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Heavy metal assessment of some eye shadow products imported into Nigeria from China

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ABSTRACT

Chinese made eye shadows (cosmetic commonly used by women and children) were analysed to determine the levels of heavy metals (Pb, Cd, Ni, Cu, Zn, Cr, Co, and Mn) in the products. Different samples of eye shadow were randomly selected from products available in the shops at Zaria, Kano and Kaduna markets in Nigeria. After digestion with concentrated acids (HNO_3 and HCl), concentrations of the selected heavy metals were determined in triplicate using a flame atomic absorption spectrophotometer. Nickel, copper, zinc, cobalt and manganese were detected in all the colours of eye shadow in varying concentrations. Chromium was also detected in all the colours except one (Diamond pink). The regulations relating to cosmetics products gave no limit values for toxic elements such as metals occurring as impurities in cosmetics products. However, it has been proposed that the levels of nickel, cobalt and chromium should preferably be less than 170 $\mu g g^{-1}$ and Lead should not exceed 20 $\mu g g^{-1}$. 85% of the colours have Ni and Co concentrations above 170 $\mu g g^{-1}$ but Cr concentrations were below this limit in all the colours. Only 2 brands (3 colours) have lead content higher than 20 $\mu g g^{-1}$. 7 out of 20 colours (35%) of the brands of eye shadows contain cadmium at low concentrations. It is obvious from the present study that the use of facial cosmetics like eye shadow exposes users to low levels of heavy metals.

Keywords: Heavy metal; Eye shadow; cosmetics.

INTRODUCTION

China is the source of 60 percent of recent cosmetics and other product recalls because of the presence of heavy metals in levels toxic to human in these products [1]. Some heavy metals have been used as cosmetics ingredients in the past. Examples include the preservative thimerosal (mercury), the progressive hair dye lead acetate and a number of tattoo pigments such as red cinnabar (mercuric sulfide). As the issue of heavy metals as deliberate cosmetics ingredients has been addressed, attention turns to the presence of these substances as impurities. Eye shadow, a

cosmetic commonly used by women and children has been reported to contain toxic metals [2, 3]. It is a typical example of a group of cosmetic products in which the significance of pigment is great. Some toxic elements and their compounds are water-soluble and moist skin can therefore promote the percutaneous absorption of elements occurring as impurities in pigments [4].

The excipients used also affect the absorption through the skin [5]. On the other hand, eye shadow is applied dry to the skin, lowering the risk of percutaneous absorption of pigments and thus also of toxic elements. The skin of the eyelid is thin and eczemas of the eyelids are common. Absorption of elements into the circulation is possible but percutaneous absorption of elements is slower than that of fat-soluble substances. Some facial (make-up) cosmetics commonly used in Nigeria were analyzed for their contents of the heavy metals; lead, cadmium, chromium, nickel, zinc and iron [6]. The study showed that the continuous use of these cosmetics may enhance the absorption of especially Cd and Pb during eating for lipsticks and during sweating for the other facial make-ups. Exposure to lead by dermal contact can contribute to significant toxicity [7].

The use of leaded eye cosmetics have been observed to be strongly correlated with elevated blood lead levels [8, 9]. The environmental and public health implications of exposure to lead in Africa have been reviewed and the use of local herbal remedies and cosmetics has been indicated as sources of lead exposure [10]. A study of the use of skin lightening creams containing hydroquinone, corticosteroid and mercury in Nigeria revealed a prevalence of dermatological side effects with exogenous ochronosis as the commonest [11]. Under arm cosmetics are being investigated as possible cause of breast cancer. A biological basis for breast carcinogenesis could result from the ability of the various constituent chemicals to bind to DNA and to promote growth of the damaged cells [12]. There is a growing concern about the physiological and behavioural effects of environmental trace metals in human population. The toxicity of lead at high levels of exposure is well known but a major concern of today is the possibility that continual exposure to relatively low levels of lead may entail adverse health effects [13].

