	7.14	0.45	2.52	2.07	97.48
017	Jelly	Yellow	W/O	7.03	0.53	2.69	2.16	97.31

TVM: Total volatile matter; TNVM: Non-volatile matter; MC: Moisture content; PM: Perfumery matter

Table 2: Physical characteristics of the cosmetic emulsions from Africa

Code	Type	Colour	Emulsion type	pH	MC (%)	TVM (%)	PM (%)	TNVM (%)
018	Lotion	White	W/O	6.34	79.15	79.83	0.68	20.17
019	Cream	Pale pink	O/W	7.2	79.09	79.83	0.74	20.17
020	Cream	White	O/W	5.93	73.78	74.34	0.56	25.66
021	Lotion	Off-white	O/W	5.89	78.83	79.64	0.81	20.36
022	Cream	White	O/W	6.23	70.48	71.02	0.54	28.98
023	Lotion	White	O/W	6.22	81.34	82.16	0.82	17.84
024	Cream	White	O/W	7.09	76.32	77.00	0.68	23.00
025	Gel	Yellow	O/W	5.29	88.93	89.67	0.74	10.33
026	Cream	White	O/W	6.45	72.93	73.69	0.76	26.31
027	Lotion	Yellow	W/O	6.92	78.04	78.93	0.89	21.07
028	Cream	White	O/W	6.98	71.14	71.63	0.49	28.37
029	Cream	White	O/W	7.09	69.83	70.61	0.78	29.39
030	White	White	W/O	6.18	76.87	77.59	0.72	22.41
031	Cream	Cream	O/W	6.48	76.84	77.23	0.39	22.77
032	Cream	Off-white	O/W	6.04	78.19	78.84	0.65	21.16
033	Jelly	White	W/O	7.12	0.52	2.43	1.91	97.57

TVM: Total volatile matter; TNVM: Non-volatile matter; MC: Moisture content; PM: Perfumery material

Table 3: Physical Characteristics of Cosmetics Emulsions from Asia

Code	Type	Colour	Emulsion type	pH	MC (%)	TVM (%)	PM (%)	TNVM (%)
034	Cream	White	O/W	6.91	80.95	1.8	18.2	0.85

TVM: Total volatile matter; TNVM: Non-volatile matter; MC: Moisture content; PM: Perfumery material

Table 4: Physical characteristics of cosmetic emulsions from Europe

Code name	Type	Colour	Emulsion type	pH	MC (%)	TVM (%)	PM (%)	TNVM (%)
035	Cream	White	O/W	7.03	79.93	80.31	0.38	19.69
036	Cream	Off-white	O/W	6.06	37.05	37.84	0.79	62.16
037	Lotion	White	O/W	6.03	81.63	82.70	1.07	17.30
038	Lotion	Pale yellow	O/W	6.52	77.41	77.51	0.10	22.49
039	Lotion	Off-white	O/W	5.73	80.36	81.14	0.78	18.86
040	Lotion	White	O/W	6.34	84.32	84.98	0.66	15.02
041	Cream	Peach	O/W	6.31	80.16	81.93	1.77	17.07
042	Lotion	White	O/W	6.50	75.84	76.45	0.61	23.55
043	Lotion	Off-white	O/W	5.02	81.54	82.39	0.85	17.61
044	Lotion	Pale pink	O/W	6.11	85.96	86.41	0.45	13.59
045	Cream	White	O/W	6.83	66.83	67.50	0.67	32.50
046	Cream	White	O/W	5.83	72.36	72.94	0.58	27.06
047	Lotion	White	O/W	6.31	81.53	82.17	0.64	17.83
048	Cream	Off-white	O/W	7.32	64.29	64.78	0.49	35.22
049	Lotion	White	O/W	5.65	79.75	80.32	0.57	19.68
050	Lotion	Yellow	O/W	5.80	78.74	79.23	0.49	20.77
051	Lotion	White	O/W	7.11	80.84	81.57	0.73	18.43
052	Lotion	White	O/W	6.84	74.57	75.45	0.88	24.55
053	Lotion	White	O/W	7.10	80.68	80.95	0.27	19.05
054	Lotion	White	O/W	6.74	78.93	79.37	0.44	20.63
055	Lotion	Lemon	O/W	7.23	84.68	85.08	0.40	14.92
056	Lotion	Pale pink	O/W	6.74	86.64	87.11	0.47	12.89
057	Cream	White	O/W	5.89	70.69	71.34	0.65	28.66
058	Jelly	White	W/O	7.09	0.52	2.43	1.91	97.57

TVM: Total volatile matter; TNVM: Non-volatile matter; MC: Moisture content; PM: Perfumery material

Table 5: Physical characteristics of cosmetic emulsions from USA

Code name	Type	Colour	Emulsion Type	pH	MC (%)	TVM (%)	PM (%)	TNVM (%)
059	Lotion	White	O/W	6.83	79.93	81.31	1.38	18.69
060	Lotion	White	O/W	6.99	76.76	77.66	0.90	22.34
061	Lotion	Off-white	O/W	5.64	81.18	81.70	0.52	18.30
062	Lotion	Light-brown	O/W	5.67	80.42	81.39	0.97	18.61
063	Lotion	White	O/W	6.48	81.10	82.93	1.83	17.07
064	Lotion	Powdered-blue	O/W	6.89	86.23	86.97	0.74	13.03
065	Lotion	White	O/W	6.42	56.23	57.74	1.51	42.26
066	Lotion	White	O/W	6.46	84.78	85.63	0.85	14.37
067	Lotion	Off-white	O/W	4.91	81.73	82.68	0.95	17.32
068	Cream	Light-brown	W/O	6.40	71.94	72.63	0.69	27.37
069	Cream	White	O/W	6.52	73.87	74.61	0.74	25.39
070	Lotion	Off-white	O/W	5.97	73.69	74.20	0.51	25.80
071	Jelly	Cream	W/O	7.12	1.07	2.89	1.82	97.11
072	Lotion	White	O/W	6.34	76.03	77.00	0.97	23.00
073	Cream	Pale pink	O/W	6.61	79.84	80.13	0.29	19.87
074	Cream	Pale green	O/W	6.69	80.36	80.97	0.61	19.03
075	Cream	Cream	O/W	4.99	79.83	80.69	0.86	19.31
076	Cream	Off- white	O/W	6.27	79.25	79.76	0.51	20.24
077	Cream	White	O/W	6.33	81.85	82.34	0.49	17.66
078	Cream	Peach	O/W	6.63	78.93	79.96	1.03	20.44
079	Cream	Off-white	O/W	6.73	76.62	77.29	0.67	22.71
080	Cream	White	O/W	6.72	72.08	72.63	0.55	27.37

TVM: Total volatile matter; TNVM: Non-volatile matter; MC: Moisture content; PM: Perfumery material

The analyses were carried out in Industrial Chemistry Laboratory of the Department of Chemistry University of Ibadan, Nigeria.

