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Full Length Research Paper

Determination of hydroquinone and mercury concentrations in some skin lightening lotions and creams sold in Southeastern Nigeria

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In this study, thirty cosmetic skin lightening emulsions (lotions and tubes) were randomly purchased from an open market in Awka and Enugu cities of Southern Nigeria with the aim of finding out if the creams contained hydroquinone and mercury at levels which were harmful to the users. Their physico-chemical properties like pH which ranged from 4.25 - 7.25 and moisture content from below 20 to 90% were also determined. The concentration of mercury in the creams ranged from below 0.00 to 200 µg/g and that of hydroquinone ranged from 0.288 - 2.35%. Mercury was not detected in most of the creams analyzed, only two samples (1 and 17) contained mercury at a much higher concentration (200 and 100 µg/g) than 1 µg/g which is the WHO limit. All the creams analyzed contained hydroquinone at concentration lower than 2% which is the recommended WHO limit except two creams with hydroquinone concentration barely higher than 2%. In conclusion, most of the creams do not contain hydroquinone or mercury at levels that are detrimental to human health and also most of the creams had pH and moisture content that will not irritate the skin, but rather provide adequate moisture and hydration to the skin.

Key words: Cosmetics, hydroquinone, mercury, emulsions, determination.

INTRODUCTION

Cosmetics are care substances used to enhance the appearance or odour of the human body. They are generally mixtures of chemical compounds, some being derived from natural sources, many being synthetic (Gunter et al., 2005). In the U.S., the Food and Drug Administration (FDA), which regulates cosmetics defines cosmetics as “intended to be applied to the human body for cleansing, beautifying, promoting attractiveness or altering the appearance without affecting the body’s structure or functions. Cosmetic preparations include skin care preparation, creams, lotions, emollients and de-pigmentation agents like hydroquinone (Encyclopedia Brit, 1979). Most of the preparations bleach the skin and eventually pose potential risk to the health of the users. The most active chemicals in creams, lotions, emollients which lighten the skin are mercury and hydroquinone although other ones like Dimethicone, Ceteareth 20, Citric acid, Benzophenone, Kojic acid, Cinnamomum Subavenium a Chinese herb, Azclaicacid, Arbutin, Vitamin C and its forms (ascorbic acid, magnesium ascorbyl phosphate are considered an effective antioxidant for the skin and help to lighten the skin), Propyl paraben, etc., are also chemicals contained in the bleaching products (Serra-Baldrich et al., 1998).

The human skin colour is determined by the amount of melanin produced. In the ages ago, humans have constantly labeled and stereotyped each other on the basis of skin colour. The quest for lightening of skin in most African communities came as a result of discrimination on the black races. Since fairness is regarded as beauty and highly social status, most women in African and Asian communities indulge in skin care products that lighten the skin (Counter, 2003). Hydroquinone is considered the primary topical ingredients for inhibiting melanin production (Cutis, 2005). Inhibition of the enzy-matic activity of tyrosinase by competitive inhibitors results in decreased or absent melanin synthesis by the melanocytes in human skin