One study in Italy investigated the connection between children's makeup with nickel, cobalt and chromium and skin irritation. They found that children do react to these metals, especially if they are prone to skin allergies or have damaged skin, such as from scrapes or cuts [14]. The book *Contact Dermatitis*, a standard text for specialists in the field, also notes that researchers "have seen patients with strong nickel sensitivity that seems to have reactions from some cosmetics" [15]. The question of skin reactions to cosmetics is much broader than just face paints. Numerous other cosmetics have been linked to Dermatitis and allergic reactions, [16] including perfumes, [17] children's bath products [18], mascara [19] and other eye-care products, hair dye (especially in children), [20, 21] facial care products, body care products and shampoo [22]. Fragrance chemicals and preservatives are some of the most significant allergens. One study in India found that reactions to cosmetics, toiletries and topical applications are the most common single reason for hospital referrals with allergic contact dermatitis [23]. However, no known work has been done to investigate the heavy metals content of Chinese eye shadows which are available in cosmetics shops in Nigeria, hence the need for this study. Therefore, this study was designed to ascertain the levels of lead, cadmium, chromium, nickel, zinc, copper, cobalt and manganese in Eye shadow. The samples were collected from Zaria, Kano, and Kaduna markets in Nigeria.

MATERIALS AND METHODS

Samples of eye shadow were homogenized in acid washed mortar and pestle. 300mg of the processed sample was weighed into a beaker for acid digestion. After the digestion and cooling, the solution was filtered through a Whatman 41 filter to remove the insoluble particles and brought to a final volume of 50ml with de-ionized water. Blank sample was also prepared similarly. Glass wares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO_3 for 24hours; cleaned with distilled-deionized water and in such a manner that no contamination occurred [24]. Standards were prepared with serial dilution technique within the range of 0.5-2.5ppm for lead, cadmium, nickel and manganese, 1-5ppm for copper and cobalt, 0.5-2ppm for zinc and 2-10ppm for chromium. The instrument was first calibrated with stock solutions of the prepared standards before analysis. The final processed samples were quantitatively analyzed using Buck Scientific VGP 210 Flame Atomic Absorption Spectrophotometer. After every five samples analyzed using AAS, the first sample was repeated for quality check. Only when the results were within 10% of earlier readings did the analysis proceed further.

RESULTS AND DISCUSSION

The distribution of heavy metals in the Eye shadows studied is shown in Table 1. 7 brands of eye shadows were randomly selected for analysis but a single brand may contain several colours which have been analyzed separately. Altogether, the study covered 20 colours of 7 brands, nickel, copper, zinc, cobalt and manganese were detected in all the colours in varying concentrations. The concentration of lead and cadmium are generally low compared to other metals. Chromium was also detected in all the colours except one (Diamond pink). The lowest concentration for lead and cadmium were below the detection limit (3 colours for Pb and 13 colours for Cd). In the majority of the products, the lead content was lower than 20 μgg^{-1}. Only 2 brands (3 colours) have lead content higher than 20μgg^{-1}. 7 out of 20 colours (35%) of the brands of eye shadows contain cadmium at low concentrations. The fact that cadmium and lead were not detected in some of the products shows that it is possible to eliminate these impurities from eye shadows.

The regulations relating to cosmetics products gave no limit values for toxic elements such as metals occurring as impurities in cosmetics products. However, it has been proposed that the levels of nickel, cobalt and chromium should preferably be less than 170 μgg^{-1} and lead should not exceed 20 μgg^{-1} [5]. Some of the colours analyzed have concentrations of nickel, cobalt and chromium above this limit. For nickel, only 4 colours ((Diamond(Pink), Qiany(White), Midle(Purple) and Qianny(White)) have concentration below 200 μgg^{-1}. The highest nickel concentrations were measured in Ladyhood (Brown (359.44 μgg^{-1}), Yellow (306.67 μgg^{-1}), Darkgrey (285.00 μgg^{-1}) and Purple (359.44 μgg^{-1}). The levels of nickel were generally higher than those of other metals.