Colour: The colour of the various cosmetic creams and lotion was determined by visual observation.

Determination of moisture content: An IR-30 Denver Instruments Moisture Analyser that has a weighing system of 30 g capacity and a 1 mg resolution was used to determine the moisture for this purpose using the inbuilt weighing capacity of the instrument. The machine was then closed and heating started automatically with the aid of two tubular inbuilt infrared heating elements. When all the moisture had been removed through drying, the percentage moisture content is automatically displaced on the screen of the moisture analyzer. The temperature of the moisture analyzer was placed at 105°C.

Determination of hydroquinone: Concentration of hydroquinone (HQ) in each of the sample was determined using the method proposed by Garcia *et al.* (2007). In this method the concentration of hydroquinone was determined using a UV spectrophotometer at a wavelength of 302 nm. According to this method, different concentrations of hydroquinone standards were prepared by dissolving it in 0.05 moles dm⁻³ sulphuric acid. The absorbance of these solutions were determined and used to prepare a calibration curve.

For the sample, 1 g of each sample was dissolve in 20 cm³ 0.05 moles dm⁻³ sulphuric acid in a beaker on a water bath. This solution was then transfer into a 25 cm³ standard volumetric flask and

made to volume with the 0.5 moles dm^{-3} sulphuric acid. The solution was then filtered with a filter paper discarding the first 5 cm^3 . The absorbance of the resulting solution was then taken and traced on the calibration curve to give the concentration of hydroquinone in each sample. This analysis was carried out at the central laboratory of Ladoke Akintola University of Technology Ogbomosho, Nigeria.

Determination of lead, iron, chromium and aluminium: Heavy metals in the emulsions were determined by atomic absorption spectrophotometer using the method of Okamoto *et al.* (1971). One gram of each sample was accurately weighed into a Kjeldahl digestion flask. The 20 cm^3 of concentrated per-chloric acid was added and the flask was clamped and placed in a heating mantle. The solution was allowed to boil until a clear solution was obtained. This solution was then poured into a 50 cm^3 standard volumetric flask and made to volume with de-ionized water. The resulting solution was then filtered if necessary and the concentration of the metals was measured using atomic absorption spectrophotometer. The analysis was carried out at the Central Laboratory of Ladoke Akintola University of Technology Ogbomosho, Nigeria.

RESULTS AND DISCUSSION

Country of manufacture: By checking the labels on the cosmetic product containers it was observed that 41.25% of these emulsions were manufactured in Africa and 51.52% of those manufactured in Africa were made in Nigeria. 1.25% were manufactured in Asia, 30.0% in Europe and 27.5 in the USA. 46.25% of these emulsions are lotions, 46.25 creams, 1.25 gel and 6.25% were petroleum jellies.

Physico-chemical analysis of the cosmetic emulsions: The results of the physical and chemical characteristics of the cosmetic emulsions were grouped into five classes depending on where the emulsions were manufactured. Those produced in Nigeria, Africa, Asia, Europe and USA.

Physical characteristics

Cosmetic emulsions from Nigeria: There were 17 emulsions manufactured in Nigeria (Table 1) made up of 8 creams, 6 lotions and 3 petroleum jellies. Four of the emulsions were coloured white, 6 off-white, 3 cream coloured, 2 yellow and 2 pale pink (Table 1). There were 14 oil-in-water (o/w) emulsions and 3-water-in oil (w/o) emulsions. The pH of the emulsions, were in the range 6.25-7.21. The % moisture content, from 0.45-81.67%, total volatile matter 2.52-82.36% and total non volatile matter content of the emulsions ranged from 17.64-97.48%. The emulsions contained perfumery matter at 0.24-2.16% level. Most of the emulsions analyzed were of the oil in water type. This is an indication of the recognition by the manufacturers that (o/w) emulsions are much more easily rubbed into the skin and are easier source of water for plasticising the skin (Oyedepi and Oderinde, 2005). This is also an indication that most of these emulsions will encourage hydration of the skin. The production of a particular emulsion type depends on the quantity of both the oil and the water phase, method of emulsion production and the type of emulsifier used.

Most of emulsions also had pH which is close to neutral pH. This implies that most of the manufacturers titrated the emulsion to acceptable pH which is not likely to irritate the skin. These values shows that the cosmetic emulsions are skin friendly in terms of their pH and should therefore not result in dermatological disorders. The pH of the cosmetic emulsions indicates the

amount of free acids and bases present in the emulsion. Ideally the pH of an emulsion should be close to the pH of the skin mantle which is 5.5 (Rieger, 1989). Because of the inclusion of various substances in the formulation of a cosmetic emulsion such as soaps that are alkaline in nature as emulsifiers, the cosmetic emulsion may not have the slightly acidic pH that is required. As a result of this, the emulsions are usually titrated to acceptable pH by the addition of components such as phosphoric acid and citric acid (Oyededeji and Oderined, 2005).

Those with high moisture content will be able to provide adequate moisture and hydration to the skin thereby making the skin to feel soft. Most of the volatile content can be related to the presence of the water used in the formulation, the rest can be attributed to the presence of perfumery material. The petroleum jellies had very low moisture levels (0.45-0.53%), therefore the total volatile matter levels (2.52-2.69%) are likely to be mostly due to perfume materials. The difference between total volatile matter and moisture is most likely attributable to perfumery material. These ranged between 0.24-2.16%. This has no significance as perfume is added into cosmetic emulsions at levels which the cosmetic designer consider adequate. The perfume is usually chosen to agree with the other components, attract consumers and /or mask any unacceptable odour from any of the ingredients. However since most perfumery materials are also allergens, care must be taken to include them at considerably low levels. Few of the emulsions have high non volatile matter content ranged from 97.31-97.48%. These are the petroleum jellies which are emulsions containing ample amount of mineral oil and petrolatum and paraffin wax. The total non-volatile matter content of the cosmetic emulsion is indicative of the total neutral fatty matter, the total fatty acids and other additives such as gums, starches, waxes and other high boiling point substances.