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(Smith et al., 2009; Halaban et al., 2002). Cosmetic skin lightening products containing hydroquinone often have a strident scent reminiscent of bleach. According to the Food and Drug Administration (FDA) and World Health Organization (WHO), non prescription skin-lightening creams can contain up to 2% hydroquinone. Some concerns about this chemical safety on skin have been expressed, but the research when it comes to topical application indicates negative reactions are minor or as result of using extremely high concentrations (USFDA, 2006). Hydroquinone are unsafe for use because it increase the risk of developing skin cancers from sun exposure, thus it makes one skin more sensitive to the sun's damaging ultraviolet rays. It has been banned in some countries like France because of fears of cancer risk (Belezal-Sandra, 2012), also in section 5 and 29 of 1995 cosmetic product regulation in Nigeria, has prohibited the use of bleaching agents which includes hydroquinone and mercury. It can harm the reproductive system and damages the immune system. It has numerous unfavorable effects with long-term application, including irritative dermatitis, melanocyte destruction, contact dermatitis and ochrono-sis (Adebanjo, 2002; Hardwick, 1989). It can be irritant particularly in higher concentrations of 4% or greater (Fuller, 2006). Many skin whiteners contain toxic mercury such as mercury (II) chloride or ammoniated mercury as the active ingredients. Some of these creams may contain up to more than 2-5% mercury that will be harmful to health thus resulting in mercury poisoning (Clarkson and Magos, 2006). However, mercury has been banned in most countries for use in skin whitening (1976 in Europe, 1990 in USA) because it accumulates on skin and it can have the opposite results in the long term. Some studies suggest that long term use could cause systemic absorption that leads to tissue accumulation of the substance. Mercury is a highly volatile element with a long atmospheric half-life. As a result of these physical properties, it is ubiquitous in the environment and exposure is not an isolated concern but rather a global threat to human health. In recent years, research has revealed that even chronic exposure to very low concentrations has the ability to cause long-lasting neurological and kidney impairment (Hutson et al., 1999). Mercury and its compounds are toxic compounds. Toxic effects especially in the case of methylmercury may be taking place at lower concentrations. It is a poison for the nervous system. Exposure during pregnancy is of most concern, because it may harm the development of the unborn baby's brain (Clifton, 2007). Some studies suggest that small increase in exposure may affect the heart and circulatory system. Mercury containing cosmetics preparation has been represented for many years as skin bleaching agents. Toning creams containing mercury in the form of inorganic mercury are mainly used by dark skinned people mostly in developing countries like Nigeria to lighten their skin tone thus inhibiting the production of the skin pigment melanin (Marzulli and Brown, 1972). The United States Food and Drugs Administration (USFDA) in 1992 established the maximum acceptable level of mercury in cosmetic to be 1 µg/g. And World Health Organization (WHO) in 1991 established the maximum acceptable level of mercury in cosmetic to be 1 µg/g also.The aim of this study is to analyze different skin whitening cosmetics present in the market for the determination of the hydroquinone and mercury contents and raising awareness on the need for more stringent control, the use and distribution of such products to prevent possible long-term adverse effect.

MATERIALS AND METHODS

Sampling and determination of country of manufacture

Thirty cosmetic emulsions were obtained by random purchase from cosmetics shops in open market in Awka and Enugu cities of Southern Nigeria. The country of manufacture was ascertained by the inspection of the labels and package of the samples.

Physiochemical analysis

The pH and moisture content of the cosmetic emulsions were carried out using standard analytical methods.

Determination of colour

The colour of the cosmetic emulsions was determined by visual observation.

Determination of pH

The pH of the samples was measured by Electrometric method using laboratory pH meter Hanna Model H1991300 (APHA, 1998). The electrodes were rinsed with distilled water and blot dry. The pH electrodes were further rinsed in a small beaker with a portion of the sample. Sufficient amount of the sample was poured into a small beaker to allow the tips of the electrodes to be immersed to a depth of about 2 cm. The electrodes were at least 1 cm away from the sides and bottom of the beaker. The temperature adjustment dial was adjusted accordingly and the pH meter was turned on and the pH of the sample was recorded.

Determination of moisture content

An 1R-30 Denver instrument moisture analyser was used to determine the moisture. The cosmetic emulsion being analysed was dried under standard condition. The weight incurred was then quantitatively determined (AOAC, 1984). To 1 ml of each of standard solution and a test sample in test tubes, 5 ml of anthrone reagent was added

Table 1. Physiochemical results of the samples with the country of manufacture.