Copper contents were generally low except in FBI (blue). This shows that Cu might have been used as a pigment in this particular colour because another colour (Ash) of the same product had copper content as low as 27.78 μgg^{-1}. 6 out of the 20 colours studied have zinc content below 200 μgg^{-1}. The highest levels of zinc were observed in 2 brands of the eye shadows (Ladyhood

and Diamond). In Ladyhood [Yellow (305 μgg^{-1}), Darkgrey (342.22 μgg^{-1}), and Purple (332.22 μgg^{-1})], In Diamond [Pink (318.89 μgg^{-1}), and Blue (334.44 μgg^{-1})].

The chromium concentrations were generally below 100 μgg^{-1} except in Qiany (Black (150 μgg^{-1}) and Brown (133.33 μgg^{-1})]. Chromium was below detection limit in Diamond (Pink). The levels of chromium are generally within the acceptable limit. Cobalt concentrations were higher than 200 μgg^{-1} in 45% of the colours. The lowest Cobalt concentration was observed in Diamond (blue) while its highest concentration was observed in Shas (Army green). Only 3 out 20 colours (15%) of the eye shadows had manganese content higher than 100 μgg^{-1}. This implies that manganese content were generally low in the products.

Analysis of Variance (ANOVA) (Table 2-Table 4) was done on each brand of the eye shadow to see if there is significant variation in the concentrations of heavy metals in different colours of each brand. In Ladyhood, there is significant difference in the levels of nickel in all the four colours analyzed. This shows that the type of pigment used in eye shadow contributes to its heavy metal content. In Diamond, four colours were also analyzed and the concentrations of nickel and zinc show significant differences of these metals in the colours. Other metals also show significant differences ($P< 0.05$).

The concentrations of 5 metals (lead, cobalt, nickel, chromium and arsenic) were determined in 25 brands of eye shadows [2]. The levels of these metals observed were generally lower than those observed in this study except for chromium. The highest concentration of chromium obtained was 5470 μgg^{-1} which is far higher than the highest obtained in this study. Some facial cosmetics available in Nigeria were also analyzed for their contents of heavy metals (lead, cadmium, chromium, nickel, zinc and iron) [6]. The results obtained are comparable to that obtained in this study. High levels of nickel, zinc and iron were observed as observed in this study.

The campaign for safe cosmetics published a report on heavy metals in face paints [25]. All the 10 products studied contained lead, 4 contained nickel, 2 contained cobalt and 5 contained chromium (ranging from 1.6 to 120ppm). The levels found in all the products exceeded the recommendation of several industries [26]. The metals analyzed in this study are not listed as ingredients on any of the products. Due to a lack of manufacturer testing and regulatory oversight, it is possible that the companies are not even aware that the products are contaminated. These contaminants likely get into the products when poor-quality ingredients are used. Most likely the metals are contaminants from one or more of the inorganic base materials. Since all the metals are found in various environments, manufacturers would have to test the raw ingredients before they are assembled into the final products in order to track the origin of these contaminants.

Eczema of the eyelids is common and may be caused by cosmetics. Mascara, eye-liner, eye shadow, and eyebrow pencil or powders are the most commonly used eye make-ups [15]. The metals which may be present in the colouring agents are often overlooked as causes of allergic contact dermatitis of the eyelids. Eye shadow should not be applied to broken skin. Eye shadows contain particles which differ in size and have various types of edges. The eyelids can therefore be mechanically broken, enabling the penetration of pigment and thus also of metals into the

body. Metals are also absorbed into the organism through healthy skin [4]. Although absorption of metals through the skin is often ignored, studies show that lead actually can be absorbed through the skin [27]. One study found that skin-absorbed lead can be detected in sweat, blood and urine within six hours of skin application [28] though more research is needed in other to understand just how skin absorbed lead is distributed in the body. In a study of nine adult males who applied hair dye containing lead acetate for 90 days, it was found that seven out of nine of them had elevated lead levels in hair on other parts of their bodies [29].