Cosmetic emulsions from Africa: Sixteen emulsions were manufactured in other countries in Africa (Table 2). There were 10 creams, 4 lotions 1 gel and 1 petroleum jelly. Twelve of the emulsions were of the oil in water type (*o/w*) and 4 water in oil (*w/o*). Ten emulsions were white in colour, 2 off-white, 1 cream coloured, 1 pale pink and 2 were yellow. The pH were in the range 5.29-7.20, %moisture 0.52-88.93, %total volatile matter 2.43-89.67, %total non volatile matter 10.33-97.57 while the emulsions contained 0.39-1.91% of perfumery matter. The colours of the cosmetic emulsions ranged from white through yellow to pale pink (Table 2) when visual observation was carried out. This is similar to the colours in Nigeria manufactured emulsions. This is probably as a result of the colours considered as acceptable by Africans. The colours are mostly pale as the manufacturers want to comply with using the minimum possible pigments to avoid evoking allergic responses. The pHs, appear to be closer to the pH of the skin mantle (5.50). This is likely to make the creams more skin compatible and less likely to cause skin problems. Other creams are closer to the neutral point showing that when the manufacturers fail to achieve a skin compatible pH, they choose the option of titrating to an acceptable pH which will reduce the likelihood of dermatological disorders.

The moisture content of the emulsions varied from 69.83-88.93% with the exception of a single emulsion with moisture level of 0.52%. This emulsion is a petroleum jelly emulsion. Interestingly even the emulsions which were water in oil contained from 76.87-79.15% of water. This is probably as a result of the emulsion having been prepared using the phase inversion method. This method of emulsion manufacture, leads to the production of more stable emulsions. The moisture will therefore be more easily available to the skin as occlusion which results from the use of water in oil cream will lead to the hydration of the stratum corneum and even though there may be increase in trans-epidermal water loss, there will be more water available to rehydrate the skin from the

cosmetic emulsions. The other creams are simple oil in water emulsions. Again with the emulsions prepared in Africa as with those prepared in Nigeria, the total volatile matter is indicative of level of moisture and perfumery materials used. For the emulsion with very low volatile matter, this is indicative of only perfume matter. The total volatile matter content of the emulsions ranged from 70.61-89.67% with the exception of the petroleum jelly which had a total volatile matter content of 2.43%. The total non-volatile matter content of the emulsions ranged from 10.33-29.39% with the exception of the petroleum jelly (97.57%).

Cosmetic emulsion from Asia: Only one of the samples obtained was manufactured in Asia (Table 3). The emulsion was white oil in water cream, with pH 6.91. It had % moisture of 80.95, total volatile matter of 81.80 and % total non volatile matter of 18.20. It contained 0.85% perfumery matter. This is indicative of the level and type of bilateral trade agreements between Nigeria and the Asian continent. It could also be because most Nigerian women who trade in cosmetic products only travel to the Europe or the Americas or other African countries, especially the west African countries. This is probably due to the fact that Nigeria is an English speaking country. The emulsion was oil-in-water emulsion. The emulsion was coloured white and had a pH of 6.91. The pH showed that there was an attempt to titrate the emulsion to neutral pH. The colour shows that pale coloured emulsions or emulsions without any pigments were usual here.

The moisture level was high (80.95%) and the emulsion probably contained perfumery matter at about 0.85% level as the total volatile matter was 81.80%. This is quite low and may suggest a situation in which intense smell was not permitted, perhaps more people from this continent were subject to allergic reactions induced by some perfumery materials.

Cosmetic emulsions from Europe: Twenty four of the emulsions purchased were made in Europe (Table 4). Of these, 7 were creams, 16 lotions and 1 jelly. Fourteen of these emulsions were white, 4 off-white, 1 peach coloured, 2 pale pink, 1 pale yellow, 1 yellow, 1 lemon coloured (yellowish green). There were 23 oil in water emulsions and 1 water in oil emulsion with pH in the range 5.02-7.32. The % moisture of the emulsions were in the range 0.52-86.64; % total volatile matter 2.43-87.11. % total non volatile matter 12.89-97.57 and perfumery matter in the range 0.10-1.91. Though majority of the emulsions were white, the use of pigments in some of the emulsions showed that the consumers from this continent are lovers of wide range of colours and that the use of colours is encouraged. Their pH showed a range in which most of them are close to the pH of the skin mantle (5.50) while others were probably titrated to close to neutral pH. The pH values shows that the emulsions are skin friendly in terms of their pH. All the emulsions were oil-in-water emulsion except the petroleum jelly which was water-in-oil emulsion.

Cosmetic emulsions from USA: Twenty two of the sample emulsions were made in the USA (Table 5). Half of these number were creams while the other half were lotions. 9 of the emulsions were white, 5 off white, 2 cream coloured, 1 peach coloured, 1 pale pink, 1 powder blue, 1 pale green and 2 light brown. Twenty of these emulsions were of the oil in water type and 2 water in oil emulsions. The pH of the emulsions were in the range 4.91-7.12; % moisture 1.07-86-23, % total volatile matter 2.89-86.97, % total non volatile matter 13.03-97.11% and perfumery matter 0.29-1.83%.

The variety of colours in these emulsion show the versatility of the industries and the preference of the consumers here for colour variations. This may be because of the multi racial nature of the

people of these region. Their moisture contents were mostly high with the exception of the 071 which consist majorly cocoa butter and petrolatum with moisture content of 1.07%. The perfumery material content of the emulsions ranged from 0.29-1.83%. This showed that most of the emulsions were relatively highly perfumed, which may be as a result of the preference of the consumers here for intense smells or requirement for more serious masking of odours.

Chemical characteristics

Cosmetic emulsions from Nigeria: The neutral fatty matter contents of the emulsions manufactured in Nigeria were in the range 11.06-86.24%, the total fatty acid from 1.53-12.37%, free acid or acid combined with weak base content from 0.16-10.31% and the free base or base combined with weak acid content from 0.01-1.44% (Table 6). The acid value of the emulsions ranged from 1.30-20.20 mg KOH g⁻¹, the ester value from 9.50-38.20 mg KOH g⁻¹ and the saponification value from 13.30-51.70 mg KOH g⁻¹. The unsaponifiable matter content of the emulsions ranged from 2.32-75.75%. The glycerol content of some of these cosmetic emulsions were in the range 1.48-2.56%. Only one of the emulsions contained sorbitol at 1.45% level. All the emulsions manufactured in Nigeria contained hydroquinone with the exception of the petroleum jellies. The hydroquinone content of the emulsions ranged from 9.50-53.30 mg g⁻¹. Heavy metals like Iron (Fe), Chromium (Ch), Lead (Pb) and Aluminium (Al) were present in the range 0.335-1.580, ND-0.087, 0/01-0.39 and ND-0.989 respectively. The neutral fatty matter content of the emulsions manufactured in Nigeria were of average values with the exception of the petroleum jellies which are the paraffin based or petrolatum based emulsions containing high amount of waxes whose neutral fatty matter content ranged from 81.95-83.24% (Table 6). The neutral fatty matter content is indicative of the fatty matters such as mineral oil, silicones, fatty alcohols, fatty esters, lanolin and most waxes present in cosmetic emulsion. Most of these especially the mineral oil, fatty alcohols and the waxes are good emollients and are useful in cleansing, massage and night creams. The neutral fatty matter is also a medium for the introduction of vitamins. The creams have higher neutral fatty matter content compared to the lotions.