Sample	Country of manufacture	Colour	pH	Moisture content (%)
1	Indonesia	White	6.65	90
2	Cote d'Ivoire	White	4.90	85
3	India	White	6.63	70
4	India	White	7.18	70
5	United Kingdom	White	5.31	50
6	Italy	White	6.87	50
7	Italy	White	5.98	20
8	Italy	White	7.15	25
9	India	White	7.08	40
10	Germany	White	7.15	40
11	Nigeria	White	6.92	85
12	Cote d'Ivoire	White	4.74	75
13	Cote d'Ivoire	White	4.25	55
14	Nigeria	White	6.86	50
15	Nigeria	White	7.10	55
16	Nigeria	White	7.11	60
17	Cote d'Ivoire	White	5.01	50
18	Nigeria	White	6.64	60
19	Cote d'Ivoire	Light pink	4.50	70
20	Nigeria	White	6.92	30
21	Philippines	White	6.85	60
22	Cote d'Ivoire	Peach	5.85	90
23	Cote d'Ivoire	Off-white	4.77	60
24	Cote d'Ivoire	White	5.85	45
25	USA	White	6.29	65
26	Cote d'Ivoire	White	6.65	70
27	Cote d'Ivoire	White	6.78	85
28	Republic du Congo	Peach	6.85	75
29	Cote d'Ivoire	Yellow	6.49	60
30	Cote d'Ivoire	White	6.32	85

and mixed properly. The tubes were covered and boiled in water for 20 mins for the colour to develop. After cooling the tubes, their absorbances were read at 620 nm against a blank containing only 1 ml of water and 5 ml of anthrone reagent. The percentage moisture content was automatically displaced on the screen of the moisture analyzer.

Digestion of samples for mercury determination

The samples were digested for total mercury determination by the method used by Adrain (1973). About 2 g of each dried sample was weighed into a digestion flask and 20 ml of the acid mixture (650 ml Conc. HNO_3; 80 ml Perchloric acid; 20 ml Conc H_2SO_4) was added. The flask was heated until a clear digest was obtained. The digest was diluted with distilled water to 100 ml mark.

Mercury determination

Determination of mercury in the samples was conducted using Varian AA240 Atomic Absorption Spectrophotometer. The sample was thoroughly mixed by shaking and 100 ml of it was transferred into a glass beaker of 200 ml volume, to which 5 ml of conc. nitric acid was added and heated to boil till the volume is reduced to about 15-20 ml. More 5 ml of conc. nitric acid was added for the entire residue to completely dissolve. The mixture was cooled, transferred and made up to 100 ml using metal free distilled water. The sample was aspirated into the oxidizing air-acetylene flame. When the aqueous sample was aspirated, the sensitivity of 1% absorption was observed.

Sample preparation

About 25.0 ml of the sample was added into a separating funnel with 4 ml of glacial acetic acid. It was swirled to allow the raid forming gas to escape. 50 ml of water saturated ethyl acetate was also added. Vigorous shaking continued and venting occasionally for 30 s. The phases were allowed to separate and acid dilution of hydroquinone extract was also done.

Determination of hydroquinone

A total of 200 ml of distilled water was added to a 250 ml volumetric flask followed by 25 ml of 1.0 M sulphuric acid. To another 50 ml volumetric flask, 20 ml of distilled water was added followed by 50 ml of 1.0 M sulphuric acid. 20 ml of the upper layer (ethyl acetate) of the prepared sample was added to both the 250 ml and 50 ml volumetric flasks. The volumetric flasks were swirled until the ethyl acetate was completely dissolved. Dilution of both volumetric flasks to volume flask was done and the contents were mixed by inverting 6 to 10 times.

A clean silica cell was rinsed and filled with a solution in the 250 ml volumetric flask. The absorbance of the solution in the cell versus air spectrophotometer at 288 nm was measured and recorded as A288. The solution in the 1 cm silica cell was discarded and rinsed with at least 6 portions of the solution in the 50 ml volumetric flask and then the cell was filled. The absorbance of the solution in the cell versus air spectrophotometer at 250 nm was done and recorded A250:

Calculation: 12:01 (A288) – 0.117 (A250) – 0.59.

RESULTS AND DISCUSSION

The results of the research are listed in Tables 1 to 3. It

Table 2. Result of mercury detected in the samples.