Three of the metals found in this study-nickel, cobalt and chromium-are well known triggers for contact dermatitis [30]. These metals are widely understood to be skin allergens in children [31]. Though the number of scientific studies on Allergic Contact Dermatitis in children is growing, routine testing at doctors' offices is infrequent. As a result, children are often misdiagnosed with eczema or other health problems and treated with unnecessary pharmaceuticals [32]. Understanding the consequences of low level human lead poisoning will depend upon an accurate assessment of the pervasiveness of toxicity in the global population. This will require that toxicity thresholds be determined as well as an understanding of the mechanisms underlying toxicity [33].

Table 2: Duncan's one way Analysis of Variance (ANOVA) of Means for heavy metal concentration (ugg^{-1}) in different colours of Ladyhood brand of eye shadow.

Metals	Ladyhood (Sample colours)			
	Brown	Yellow	Darkgrey	Purple
Pb	12.22^{ab}	8.33^{a}	15.56^{bc}	18.89^{c}
Cd	2.78^{a}	ND^{b}	8.89	1.67^{ab}
Ni	359.44^{a}	306.67^{b}	285.00^{c}	359.44^{d}
Cu	5.56^{a}	21.11^{b}	1.67^{a}	21.67^{b}
Zn	83.33^{a}	305.00^{b}	342.22^{c}	332.22^{c}
Cr	38.89^{ab}	61.11^{bc}	83.33^{c}	33.33^{a}
Co	217.22^{a}	122.78^{b}	192.77^{c}	221.11^{a}
Mn	37.78^{a}	270.56^{b}	63.33^{c}	42.78^{ac}

ND-Not Detected

(P<0.05); Means with the same superscript in the same row are not significantly different.

Table 1: Mean (±SD) heavy metal concentration (ugg^{-1}) in Eye shadow

Samples		Metals							
Brand	Colour	Pb	Cd	Ni	Cu	Zn	Cr	Co	Mn
Ladyhood	Brown	12.22±1.92	2.78±0.96	359.44±5.85	5.56±1.92	83.33±6.01	38.89±19.24	217.22±4.19	37.78±0.96
	Yellow	8.33±1.67	0.00±0.00	306.67±4.41	21.11±1.92	305.00±6.01	61.11±9.62	122.78±9.08	270.56±22.38
	Darkgrey	15.56±2.55	8.89±1.92	285.00±4.41	1.67±0.00	342.22±13.57	83.33±16.67	192.77±17.51	63.33±6.01
	Purple	18.89±2.55	1.67±0.00	359.44±3.85	21.67±4.41	332.22±8.22	33.33±0.00	221.11±5.09	42.78±5.36
Diamond	Pink	55.00±11.67	6.67±1.67	153.89±5.85	18.89±0.46	318.89±8.39	ND	217.78±2.55	30.56±5.85
	Blue	46.67±5.00	3.33±0.00	230.56±19.53	75.56±3.47	334.44±10.72	16.67±0.00	162.78±18.58	25.56±3.47
	Green	19.44±4.19	3.89±1.92	282±1.97	136.67±19.65	211.67±7.64	22.22±9.62	176.67±4.41	15.00±3.33
	Golden Brown	11.11±0.96	ND	206.67±3.33	4.44±0.96	103.33±4.41	51.67±6.01	190.56±5.09	59.44±4.19
Qiany1	White	12.22±2.55	ND	80.56±5.36	1.67±0.00	109.44±7.51	38.89±9.62	253.33±6.67	67.22±10.84
	Black	6.11±2.55	ND	350.00±1.67	6.11±0.96	81.67±3.33	150.00±16.67	200.56±11.10	131.11±23.82
	Brown	12.78±2.55	ND	213.33±10.41	8.89±1.93	112.78±2.55	133.33±33.33	188.33±3.33	95.00±9.28
	Pink	13.89±2.55	ND	217.22±21.43	3.89±0.96	28.33±1.67	33.33±0.00	184.44±4.81	56.11±4.81
Shas	Army green	ND	ND	228.89±2.55	88.98±19.20	208.89±6.94	72.22±9.62	258.33±6.01	32.22±2.55
	Brown	ND	ND	227.2±21.1	21.11±2.55	210.56±5.09	77.8±19.20	201.11±5.09	36.67±2.89
Midle	Purple	ND	ND	192.22±3.47	8.33±1.67	274.40±17.70	22.22±9.62	190.00±10.10	27.78±3.47
	Light Yellow	23.33±1.67	ND	262.22±1.92	2.22±0.96	288.89±5.09	44.44±9.62	167.78±6.94	58.33±4.41
Qianny	White	17.78±2.55	ND	77.22±3.47	1.67±0.00	208.30±10.40	33.33±0.00	197.78±5.85	50.00±8.82
	Light Brown	8.89±1.92	ND	352.22±5.09	137.22±9.18	203.33±1.67	122.22±9.62	211.11±6.94	107.22±1.92
FBI	Blue	5.00±0.00	4.44±0.96	278.89±6.31	465.00±5.00	257.20±17.80	16.67±0.00	201.11±6.74	34.44±2.55
	Ash	9.44±0.96	ND	222.78±3.47	27.78±2.55	218.30±20.20	27.78±9.62	193.33±9.28	32.22±0.96