Table 6: Chemical characteristics of cosmetic emulsions from Nigeria

Code name	% NFM	% TFA	% FAWB	% FBWA	AV (mg KOH g ⁻¹)	EV (mg KOH g ⁻¹)	SV (mg KOH g ⁻¹)	% USM	% GLYCEROL	% SORBITOL	HQ (mg g ⁻¹)
001	17.19	6.84	3.59±0.01	ND	11.40±0.05	16.60±0.11	28.00±0.14	11.19	2.56±0.05	ND	32
002	11.83	5.19	3.75±0.02	0.01±0.05	7.60±0.09	38.20±0.06	45.80±0.13	2.32	ND	ND	9.5
003	11.84	12.37	6.40±0.01	ND	12.60±0.13	33.20±0.07	45.80±0.19	3.55	1.87±0.10	ND	33.5
004	17.43	6.75	3.43±0.01	ND	10.10±0.20	18.20±0.04	28.30±0.22	9.65	2.52±0.10	ND	29.5
005	17.89	8.58	5.62±0.04	ND	16.30±0.30	16.60±0.07	32.90±0.33	12.35	ND	ND	18.6
006	18.63	6.84	3.12±0.02	0.27±0.01	3.80±0.15	9.50±0.10	13.30±0.23	15.66	ND	ND	16.8
007	12.23	12.27	10.31±0.06	ND	20.20±0.13	31.50±0.10	51.70±0.20	4.68	1.48±0.07	ND	19.5
008	11.06	5.75	10.07±0.05	ND	7.60±0.09	19.90±0.10	27.50±0.17	6.27	1.75±0.13	ND	27.6
009	18.23	6.48	6.25±0.01	ND	13.90±0.04	23.20±0.10	37.10±0.12	11.15	1.80±0.06	ND	36.0
010	11.67	6.84	6.56±0.03	ND	12.60±0.07	23.20±0.10	35.80±0.15	5.09	2.42±0.09	ND	27.8
011	17.72	6.29	4.37±0.00	ND	8.80±0.11	13.30±0.20	22.10±0.29	12.52	2.33±0.10	ND	53.3
012	17.64	6.67	3.59±0.01	ND	12.60±0.17	21.60±0.10	34.20±0.25	10.45	2.46±0.07	ND	46.8
013	11.43	6.81	5.55±0.01	ND	12.60±0.05	19.90±0.10	32.50±0.12	6.01	1.76±0.05	ND	32.9
014	16.58	6.28	9.68±0.02	1.44±0.02	16.40±0.18	29.90±0.15	46.30±0.30	8.38	ND	1.45±0.10	ND
015	82.95	1.67	0.16±0.00	ND	1.30±0.00	20.50±0.20	21.80±0.19	75.3	ND	ND	ND
016	81.27	153	0.16±0.00	ND	1.30±0.00	20.90±0.10	22.20±0.09	75.75	ND	ND	ND
017	83.24	1.95	0.16±0.00	ND	1.30±0.00	21.20±0.10	22.50±0.10	74.5	ND	ND	ND

% NFM: % Neutral fatty matter, % TFA: % Total fatty acids, % FAWB: % Free acid combined with weak base, % FBWA, % Free base combined with weak acid, AV: Acid Value, EV: Ester Value, SV: Saponification Value, % USM, % unsaponifiable matter

The total fatty acids includes all the fatty acids present in the cosmetic emulsion. This fatty acids are known to be precursors of emulsifiers that stabilize the cosmetic emulsions. Some of this fatty acids are essential ones that are good for healing of the skin (Van Boekel *et al.*, 1981). Those with very low total fatty acid content are those that contain ample amount of mineral oil or petrolatum and small amount of vegetable oil. When the content of the petrolatum is higher compared to that of fatty acids, this can lead to dehydration of the skin due to TEWL. The values for the petroleum jellies was 0.16%. The free acid or acid combined with weak bases in cosmetic emulsions are acids added to emulsions in order to present an emulsion that is a fat at body temperature. The most commonly used acid is stearic acid. Very high free acid content may lead to skin irritations. Majority of the emulsions had no detectable base in them. This might be due to the fact that soaps that were used as emulsifiers and the little base that might have being present had being titrated to close to neutral pH. The free base or base combined with weak acid in cosmetic emulsions are bases usually acting as emulsifiers. Some are in form of soaps of alkaline metals, some are hydroxides of alkaline metals while some are quaternary ammonium bases such as urea and triethanolamine. Quaternary ammonium bases at low levels are useful for skin softening and also useful as surface active agent thereby reducing the surface tension of water and allowing permeability of skin substansive components into the skin.

The acid value of the petroleum jellies are quite low with all of them having a value of 1.30 mg KOH g⁻¹. The acid values indicates the quantity of fatty acids remaining in the cosmetic emulsions from the lipid oil used in their production. This fatty acids acts as thin films that cover the skin in order to prevent TEWL. The low acid values of some of these emulsions is indicative of presence of very low amount of fatty acid or absence of fatty acids and also an indication of high paraffin content. Those with high acid values is indicative of the near absence or paraffin oil or petrolatum content but high amount of animal or vegetable fats. Also, the low fatty acid content or acid value could also be as a result of saponification of the fatty acids by the bases added during the emulsion formation. Those with very high acid value are likely to make the skin feel warm resulting in intense sweating because of their occlusive properties thereby blocking of the skin pores. The ester value is indicative of the esters present in the cosmetic emulsions. These esters are either present in the fat or oil used in their production or are added during the cause of emulsion formation. These esters have skin substansive properties that makes the emulsion to be skin friendly. The low ester value of some of these cosmetic emulsion is either due to the absence of animal or vegetable oil and presence of more paraffin oil or petrolatum or due to the fact that most of them have been saponified during emulsion formulation. The saponification values is indicative of both the acid values and the ester values of the cosmetic emulsions.