Sample	Quantity of Hg detected (µg/g)	Quantity of Hg indicated by the manufacturer	WHO standard (µg/g)
1	200	NI	1
2	NIL	NI	"
3	NIL	NI	"
4	NIL	NI	"
5	NIL	NI	"
6	NIL	NI	"
7	NIL	NI	"
8	NIL	NI	"
9	NIL	NI	"
10	NIL	NI	"
11	NIL	NI	"
12	NIL	NI	"
13	NIL	NI	"
14	NIL	NI	"
15	NIL	NI	"
16	NIL	NI	"
17	100	NI	"
18	NIL	NI	"
19	NIL	NI	"
20	NIL	NI	"
21	NIL	NI	"
22	NIL	NI	"
23	NIL	NI	"
24	NIL	NI	"
25	NIL	NI	"
26	NIL	NI	"
27	NIL	NI	"
28	NIL	NI	"
29	NIL	NI	"
30	NIL	NI	"

Key note: Hg = Mercury; WHO = World Health Organization; NI = Not indicated.

was observed that 55% of these emulsions were manufactured in Africa and 45% were from foreign countries. There were 19 emulsions manufactured in Africa, while 11 emulsions were manufactured in foreign countries. 25 samples studied were white, 2 peach, 1 off-pink and 1 light pink in colour. 20% of the sample studied had pH which is acidic (4.25 - 4.90), 50% is slightly acidic (5.01 - 6.92) and 30% is neutral (7.10 - 7.25). The manufacturers of the samples whose pH are neutral and slightly acidic titrated the emulsion to a point that it cannot irritate the skin. The pH of cosmetics creams and lotions indicates the amount of free fatty acids and bases present in them. The pH of the skin is acidic, that is, 3 to 5 (Raven and Johnson, 1999). Acidic creams should not be used rather neutral creams are advisable. Most of the cosmetic sample have high percentage moisture content (50 - 90) and thus will provide adequate moisture and hydration to the skin thereby making the skin feel soft (Oyedeji and Oderined, 2005). All the cosmetic emulsion with low percentage moisture content (20 - 40) will keep the skin dry and thus inhibit the comfort. 90% of the samples did not contain mercury. Samples 1 and 17 (from Indonesia and Cote D' Ivoire) mercury content is alarming as compared with the standard of World Health Organization which is 1 µg/g. Skin lightening emulsions that contain mercury to any extent is detrimental to the skin since it accumulate gradually on skin on constant usage. The result of this research also revealed that all the samples contain hydroquinone but not above the standard recommended by World Health Organization. The manufacturers adhered to the standard of quantity of hydroquinone in cosmetic emulsions thus reducing the effect of hydroquinone on skin.

Conclusion

This study establishes the presence of hydroquinone in all the samples while mercury was found in only samples

Table 3. Result of hydroquinone content detected in the sample.

Sample	Quantity of hydroquinone detected (%)	Quantity of hydroquinone indicated by the manufacturer	WHO standard (2%)
1	1.754	NI	"
2	0.312	Present but the quantity was not indicated	"
3	1.207	NI	"
4	0.350	NI	"
5	0.288	2%	"
6	0.540	NI	"
7	NIL	NI	"
8	0.860	NI	"
9	0.490	NI	"
10	0.491	NI	"
11	0.589	NI	"
12	0.297	NI	"
13	0.487	2%	"
14	0.608	NI	"
15	0.604	NI	"
16	0.655	NI	"
17	0.372	NI	"
18	0.563	NI	"
19	0.294	NI	"
20	0.634	NI	"
21	2.350	N1	"
22	0.660	None (free)	"
23	1.010	2%	"
24	0.350	2%	"
25	0.620	2%	"
26	0.560	NI	"
27	0.480	2%	"
28	0.930	2%	"
29	0.890	2%	"
30	0.900	NI	"

Key note: NI = Not indicated; WHO = World Health Organization.

A and Q at an alarming rate. The pH of the cosmetic creams is not too acidic to irritate the skin since most of them have pH from 5.01 to 7.25. The percentage moisture content of most of the samples is normal for soft and hydrated skin. Also there is need for more stringent control by regulatory bodies appointed by the government to check the quality of cosmetics in the market.

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