Table 3: Duncan's one way Analysis of Variance (ANOVA) of Means for heavy metal concentration (ugg^{-1}) in different colours of Diamond brand of eye shadow.

Metals	Diamond (Sample colours)			
	Pink	Blue	Green	Golden Brown
Pb	55.00^{a}	46.67^{a}	19.44^{b}	11.11^{b}
Cd	6.67^{a}	3.33^{b}	3.89^{b}	ND^{ab}
Ni	153.89^{a}	230.56^{b}	282.22^{c}	206.67^{d}
Cu	18.89^{a}	75.56^{b}	136.67^{c}	4.44^{a}
Zn	318.89^{a}	334.44^{b}	211.67^{c}	103.33^{d}
Cr	ND^{a}	16.67^{a}	22.22^{a}	51.67^{b}
Co	217.78^{a}	162.78^{b}	176.67^{bc}	190.56^{c}
Mn	30.56^{a}	25.56^{a}	15.00^{b}	59.44^{c}

ND-Not Detected

(P<0.05); Means with the same superscript in the same row are not significantly different.

Table 4: Duncan's one way Analysis of Variance (ANOVA) of Means for heavy metal concentration (ugg^{-1}) in different colours of Qiany brand of eye shadow.

Metals	Qiany (Sample colours)			
	Brown	Yellow	Darkgrey	Purple
Pb	12.22^{ab}	6.11^{b}	12.78^{a}	13.89^{a}
Cd	ND^{a}	ND^{a}	ND^{a}	ND^{a}
Ni	80.56^{a}	350.00^{b}	213.33^{c}	217.22^{c}
Cu	1.67^{a}	6.11^{b}	8.89^{c}	3.89^{d}
Zn	109.44^{a}	81.67^{b}	112.78^{a}	28.33^{c}
Cr	38.89^{a}	150.00^{b}	133.33^{b}	33.33^{a}
Co	253.33^{a}	$200.56.^{b}$	188.33^{bc}	184.44^{c}
Mn	67.22^{a}	131.11^{b}	95.00^{c}	56.11^{a}

ND-Not Detected

(P<0.05); Means with the same superscript in the same row are not significantly different.

CONCLUSION

It is obvious from the present study that the use of facial cosmetics like eye shadow exposes users to low levels of heavy metals. Continuous use of these cosmetics could result in an increase in the heavy metal level in human body beyond acceptable limits.

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