The petroleum jellies had very high unsaponifiable matter content ranging from 74.50-75.75%. The unsaponifiable matter of cosmetic emulsion is indicative of unsaponifiable components of the emulsion such as fatty alcohols, sterols and so on. These materials provides essential moisture to the skin. Some of them have surface-active properties hence acts as emulsifiers and stabilizers in the cosmetic emulsion. Those with very high unsaponifiable matter ie the petroleum jellies contain mainly paraffin oil and/or petrolatum or paraffin waxes which are mainly hydrocarbons. The glycerol content is indicative of quantity of the chemical used to solubilize the perfumery material or the amount added for the purpose of moisturization. The inability to detect sorbitol may indicate that sorbitol is not commonly used in this part of the world. The presence of small amount of hydroquinone might be as a result of the use of hydroquinone as antioxidant in such emulsions. Those with percentage hydroquinone content below 3.0% do not cause skin injuries but can be used

Table 7: Chemical characteristics of cosmetic emulsions from Africa

Code name	% NFM	% TFA	% FAWB	% FBWA	AV (mg KOH g ⁻¹)	EV (mg KOH g ⁻¹)	SV (mgKOH g ⁻¹)	% USM	% GLYCEROL	% SORBITOL	HQ (mg g ⁻¹)
018	11.36	10.67	10.86±0.05	ND	17.70±0.10	38.20±0.05	55.90±0.13	2.17	1.45±0.10	ND	47.5
019	16.29	8.16	1.80±0.00	0.27±0.01	6.30±0.10	33.20±0.09	39.50±0.15	7.31	ND	ND	ND
020	18.36	8.48	18.59±0.03	ND	20.20±0.05	28.20±0.10	48.40±0.13	10.78	1.34±0.09	ND	7.8
021	11.83	10.74	3.59±0.02	0.18±0.00	3.80±0.10	48.10±0.20	51.90±0.27	1.32	1.25±0.05	ND	ND
022	18.71	7.23	9.68±0.01	ND	30.30±0.30	18.20±0.10	48.50±0.36	11.88	1.36±0.10	ND	27
023	12.08	11.63	9.22±0.01	ND	21.50±0.04	16.60±0.09	38.10±0.11	7.49	ND	ND	8.8
024	17.64	6.32	4.37±0.00	0.36±0.01	10.10±0.09	14.90±0.13	25.00±0.10	13.06	1.87±0.60	ND	ND
025	10.69	12.13	22.49±0.02	ND	45.50±0.06	48.10±0.10	93.60±0.14	ND	ND	ND	ND
026	18.95	6.73	12.34±0.02	ND	22.80±0.10	23.20±0.06	46.00±0.12	11.37	1.36±0.10	ND	45.6
027	11.29	10.04	5.39±0.03	0.18±0.01	20.20±0.20	34.80±0.09	55.00±0.24	2.29	1.48±0.10	ND	53.5
028	22.79	7.65	5.62±0.01	0.36±0.01	10.10±0.17	16.60±0.06	26.70±0.21	16.83	ND	ND	ND
029	18.24	8.13	3.91±0.02	ND	13.90±0.12	31.50±0.10	45.40±0.20	9.66	ND	ND	26.2
030	18.96	12.12	13.04±0.03	ND	32.90±0.10	19.90±0.09	52.80±0.16	11.96	1.44±0.10	ND	27
031	18.38	8.29	16.56±0.02	ND	26.50±0.10	9.95±0.07	36.50±0.14	13.89	1.36±0.06	ND	45.3
032	18.58	12.14	9.92±0.02	ND	34.10±0.20	51.40±0.05	85.50±0.22	4.23	ND	ND	19.1
033	81.52	1.32	0.16±0.00	ND	1.30±0.00	20.00±0.03	21.30±0.02	75.45	ND	ND	ND

% NFM: % Neutral fatty matter, % TFA: % Total fatty acids, % FAWB: % Free acid combined with weak base, % FBWA: % Free base combined with weak acid, AV: Acid Value, EV: Ester Value, SV: Saponification Value, % USM: % unsaponifiable matter, % HQ: % Hydroquinone

to remove localised hyperpigmentation and generally tone the skin. Values above this may provoke local irritation to the skin leading to hyperpigmentation, skin thinning or skin cancer (Bleehen, 1977).

Cosmetic emulsions from Africa: The emulsions from Africa had their neutral fatty matter contents varying from 10.69-81.52% (Table 7). The total fatty acid content ranged from 1.32-12.14%. Their free acid or acid combined with weak base content ranged from 1.80-22.49% while the free base or base combined with weak acid content of from 0.18-0.36%. The acid value of the emulsions ranged from 1.30-45.50 mg KOH g⁻¹. The ester value of the emulsions ranged from 9.95-51.40 mg KOH g⁻¹. The saponification value ranged from 21.30-85.50 mg KOH g⁻¹. The unsaponifiable matter content of the emulsions ranged from 1.32-75.45% The unsaponifiable matter content of 025 could not be detected, this is probably because it contained none. The petroleum jelly had a value of 75.45% which contain mostly the paraffin wax. The glycerol content of the emulsions ranged from 1.25-1.87%, which might be the amount added the solubilize the perfumery material. None of the emulsions contained sorbitol which is an indication that sorbitol is not commonly used in this part of the world, unlike glycerol which is readily available in market as a byproduct of the soap manufacturing process. Majority of these emulsions contained hydroquinone ranging from 7.80-53.50 mg g⁻¹ some of which might have been used as antioxidant rather for lightening. The percentage content of hydroquinone ranged from 0.78-5.35%. with the exception of the petroleum jelly with 81.52% (Table 8).

Cosmetic emulsion from Asia: The emulsion from Asia has its neutral fatty matter content to be 16.29% being a cream (Table 8). The total fatty acid content is 6.17%. The free acid or acid combined with weak base content is 5.39% while the free base or base combined with weak acid content is 0.90%. The acid value of the emulsion is 11.40 mg KOH g⁻¹. The ester value of the emulsion is 36.50 mg KOH g⁻¹. The saponification value of this emulsion is 47.90 mg KOH g⁻¹. The

Table 8: Chemical characteristics of the cosmetic emulsion from Asia

Code	NFM	TFA	FAWA	FBWA	AV	EV	SV	USM	GLYCEROL	SORBITOL	HQ
name	%	%	%	%	(mg KOH g ⁻¹)	(mg KOH g ⁻¹)	(mg KOH g ⁻¹)	%	%	%	(mg g ⁻¹)
034	16.32	6.17	5.39±0.01	0.90±0.01	11.40±0.10	36.50±0.05	47.90±0.13	10.54	1.62±0.09	ND	ND

% NFM: % Neutral fatty matter, %TFA: %Total fatty acids, %FAWB: %Free acid combined with weak base, %FBWA: %Free base combined with weak acid, AV: Acid value, EV: Ester value, SV: Saponification value, %USM: %unsaponifiable matter, %HQ: %Hydroquinone

Table 9: Chemical characteristics of cosmetic emulsion from Europe

Code	NFM	TFA	FAWB	FBWA	AV	EV	SV	USM	Glycerol	Sorbitol	HQ
name	%	%	%	%	(mg KOH g ⁻¹)	(mg KOH g ⁻¹)	(mg KOH g ⁻¹)	%	%	%	(mg g ⁻¹)
35	17.8	5.46	2.42±0.01	0.54±0.01	6.30±0.10	41.50±0.08	47.80±0.15	7.64	ND	ND	ND
36	16.45	8.19	10.42±0.01	1.20±0.02	27.80±0.20	31.50±0.06	59.30±0.22	8.07	1.96±0.12	ND	ND
37	11.63	8.09	10.73±0.04	0.72±0.02	22.80±0.10	29.90±0.06	52.70±0.13	4.32	ND	ND	ND
38	11.14	5.36	4.76±0.02	1.08±0.00	7.60±0.30	19.90±0.05	27.50±0.32	6.39	1.75±0.06	ND	12
39	11.25	10.03	19.44±0.05	ND	10.10±0.10	28.20±0.05	38.30±0.13	4.47	1.65±0.08	ND	47
40	11.18	10.16	8.20±0.01	0.90±0.01	21.50±0.10	38.20±0.10	59.70±0.17	2	1.76±0.15	ND	ND
41	12.57	6.85	6.33±0.00	0.45±0.02	15.20±0.20	8.30±0.05	23.50±0.23	9.67	2.48±0.10	ND	ND
42	11.63	11.95	6.64±0.02	0.18±0.01	10.10±0.17	5.00±0.09	15.10±0.26	10.43	ND	ND	ND
43	11.07	14.86	22.59±0.03	ND	51.80±0.15	31.50±0.06	83.30±0.19	3.49	ND	ND	14.8
44	11.45	11.76	11.87±0.03	0.99±0.01	32.90±0.12	33.20±0.20	66.10±0.27	2.48	ND	ND	ND
45	26.05	7.76	3.98±0.02	0.29±0.01	16.40±0.07	26.50±0.13	42.90±0.18	18.27	ND	ND	ND
46	18.27	9.09	17.34±0.02	ND	26.50±0.09	21.60±0.15	48.10±0.22	12.95	ND	ND	28.6
47	16.32	13.89	25.93±0.03	ND	40.40±0.05	61.40±0.06	101.80±0.09	7.1	ND	ND	19.3
49	11.13	10.96	16.71±0.02	0.72±0.01	19.00±0.10	43.10±0.05	62.10±0.13	1.76	1.15±0.07	ND	22.6
50	11.21	12.23	15.62±0.01	0.45±0.03	27.800±0.20	43.10±0.10	70.90±0.27	1.84	1.21±0.09	ND	17.5
51	11.58	5.95	2.97±0.00	ND	7.60±0.10	24.90±0.09	32.50±0.17	5.59	ND	ND	30.1
52	11.45	6.63	5.47±0.01	0.18±0.00	10.10±0.05	51.40±0.10	61.50±0.13	7.98	ND	ND	ND
53	11.08	6.94	3.05±0.01	ND	10.10±0.13	38.20±0.10	48.30±0.20	1.89	1.23±0.10	ND	ND
54	11.19	11.74	10.15±0.02	0.90±0.02	26.50±0.08	26.50±0.10	53.00±0.15	3.81	ND	ND	ND
55	10.97	6.56	3.59±0.01	0.54±0.01	7.60±0.10	23.20±0.06	30.80±0.13	5.39	1.36±0.08	ND	ND
56	11.54	12.97	7.73±0.03	1.17±0.01	22.80±0.09	14.90±0.10	37.70±0.16	6.96	ND	1.39±0.10	ND
57	21.57	15.86	17.34±0.01	0.99±0.00	51.80±0.13	29.90±0.10	81.70±0.20	12.5	1.85±0.10	ND	ND
58	82.63	1.32	0.16±0.00	ND	1.30±0.00	20.50±0.05	21.80±0.03	75.45	ND	ND	ND

unsaponifiable matter content of the emulsion is 10.54% which is quite high, implying that the cream may contain skin substansive components. The glycerol content of the emulsion is 1.62% which might be the amount added to dissolve the perfumery material added to the emulsion. The emulsion does not contain sorbitol or hydroquinone.

Cosmetic emulsions from Europe: The emulsions from Europe had their neutral fatty matter content ranging from 10.97-26.05% with the exception of the petroleum jelly with 82.63% (Table 9). The total fatty acid content ranged from 6.36-15.86%. The petroleum jelly has a fatty acid content of 1.32%. Their free acid or acid combined with weak base content ranged from 2.42-25.93%. Majority of the emulsions contain free base or base combined with weak acid in the range 0.18-1.20%. The acid value of the emulsions ranged from 6.30-51.80 mg KOH g⁻¹ and the petroleum jelly had a value of 1.30 mg KOH g⁻¹. The ester value of the emulsions ranged from 5.00-61.40 mg KOH g⁻¹. The saponification value of these emulsions ranged from

Table 10: Chemical characteristics of cosmetic emulsions from USA

Code name	NFM %	TFA %	FAWB %	FBWA %	AV (mg KOH g ⁻¹)	EV (mg KOH g ⁻¹)	SV (mgKOH g ⁻¹)	USM %	Glycerol %	Sorbitol %	HQ (mg g ⁻¹)
059	10.95	11.63	3.98±0.05	0.54±0.01	6.30±0.10	44.80±0.20	51.10±0.29	3.58	2.43±0.10	ND	ND
060	10.19	12.15	3.20±0.04	0.09±0.01	6.30±0.11	23.70±0.05	30.00±0.15	4.45	2.54±0.08	ND	ND
061	11.27	12.19	19.99±0.03	ND	37.90±0.10	26.50±0.24	64.40±0.29	4.79	1.95±0.04	ND	16
062	11.45	12.57	20.12±0.05	ND	51.80±0.32	23.20±0.05	75.00±0.35	4.68	1.83±0.10	ND	35
063	12.19	12.84	5.55±0.01	0.04±0.02	12.60±0.10	24.90±0.15	37.50±0.23	5.2	2.53±0.06	ND	ND
064	12.86	11.31	6.00±0.01	0.54±0.01	10.10±0.20	48.10±0.35	58.20±0.52	2	ND	ND	ND
065	16.23	8.06	5.60±0.00	0.90±0.03	12.60±0.10	44.80±0.06	57.40±0.15	4.56	2.51±0.08	ND	ND
066	10.17	10.11	5.70±0.02	0.72±0.01	20.20±0.15	21.60±0.09	41.80±0.21	4.83	ND	ND	ND
067	11.96	12.37	25.46±0.06	ND	46.80±0.07	31.50±0.20	78.30±0.32	3.38	1.83±0.10	ND	13.6
068	21.93	7.19	5.47±0.02	ND	17.70±0.09	23.20±0.10	40.90±0.15	15.25	ND	ND	10.2
069	18.15	6.81	5.55±0.02	ND	11.40±0.10	23.20±0.05	34.60±0.12	11.57	ND	ND	18.2
070	10.95	12.69	17.57±0.04	0.18±0.05	27.80±0.20	43.10±0.22	70.90±0.38	10.54	1.73±0.10	ND	ND
071	69.3	12.35	0.16±0.00	ND	1.30±0.02	21.90±0.05	22.20±0.05	63.33	ND	ND	ND
072	20.36	11.84	7.03±0.01	ND	19.00±0.05	18.20±0.15	37.20±0.17	15.26	ND	ND	31.3
073	18.13	7.29	4.37±0.01	0.72±0.00	13.90±0.15	28.20±0.09	42.10±0.24	10.72	ND	ND	18.1
074	17.94	6.11	9.06±0.02	1.08±0.02	19.00±0.12	51.40±0.05	70.40±0.14	5.23	ND	1.43±0.05	ND
075	18.19	6.24	24.52±0.05	ND	35.40±0.20	38.20±0.01	73.60±0.27	7.75	ND	ND	50.2
076	17.83	5.93	9.84±0.03	0.36±0.03	11.40±0.07	48.10±0.15	59.50±0.20	6.54	1.30±0.10	ND	ND
077	17.26	6.89	5.08±0.02	0.45±0.01	27.80±0.03	23.20±0.07	46.00±0.09	11.37	2.34±0.7	ND	ND
078	17.89	5.67	10.15±0.01	0.99±0.01	20.20±0.06	28.40±0.17	48.60±0.23	10.05	ND	ND	ND
079	18.25	6.39	8.04±0.01	ND	15.20±0.13	36.50±0.07	51.70±0.19	9.47	ND	ND	ND
080	17.82	6.1	3.98±0.01	ND	12.60±0.15	33.20±0.01	45.80±0.13	8.84	ND	ND	19.6

15.10-101.80 mg KOH g⁻¹. The unsaponifiable matter content of the emulsions ranged from 1.76-18.27%. The petroleum jelly had a value of 75.45% which contain mostly petrolatum. The glycerol content of the emulsions ranged from 1.15-2.48% which might be the amount added to dissolve the perfumery material added to the emulsion. Only one of the emulsions contained sorbitol at 1.39% level. The hydroquinone content of the emulsions, were quite low ranging from 12.00-47.00 mg g⁻¹. The hydroquinone may have been included in most cases as an antioxidant rather than for skin lightening. The percentage content of hydroquinone ranged from 1.20-4.70%. Only one of these emulsion had a value higher than 3.0%.

Cosmetic emulsions from USA: The emulsions from USA have their neutral fatty matter content ranging from 10.19-69.30% (Table 10). The emulsion with 69.30% is 071 which contains ample amount of cocoa butter, mineral oil and microcrystalline wax. The total fatty acid content ranged from 5.67-12.84%. Their free acid or acid combined with weak base content ranged from 3.20-25.45%. 071 had a value of 0.16%, showing that the most of the fatty acids in the cocoa butter may have been saponified during the process of manufacture of the cream to produce a mix emulsifier system which results in increased stability of the emulsion system. Majority of the emulsions contain free base or base combined with weak acid ranging from 0.04-1.08%. The acid value of the emulsions ranged from 1.30-51.80 mg KOH g⁻¹, 071 had the smallest value. The ester value of the emulsions ranged from 18.20-51.40 mg KOH g⁻¹. The saponification value of these emulsions ranged from 22.20-78.30 mg KOH g⁻¹. The unsaponifiable matter content of the emulsions ranged from 2.00-15.25%, 071 had a value of 63.33%. This shows that the fatty alcohols level of the cream must be quite high; it also reflects the presence of hydrocarbons and waxes present in

Table 11: Metal levels of cosmetic emulsions from Nigeria

Code name	Fe (mg L ⁻¹)	Cr (mg L ⁻¹)	Pb (mg L ⁻¹)	Al (mg L ⁻¹)
001	0.335	ND	0.15	0.481
002	0.57	ND	0.1	0.989
003	0.71	0.043	0.2	ND
004	0.82	0.043	0.18	ND
005	1.18	0.008	0.39	ND
006	0.62	0.037	ND	ND
007	0.97	ND	0.01	ND
008	0.61	0.087	0.06	ND
009	0.69	0.051	0.08	ND
010	0.732	ND	0.12	0.597
011	0.816	ND	0.09	ND
012	0.57	0.085	0.02	ND
013	1.58	ND	0.04	ND
014	0.91	ND	0.05	ND
015	1.28	ND	0.12	ND
016	1.22	ND	0.12	ND
017	1.2	ND	0.12	ND

ND: Not detected by the method employed

the mineral oil or the wax used for its production. If sterols are present, it may make the cream to have skin smoothening and softening effect when it is used. The emulsions from USA had the highest amount of glycerol content which ranged from 1.30-2.54% which might be the amount added to solubilize the perfumery material and the quantity added to the emulsion for the purpose of moisturization. One emulsion contained sorbitol at 1.43% level. The hydroquinone content of the emulsions was quite low ranging from 10.20-50.20 mg g⁻¹ which might have been used as antioxidant and toner. Only two emulsions have values higher than 3.0 mg g⁻¹. Their percentage hydroquinone range therefore is 1.02-5.20%.

Metal analysis

Cosmetic emulsions from Nigeria: All the cosmetic emulsions from Nigeria contained iron (Table 11) and this is indicative of the type of water used in the preparation of the emulsions. It is most likely that the water used was utility water or distilled water instead of de-ionized water that was claimed to have been used by some manufacturers. The concentration of iron in the emulsions ranged from 0.335-1.580 mg L⁻¹. Some of these emulsions contained chromium, lead and aluminium. The concentration of chromium ranged from 0.008-0.087 mg L⁻¹. The presence of chromium in these cosmetic emulsions might be due the use of chromium coated apparatus in the course of their production. The concentration of lead ranged from 0.01-0.39 mg L⁻¹. This might be due to use of utility water obtained from lead pipes. The concentration aluminium ranged from 0.481-0.989 mg L⁻¹. Only three of these emulsions contain aluminium and these are likely to be as a result of using magnesium aluminium silicate for interfacial strengthening of the emulsion or due to treatment of utility water with industrial alum. The presence of these metals might also be as a result of the use of polluted water or hydrocarbons from the petroleum refining process.

The presence of these heavy metals in cosmetic emulsions may make it toxic to the skin. Some of these metals could be absorbed through some areas of the skin into the body and most of these metals can only be tolerated by human beings at very low concentrations. Apart from the fact that they cause blood poisoning; they also, destabilize emulsion system by forming free radicals thereby

Table 12: Metal levels of cosmetic emulsions from Africa

Code name	Fe (mg L ⁻¹)	Cr (mg L ⁻¹)	Pb (mg L ⁻¹)	Al (mg L ⁻¹)
018	0.81	ND	0.22	ND
019	0.61	0.003	0.05	ND
020	1.12	ND	0.05	ND
021	0.53	ND	ND	ND
022	0.63	ND	ND	0.705
023	0.75	0.05	0.2	ND
024	0.72	ND	0.05	0.861
025	0.69	ND	0.08	ND
026	0.77	0.054	ND	ND
027	0.64	0.013	0.07	ND
028	0.75	ND	0.08	ND
029	0.58	ND	0.11	ND
030	0.81	0.048	0.08	ND
031	0.72	ND	0.22	ND
032	0.81	ND	0.18	ND
033	0.93	ND	0.03	ND

ND: Not detected by the method employed

Table 13: Metal levels of the cosmetic emulsion from Asia

Code name	Fe (mg L ⁻¹)	Cr (mg L ⁻¹)	Pb (mg L ⁻¹)	Al (mg L ⁻¹)
034	0.61	0.049	0.25	ND

ND: Not detected by the method employed

reducing their shelf life (Health Canada, 2009). Therefore, effort should be made to make sure that these metals are absent in cosmetic emulsions as much as possible. This can be achieved by complexing such metal ions with chelating compounds like EDTA (Oyedeki and Oderined, 2005) which some of the manufacturers have done and also by using de-ionized water.

Cosmetic emulsions from Africa: All the cosmetic emulsions from Africa like those from Nigeria contained iron (Table 12) and this is indicative of the type of water used in the preparation of the emulsions. The concentration of iron in the emulsions ranged from 0.530-1.120 mg L⁻¹. Some of these emulsions contained chromium, lead and aluminium though their levels are low compared to those manufactured in Nigeria. The concentration of chromium ranged from 0.003-0.054 mg L⁻¹. The concentration of lead ranged from 0.030-0.220 mg L⁻¹. Only two of these emulsions contain aluminium at 0.705 and 0.861 mg L⁻¹ levels.

Cosmetic emulsion from Asia: The cosmetic emulsion from Asia (Table 13) had an iron level of 0.610 mg L⁻¹. Its chromium level was 0.049 mg L⁻¹. The concentration of lead in this emulsion was 0.250 mg L⁻¹ and its aluminium level could not be detected.

Cosmetic emulsions from Europe: All the cosmetic emulsions from Europe contained iron (Table 14). The concentration of iron in the emulsions ranged from 0.060-1.090 mg L⁻¹. The concentration of chromium ranged from 0.011-0.097 mg L⁻¹. The concentration of lead ranged from 0.040-0.240 mg L⁻¹. Only four of these emulsions contain aluminium at 0.340-0.958 mg L⁻¹ levels.

Cosmetic emulsions from USA: The iron levels of the cosmetic emulsions from USA (Table 15) ranged from 0.050-1.830 mg L⁻¹. The emulsion with the highest iron level so far is 080 with a level

Table 14: Metal levels of cosmetic emulsions from Europe

Code name	Fe (mg L ⁻¹)	Cr (mg L ⁻¹)	Pb (mg L ⁻¹)	Al (mg L ⁻¹)
035	0.36	ND	ND	ND
036	0.48	ND	ND	0.767
037	0.518	ND	ND	ND
038	0.28	ND	ND	ND
039	0.34	ND	ND	ND
040	0.82	ND	ND	0.958
041	0.63	ND	ND	ND
042	0.5	0.093	0.18	ND
043	0.35	0.065	0.14	0.34
044	0.495	0.018	0.12	ND
045	0.74	0.03	0.22	ND
046	0.94	0.097	0.19	ND
047	0.06	0.016	0.24	0.579
048	0.92	0.063	0.04	ND
049	0.56	0.051	ND	ND
050	0.55	0.031	ND	ND
051	0.62	ND	0.04	ND
052	0.68	ND	0.13	ND
053	0.48	ND	0.13	ND
054	0.59	0.016	0.22	ND
055	0.7	0.011	0.18	ND
056	0.76	0.038	0.24	ND
057	0.59	0.016	0.08	ND
058	1.09	ND	0.12	ND

ND: Not detected the method employed

Table 15: Metal levels of cosmetic emulsions from USA

Code name	Fe (mg L ⁻¹)	Cr (mg L ⁻¹)	Pb (mg L ⁻¹)	Al (mg L ⁻¹)
059	0.78	ND	0.06	0.862
060	0.42	ND	ND	ND
061	0.1	ND	ND	0.38
062	0.05	ND	ND	0.461
063	0.31	ND	ND	ND
064	0.7	0.002	ND	ND
065	0.54	ND	ND	ND
066	0.463	ND	ND	0.312
067	0.35	ND	0.28	0.895
068	0.55	ND	ND	ND
069	0.59	ND	ND	ND
070	0.658	ND	ND	1.002
071	0.34	ND	ND	0.32
072	0.57	0.021	0.19	ND
073	0.88	0.019	0.26	ND
074	0.591	0.006	0.1	0.648
075	0.56	0.051	ND	ND
076	0.59	0.071	0.04	ND
077	0.71	0.067	ND	ND
078	0.79	0.043	0.11	ND
079	0.64	ND	0.1	ND
080	1.83	ND	0.26	0.967

ND: Not detected with the method employed

of 1.830 mg L⁻¹. This may also be as a result of using all steel reactors which may have started to corrode. The concentration of chromium ranged from 0.002-0.071 mg L⁻¹. The concentration of lead ranged from 0.040-0.280 mg L⁻¹. The aluminium levels of the emulsions ranged from 0.312-1.002 mg L⁻¹.

CONCLUSIONS

Most of the cosmetic emulsions did not contain hydroquinone at levels that could be detrimental to skin health. The heavy metal levels were also within acceptable values as iron levels experienced could only be as a result of presence in utility water

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